Thermoreversible cross-linking of elastomers: a comparative study between ionic interactions, hydrogen bonding and covalent cross-links

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Thermoreversible Cross-linking of Elastomers
A Comparative Study between Ionic Interactions, Hydrogen Bonding and Covalent Cross-links

PROEFSCRIJT

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Thermoreversible Cross-linking of Elastomers
A Comparative Study between Ionic Interactions, Hydrogen Bonding and Covalent Cross-links

Summary

Elastomers have to be cross-linked to obtain typical rubber properties, such as good elasticity, high toughness and solvent resistance. The main industrial rubber cross-linking techniques, i.e., sulfur vulcanization and peroxide curing, yield permanent (irreversible) chemical cross-links, which prevent melt (re)processing and result in time-consuming and, hence, expensive multi-step production processes. This has led to the development of thermoplastic elastomers (TPEs), which ideally combine the service properties of cross-linked elastomers with the melt processability of thermoplastics. The cross-links in TPEs are of thermoreversible nature: they weaken or disappear at elevated temperatures, thereby allowing flow, and behave effectively similar to permanent cross-links at service temperatures. This behavior allows the use of standard thermoplastic processing techniques, in particular extrusion and injection molding, resulting in short production times and lower production costs.

The main objective of this study is to compare several alternative approaches for the thermoreversible cross-linking of the same precursor, i.e., maleated ethylene/propylene rubber (MAn-g-EPM). These methods include ionic interactions, (multiple) hydrogen bonds and covalent cross-links. The versatile and high reactivity of the grafted maleic anhydride groups allows the use of a variety of modification and cross-linking reactions. Structure-property and structure-processing relationships are established with the final objective to determine which thermoreversible cross-linking method(s) yield(s) the best property-processing balance. All reactions are initially performed via a solution route to obtain homogeneously cross-linked materials, while no processing oil or reinforcing fillers are added to keep the analysis as straightforward as possible.

Small-angle X-ray scattering (SAXS) experiments demonstrated that microphase-separated anhydride-rich aggregates are already formed for the MAn-g-EPM precursor, due to the large polarity difference between the anhydride groups and the EPM chain segments. These aggregates act as physical cross-links that increase the network density compared to the parent EPM and persist upon cross-linking with any of the applied thermoreversible cross-linking methods. Dynamic mechanical thermal analysis (DMTA) showed that the network density is not affected upon cross-linking, which suggests that the cross-links are solely formed within the aggregates. The strength of the aggregates is increased, which therefore prevail to higher temperatures than for MAn-g-EPM.

Ionic interactions with metal cations were introduced via neutralization of hydrolyzed MAn-g-EPM with potassium (K) and zinc (Zn) acetate, yielding ionomers with di-carboxylate functionalities. The type of cation has an important influence on the morphology, since the particular coordination
of Zn cations with di-carboxylates results in a relatively ill-defined aggregate structure, as demonstrated by SAXS. The tensile and elastic properties of the ionomers improve significantly upon increasing degree of neutralization and are much better for the K-ionomers than for the Zn-ionomers. Ionomers with relatively weak ammonium cations were obtained via neutralization with tertiary amines and have a reduced performance compared to the K- and Zn-ionomers.

Hydrogen-bonded materials were obtained via the reaction of MAn-g-EPM with an equimolar amount of primary N-alkylamine, resulting in amide-acids, while the addition of an excess of N-alkylamine yielded amide-salts that combine hydrogen bonds with ionic interactions. The tensile and elastic properties of the amide-acids are somewhat better than for MAn-g-EPM, but are significantly improved for the amide-salts, due to the additional ionic interactions. Processing temperatures of 120 °C and higher have to be avoided, since irreversible imide formation for all the amide-acids and amide-salts results in the loss of the thermoreversible cross-links and, hence, in a deterioration of the properties. Fortunately, all amide-acids and -salts can be easily compression molded at temperatures as low as 80 °C.

Different multiple hydrogen bonding arrays, i.e., imide-diaminopyridine, triazole, imidazolidone, (bis)urea and 2-ureido-4-pyrimidone (UPy) arrays, were introduced into MAn-g-EPM and compared to “non-organized” hydrogen-bonded materials, such as the amide-acids, hydrolyzed MAn-g-EPM and hydrogen-imide (NH$_3$-imide). The type of (multiple) hydrogen bonding (array) has a significant influence on the tensile and elastic properties, which improve in the following order: MAn-g-EPM < “non-organized” << triazole < imidazolidone < urea < bisurea < UPy. Specific stacking of the urea and bisurea groups within the aggregates results in an improved elasticity at elevated temperatures for the (bis)urea materials.

Materials with reversible covalent cross-links were obtained by using the equilibrium reaction of the anhydride groups of MAn-g-EPM with (aliphatic) diols, diamines and amino-alcohols, while a shift of the equilibrium at elevated temperatures was expected to result in their (partial) removal. High conversions are achieved at relatively low temperatures (50-75 °C) for all cross-linkers, although the addition of a suitable catalyst (p-toluene sulfonic acid) is necessary for the reaction with diols. The tensile strength and elasticity are significantly improved for increasing levels of cross-linking, whereas the influence of the type of cross-linker is less pronounced. The use of cross-linkers containing solely alcohol and secondary amine groups results in materials that are repeatedly reprocessable via compression molding at elevated temperatures. The reprocessability of these materials does not originate from the expected shift of the equilibrium, but from a continuous, dynamic exchange between cross-linked and non-cross-linked groups.

All cross-linked materials proved to be repeatedly reprocessable via compression molding, which indicates that the cross-links are thermoreversible in nature and suggests that these materials are in principle recyclable. The only exceptions are the K-ionomers at high degrees of neutralization, due to their extremely strong ionic interactions. All types of cross-links have a characteristic average lifetime (relaxation time), after which they can disconnect and the corresponding chain segments can diffuse between aggregates, eventually resulting in flow via hopping-like processes. These relaxation times are sufficiently short at the respective processing temperatures for ammonium-
ionomers, “non-organized” hydrogen bonds, amide-salts and some of the multiple hydrogen bonding arrays (triazole and imidazolidone) to allow the use of thermoplastic processing techniques, which are characterized by short timescales. Short-timescale processing is not possible for Zn- and K-ionomers, covalent cross-links and the other multiple hydrogen bonding arrays (urea, bisurea and UPy), since the relaxation times are still too long at the respective processing temperatures, although compression molding is feasible due to the long experimental timescales.

A comparison of the different thermoreversible cross-linking methods showed that a wide range in tensile and elastic properties can be obtained depending on the chosen cross-linking method. Both the strength of the aggregates and the timescale of the hopping-like process have a profound influence on the rubber properties. The best property-processing balance is obtained for some of the multiple hydrogen bonding arrays (triazole and imidazolidone) and the amide-salts, although their elastic behavior at elevated temperatures is rather poor, which is the case for all materials anyway. The other materials that are suitable for thermoplastic processing techniques have relatively poor properties, whereas the materials with good properties are not suitable for thermoplastic processing.

Two different approaches were applied to improve the property-processing balance of the current materials, namely the addition of processing oil and the use of lower anhydride contents. Both approaches do not improve the processability of the covalently cross-linked materials, because the characteristic relaxation times of the prevailing covalent networks are still too long. However, it was shown that these materials can be compounded with relatively large amounts of processing oil without affecting the elasticity, which can be advantageous in certain applications. Melt viscosities do decrease with both approaches for the materials with multiple hydrogen bonding arrays, which are already suitable for thermoplastic processing techniques, but at the expense of the properties.

The results discussed so far are based on an academic study on the thermoreversible cross-linking of MAn-g-EPM via a solution route. Melt modification or cross-linking is obviously the desired production route from a commercial point of view. Most types of reactions could indeed be performed in the melt using an internal mixer. For actual commercial applications, these materials have to be further optimized by compounding with, amongst others, processing oil and reinforcing filler, similarly to conventionally cross-linked elastomers. However, this falls outside the scope of this thesis. Some of the current materials without additives have superior tensile strength and elongation at break compared to peroxide-cured gumstock EP(D)M and thermoplastic vulcanizates (TPVs) based on dispersions of cross-linked EPDM in poly(propylene). Unfortunately, all current materials are significantly less elastic, especially at elevated temperatures. The current materials have a distinct processing advantage over conventionally cross-linked elastomers, since they are all repeatedly (re)processable. Unfortunately, their property-processing balance is much less optimal than for the TPVs in all cases. Possible approaches to improve this balance include the use of different MAn-g-EPM precursors or polar elastomer backbones and the addition of polar plasticizers. Finally, potential commercial applications have to be found in applications that require good tensile properties without high requirements on the elasticity.
Chapter 1

Introduction

1.1. Polymers

Nature has “used” polymers as building blocks of life ever since its beginning. Important natural polymers are DNA, poly(peptides) (proteins) and poly(saccharides). Naturally occurring polymers like wood, cotton, rubber and silk have been used by man for centuries. The first synthetic polymers were developed in the 19th century and were initially chemically-modified variations of natural polymers. The development of fully synthetic polymers started in the beginning of the 20th century. Since then, the production volume of polymers has increased enormously, resulting in an industry that currently produces over 100 million tons per year.

Polymers have more and more replaced traditional construction materials like metals, wood, glass and ceramics. Nowadays, polymers are used everywhere around us, in a wide range of applications, such as textiles, packaging materials, car parts, coatings and electronic and optical devices. Polymers are long-chain molecules built up from a large number of chemically-linked building blocks, so-called monomers. These monomers can be connected in different ways to obtain completely different properties, like in linear or branched chains, 3-dimensional networks or copolymers of different monomers. The main advantages of polymers are the relatively low cost, the ease of manufacturing complex shapes, the low density and the vast range of properties.

Polymers can be divided into three main classes, depending on their (processing) behavior at elevated temperatures, namely thermoplastics, thermosets and rubbers.

*Thermoplastics* are linear or branched polymers that soften or melt into a flowable state upon heating, thereby allowing shaping of the material. They solidify again upon cooling via vitrification for amorphous thermoplastics, for instance poly(styrene) (PS) and poly(methyl methacrylate) (PMMA), or via crystallization for semi-crystalline thermoplastics, e.g., poly(ethylene) (PE), poly(propylene) (PP) and poly(amide) (PA). Processing cycles can be repeated if desired, since no irreversible connections between polymer chains are formed.

*Thermosets* are low-molecular-weight resins that are cured into a 3-dimensional network during the final processing step. Irreversible covalent bonds are formed between the polymer chains, which are called *cross-links*. In general, thermosets have superior thermo-mechanical properties and dimensional stability compared to thermoplastics and are better suited for high-temperature applications. The first synthetic thermoset was developed in 1907 by Leo Baekeland and was based on a phenol-formaldehyde resin. This material, which he named Bakelite, quickly found commercial application in electrical insulators. Other examples of thermosets include epoxy, urea, melamine, and poly(ester) resins.
Rubbers, or alternatively elastomers, are soft, flexible and elastic materials and are applied in a wide range of applications, such as tires, tubes, seals and gloves. Rubbers have a glass transition temperature \( (T_g) \) below room temperature and, as a result, have highly flexible chain molecules. Virgin elastomers are rather viscous materials with low strength, since chain disentanglement occurs readily under stress conditions, resulting in viscous flow and permanent deformation.\(^4,5\) The typical rubber properties, such as elasticity, high toughness and solvent resistance, are only obtained after cross-linking, since this severely restricts the motion of the chain molecules. The main industrial techniques for rubber cross-linking are sulfur vulcanization and peroxide curing.\(^6\) The process of sulfur vulcanization was discovered already in 1839 by Charles Goodyear after heating natural rubber in the presence of sulfur.\(^6,7\) Sulfur vulcanization is limited to rubbers with unsaturated moieties, which resulted in the industrial development of peroxide curing of elastomers, because of its ability to cross-link both saturated and unsaturated elastomers.\(^4,8\) Rubber cross-linking results in a three-dimensional network via sulfur bridges for sulfur vulcanization and via C-C bonds for peroxide curing,\(^8,9\) similar to thermosets, although the degree of cross-linking is generally lower for elastomers. The most important types of rubber are natural rubber (NR) and the synthetic styrene-butadiene (SBR), butadiene (BR) and ethylene-propylene-diene (EPDM) rubbers.

The formation of an irreversible network upon cross-linking prevents melt (re)processing of both thermosets and elastomers, which gives them a distinct processing disadvantage compared to thermoplastics. Materials have to be shaped before the relatively slow curing reactions take place, resulting in time-consuming and expensive multi-step processes. Thermoplastics, on the other hand, are typically processed using one-step, short-timescale techniques, such as extrusion or injection molding. In addition, simple recycling of scrap material and used products is not possible for thermosets and elastomers.\(^10,11\)

In this respect, thermoplastic elastomers (TPEs) are an interesting subclass of materials, since they ideally combine the service properties of cross-linked elastomers with the melt processability of thermoplastics.\(^12,13\) The cross-links in TPEs are of thermoreversible nature; i.e., they weaken or disappear at elevated temperatures, thereby allowing flow, while they behave as permanent cross-links at the service temperature. This behavior gives TPEs a processing advantage over conventional elastomers, since standard thermoplastic processing equipment can be used.\(^12\) Furthermore, scrap material and used products can be recycled. A main disadvantage of TPEs is the relatively poor behavior at elevated temperatures.

### 1.2. Thermoreversible cross-linking methods

Thermoreversible cross-links can be of physical nature, e.g., crystallization, phase separation, ionic interactions or hydrogen bonds, or of chemical nature, using reversible covalent bonds. Phase separation of hard and soft blocks in TPEs and ionic interactions in so-called ionomers have been used commercially for quite some time. The use of hydrogen bonding and reversible covalent bonds to obtain thermoreversible polymers or networks has received a lot of attention recently, although it has so far not resulted in actual commercial applications. Lehn recently introduced the name “dynamers” for polymers that consist of monomers connected by reversible connections, which can
be either reversible covalent bonds or non-covalent interactions, such as hydrogen bonds.\textsuperscript{14} An overview of several different thermoreversible cross-linking methods is given in the next sections.

1.2.1. Hard/soft phase separation in TPEs

Virtually all TPEs consist of two different phases: a hard and rigid thermoplastic phase and a soft and flexible elastomeric phase.\textsuperscript{12,13} In TPEs, these phases are phase-separated, since two different polymers are generally not thermodynamically miscible. Commercial TPEs can be divided into two main classes, namely block copolymers and polymer blends.\textsuperscript{13}

For the block copolymers, a further division into tri-block and multi-block copolymers can be made.\textsuperscript{13} TPE tri-block copolymers consist of a flexible mid-block end-capped with relatively short, ‘rigid’ blocks, such as poly(styrene)-poly(butadiene)-poly(styrene) (SBS). Multi-block copolymers are usually based on poly(urethanes), poly(esters) or poly(amides) as hard blocks and consist of alternating hard and soft blocks. Below their $T_g$ or melting point ($T_m$), the hard blocks form microphase-separated domains within the soft matrix, as shown schematically for an ABA tri-block copolymer in Figure 1.1. The small rigid domains act as physical cross-links, resulting in the formation of a three-dimensional network and in rubber-like behavior at the service temperature. The two phases become miscible above the order-disorder transition temperature, resulting in a one-phase system and a significant drop in the viscosity, which enables flow of the material. This process is fully reversible, since the network is re-formed upon solidification of the hard phase during cooling. It should be noted that hydrogen bonds may be used to strengthen the hard domains, for instance in poly(urethane)-based multi-block copolymers.\textsuperscript{13}

![Figure 1.1. Schematic representation of the morphology of an ABA tri-block copolymer.\textsuperscript{15}]

TPE polymer blends are dispersions of an elastomer in a semi-crystalline thermoplastic matrix.\textsuperscript{13,16} They can contain a non-cross-linked elastomer, yielding relatively soft and flexible materials, and are usually blends of PP and ethylene/propylene (EPM) rubber. Cross-linking of the rubber phase results in thermoplastic vulcanizates (TPVs), which have superior elastic and tensile properties compared to blends with non-cross-linked rubber particles. Most commercial TPVs are blends of PP and cross-linked EPDM rubber. The homogeneously dispersed rubber particles give TPE blends their elastic properties, whereas the thermoplastic matrix is responsible for the melt processability.
1.2.2. Ionic interactions

Ionomers are another class of materials with thermoreversible cross-links. These are polymers that contain small amounts of ionic groups either pendant to or incorporated in the backbone. The ionic groups are generally obtained via partial or full neutralization of acid groups, usually carboxylic or sulfonic acids, with (metal) cations. In most cases, microphase-separated ionic aggregates are formed, dispersed in the non-ionic matrix, due to the large difference in polarity between the ionic groups and the relatively apolar backbone chains. The corresponding polymer chain segments are anchored to the ionic aggregates, which therefore act as strong physical cross-links and are responsible for the unique physical, mechanical and rheological properties of ionomers. Several types of ionomers have been developed up to date, including commercially successful ionomers, such as Surlyn®, which is a zinc- or sodium-neutralized ethylene-methacrylic acid copolymer, and Nafion®, which is based on sulfonated poly(tetrafluoroethylene).

The morphology of ionomers has been extensively studied, mainly using small-angle X-ray and neutron scattering techniques (SAXS and SANS). A large number of structural models has been proposed to describe the microphase-separated structure of ionomers, but a consensus on the correct model is still lacking. Despite this, it is well established that several parameters determine the morphology of ionomers and, concomitantly, their properties. These include the amount of acid groups and the extent of their neutralization and the choice of the (metal) cation. Another important parameter is the architecture of the ionomer, i.e., the location of the ionic groups on the polymer chains, for which random ionomers are distinguished from telechelic and block ionomers. Finally, the type of acid group is important. Lundberg et al. showed that the ionic associations are much stronger for sulfonated ionomers than for their carboxylated analogues, which makes the former ionomers difficult or even impossible to process. Additionally, full neutralization is necessary for sulfonated ionomers to avoid thermal degradation of residual sulfonic acid groups at elevated temperatures. Therefore, carboxylated ionomers are preferred for practical applications.

Although ionomers are more viscous than their non-ionic precursors, melt processing in low shear applications, such as compression molding, is usually possible, especially in the case of carboxylated ionomers. SAXS experiments have consistently shown that ionic aggregates persist to temperatures as high as 300 °C, which is far above the melt processing temperatures. This indicates that flow of ionomers does not require full elimination of the ionic aggregates. It is generally assumed that an “ion hopping” mechanism, as originally proposed by Cooper, is responsible for the flow of ionomers, as shown schematically in Figure 1.2. The ionic interactions have a characteristic lifetime, after which they can disconnect. The “free” ionic groups can leave the aggregates and “hop” between aggregates, which allows stress relaxation in the polymer chain segments containing the ionic groups. In this way, ionomer chains can flow without breaking all their ionic associations simultaneously.

Ionomers based on rubbery polymers can be used as “ionic TPEs”, because the thermoreversible nature of ionic interactions allows flow at elevated temperatures. One example is metal-neutralized sulfonated EPDM. The mechanical properties of EPDM are significantly improved upon the introduction of small amounts of zinc sulfonate groups and can even approach those of
vulcanized EPDM. However, the ionic interactions are extremely strong, resulting in (too) high melt viscosities. The addition of polar plasticizers, such as zinc stearate, enhances the processability, but also deteriorates the mechanical properties. Other attempts to obtain ionic TPEs resulted in too high melt viscosities as well and required the addition of polar plasticizers. In most of the reported cases, the ionomer precursor was an elastomer with a relatively high molecular weight. Therefore, the use of an ionomer precursor with low molecular weight and with carboxylic acid groups was proposed during previous work in our group, using maleated EPM (MAN-g-EPM). However, the melt viscosities were still relatively high, most probably due to the high ion contents that were necessary to obtain acceptable properties.

Figure 1.2. Schematic representation of the “ion hopping” mechanism.

This demonstrates that it is difficult to find a proper balance between the solid-state properties and the processability of ionomers, although the adjustment of (some of) the ionomer variables discussed above or the addition of processing aids may improve this balance to a certain extent.

1.2.3. Hydrogen bonding

Hydrogen bonds weaken significantly at elevated temperatures and can therefore be used for thermoreversible cross-linking. Hydrogen bonds are attractive interactions between a positively-charged hydrogen atom bonded to a negatively-charged atom (the donor) and a negatively-charged atom with a lone electron pair (the acceptor). The strength of a hydrogen bond is dependent on the donor (D) and acceptor (A) properties of the two species and their directionality. The O-H and N-H donors and the C=O and R3N acceptors are most common in both nature and synthetic materials, but result in hydrogen bonding donor and acceptor pairs with limited strength. Fortunately, the strength of hydrogen bonds can be improved rather easily by combining them in linear arrays of hydrogen bonding sites. The development of multiple hydrogen bonding arrays was inspired by nature, which uses double and triple hydrogen bonding arrays between the base pairs to store the information of life in DNA.

The cooperation of hydrogen bonds within an array increases the strength and especially the specificity and directionality. As a result, linear multiple hydrogen bonding arrays will generally form dimers, which can be divided into two classes: complementary dimers, which are formed between two dissimilar arrays, and self-complementary ones, formed between two identical arrays. Two different types of double hydrogen bonding dimers exist (DA-AD and AA-DD),
while there are three types of triple hydrogen bonding dimers (AAA-DDD, ADA-DAD and AAD-DDA) and six types of quadruple units, including two self-complementary ones.\textsuperscript{49} Besides the strength of the separate hydrogen bonds and their number, the attractive and repulsive secondary interactions between adjacent donor and acceptor sites play an important role in determining the final strength of an array, according to Jorgenson’s model.\textsuperscript{52,53} This explains for example the much lower association constant of ADA-DAD dimers compared to AAA-DDD dimers.\textsuperscript{49,50,54}

The recent developments in supramolecular chemistry resulted in an increased interest in the development of multiple hydrogen bonding arrays. In most cases, both thermoreversible linear polymers and networks are possible, as dimers are formed between arrays. Examples of thermoreversible polymer networks obtained with multiple hydrogen bonding arrays are discussed in the remainder of this section.

Stadler and co-workers reported on the modification of poly(butadiene) with grafted phenylurazole groups.\textsuperscript{55-58} The phenylurazole groups form double hydrogen bonding dimers (Figure 1.3a) and improved the mechanical properties compared to the non-modified poly(butadiene), while rheological experiments suggested the formation of a thermoreversible network. However, the properties of the materials remained rather poor, due to the relatively low association constant of the phenylurazole groups (10\textsuperscript{2} L/mol in chloroform).\textsuperscript{59} In an alternative approach, phenylurazole groups with an additional carboxylic acid group, i.e., 4-carboxyphenylurazole, were grafted (Figure 1.3b).\textsuperscript{60,61} Each functional group is now capable of forming two double hydrogen bonds, which resulted in the formation of hydrogen-bonded, phase-separated structures within the poly(butadiene) matrix and in impressive mechanical and rheological properties.\textsuperscript{62}

![Figure 1.3. (a) Double hydrogen bonding dimer of two phenylurazole groups\textsuperscript{55,56} and (b) a 4-carboxyphenylurazole group, capable of self-assembly via two double hydrogen bonds.\textsuperscript{60,61}](image)

Lange and Meijer studied the imide-diaminopyridine (DAD-ADA) triple hydrogen bonding array between melamine and the imide groups of styrene-maleimide copolymers. They proposed the complexation of one melamine molecule with three imide groups to form a polymer network (Figure 1.4).\textsuperscript{63,64} Loontjens et al. obtained polymer networks from melamine and low-molecular-weight poly(tetramethylene oxide) with two imide end-groups, which displayed a melt rheological behavior similar to covalent polymer networks.\textsuperscript{65} In both cases, the materials remained soluble, indicating that the networks are indeed reversible. However, the networks were relatively weak, again due to the relatively low association constant of the complexes (10\textsuperscript{2} L/mol).\textsuperscript{64}
Sijbesma, Meijer and co-workers developed a self-complementary quadruple hydrogen bonding array (DDAA), i.e., the nowadays well-known 2-ureido-4-pyrimidone (UPy) unit. UPy groups form extremely strong dimers with an association constant of $6 \times 10^7$ L/mol in chloroform (Figure 1.5). Reversible polymer networks were obtained from low-molecular-weight poly(ether) polyols, functionalized with three UPy groups. The rheological behavior of these materials resembled that of covalent polymer networks without the need for additional stabilization by phase separation. Coates and co-workers introduced small amounts of UPy units into poly(olefins) via the copolymerization of olefins with vinyl-functionalized UPy groups. The resulting polymer networks displayed tensile properties typical for cross-linked elastomers, while solution viscosity measurements showed that the cross-links are reversible.

Recently, two research groups reported on the use of bisurea groups in the development of TPEs. Bouteiller and co-workers studied poly(dimethylsiloxanes) with grafted bisurea groups, while Versteegen et al. prepared segmented block copoly(ether ureas) with small bisurea blocks. Urea groups are able to self-assemble into long stacks of hydrogen bonding arrays via strong bifurcated hydrogen bonds, as shown in Figure 1.6 for bisurea groups. As a consequence, large stacks of hydrogen-bonded urea groups are formed, which act as multiple cross-linking units. Both groups obtained TPEs with excellent mechanical properties, while melting of these stacks resulted in processable materials at elevated temperatures.
Figure 1.6. Self-association of bisurea units, where R is a phenyl ring in the work of Bouteiller and co-workers\textsuperscript{71} and a butylene spacer in the work of Versteegen et al.\textsuperscript{74}

Chino et al. introduced triazole groups into elastomers via the reaction of maleated elastomers with 3-amino-1,2,4-triazole (ATA) (Figure 1.7).\textsuperscript{76,77} The authors speculated that each functional group is capable of interacting with other groups via a six-point hydrogen bonding geometry, but its real existence may be questioned from an entropic point of view. The mechanical properties were significantly improved, indicating the formation of relatively strong hydrogen bonding interactions, while the materials could be reprocessed at least ten times without affecting the properties.

Figure 1.7. Modification of maleated poly(isoprene) with 3-amino-1,2,4-triazole (ATA).\textsuperscript{76}

Very recently, Leibler and co-workers reported on the use of imidazolidone groups, which are capable of forming double hydrogen bonding dimers (Figure 1.8), to obtain supramolecular polymers.\textsuperscript{78} Polymer networks were obtained via grafting of the functional groups onto polymers\textsuperscript{79} or via the use of tri-functional, low-molecular-weight compounds.\textsuperscript{80}

Figure 1.8. Double hydrogen bonding dimer of two imidazolidone groups.\textsuperscript{78}
1.2.4. Reversible covalent cross-linking

Another intriguing possibility is the use of thermoreversible covalent cross-links, using the inherent temperature dependence of equilibrium reactions and the related ceiling temperature. Covalent cross-links are formed via the forward reaction between suitable chemical functionalities at low temperatures, while a shift in the equilibrium may result in their (partial) removal at elevated temperatures.\textsuperscript{81} The properties of the resulting thermoreversible network are expected to be similar to those of an conventionally cross-linked network.

Reversible covalent bonds can be applied for the formation of thermoreversible linear polymers and polymer networks. Not much success has been achieved in the formation of reversible linear polymers, since polymers with sufficiently high molecular weight are only obtained if the forward reaction results in very high conversions.\textsuperscript{81,82} Additionally, the equilibrium has to shift significantly to achieve sufficiently low viscosities and melt processing temperatures to avoid irreversible side reactions or thermal degradation. A similar problem occurs for multiple hydrogen bonding arrays, for which high-molecular-weight polymers are only obtained in the case of (extremely) strong arrays, while small amounts of impurities already have a detrimental effect.\textsuperscript{50} More success has been achieved in thermoreversible covalent cross-linking, since small amounts of cross-links are generally already sufficient to obtain a network, while complete reversion of the reaction is not necessary. Only sufficient chemical bonds need to disconnect to allow adequate melt flow.\textsuperscript{81} The remainder of this section focuses on examples of covalent cross-linking reactions.

A particularly suitable reaction for this purpose is the Diels-Alder \([4+2]\) cycloaddition between a dienophile and a diene, because of the readiness of Diels-Alder adducts to undergo the reverse (retro-Diels-Alder) reaction upon heating.\textsuperscript{81,83} Especially the reaction between maleimide and furan groups (Figure 1.9) has received a lot of attention. Several authors reported on the cross-linking of maleimide- or furan-functionalized polymers with bisfurans or bismaleimides, respectively.\textsuperscript{83-88} Polymer networks were obtained at low temperatures, while decross-linking at elevated temperatures resulted in soluble materials. Wudl and co-workers obtained “self-healing” networks via the Diels-Alder reaction between multi-functional maleimide and furan compounds, which were able to repeatedly “heal” cracks at elevated temperatures.\textsuperscript{89,90} The Diels-Alder reaction between two cyclopentadiene groups has also been used for thermoreversible network formation, although monofunctional dienophiles, such as maleic anhydride, had to be added to obtain soluble materials at high temperatures.\textsuperscript{91-93}

\[
\begin{align*}
\text{R} - \text{O} & \quad \text{+} \quad \text{N} - \text{R}' \\
\text{O} & \quad \text{\textDelta T} \quad \text{N} - \text{R}' \\
\text{R} - \text{O} & \quad \text{O} \\
\end{align*}
\]

**Figure 1.9.** (Retro-)Diels-Alder reaction between furan and maleimide groups.\textsuperscript{85,89}

Urethane formation from isocyanate and hydroxyl groups is thermoreversible\textsuperscript{94,95} and has been used for polymer cross-linking.\textsuperscript{96-98} Previous work in our group showed that the depolymerization of linear poly(urethanes) is completely reversible up to temperatures of 250 °C.\textsuperscript{99-101} Unfortunately, the
required processing temperatures for poly(urethanes) with relatively high molecular weights were above the degradation temperature, which agrees with the general observations discussed above. The required processing temperatures decreased upon lowering the molecular weights, eventually resulting in easily processable materials below the degradation temperature.

The reaction of cyclic anhydrides with amines to form amide-acids (Figure 1.10) and with alcohols to form hemi-esters (Figure 1.11) were reported to be thermoreversible.\textsuperscript{102-105} Amide-acids obtained from primary amines subsequently undergo irreversible imide formation already at moderately elevated temperatures (Figure 1.10),\textsuperscript{106-108} which limits the thermoreversibility. Imide formation is not possible for secondary amines, resulting in a thermoreversible reaction. Di- or multi-functional cross-linkers, containing at least one alcohol or secondary amine group, such as diols, polyols, amino-alcohols and secondary diamines, have been used for the thermoreversible cross-linking of polymers containing cyclic anhydride groups.\textsuperscript{103,105,109-111}

![Figure 1.10. The reaction of cyclic anhydrides with primary (above) and secondary amines (below).\textsuperscript{105}](image1)

![Figure 1.11. Reaction between cyclic anhydrides and alcohols.\textsuperscript{102,105}](image2)

Several other reactions have been applied for thermoreversible cross-linking of polymers. The reaction between vinyl ethers and carboxylic acids is thermoreversible and was used to cross-link carboxylic acid copolymers with divinyl ethers.\textsuperscript{112} Another possibility is the reaction of azlactones groups with phenols. Although linear polymerization reactions were unsuccessful,\textsuperscript{113} poly(azlactones) could be thermoreversibly cross-linked with bisphenols, resulting in materials that were soluble at elevated temperatures for several cycles.\textsuperscript{114} Finally, nitroso groups form dimers at low temperatures that dissociate at elevated temperatures and have been used to obtain thermoreversible networks.\textsuperscript{115}
1.3. Aim of the thesis

In the previous sections, the concept of thermoreversible cross-linking was explained and several examples and commercial applications were reviewed. However, a direct comparison between different routes towards thermoreversible cross-linking has never been made to the authors’ knowledge. The main objective of this thesis is to compare different thermoreversible cross-linking methods for the same starting material.

For this purpose, a maleated EPM rubber (MAn-g-EPM) is used, which ideally results in new types of TPEs, but the same principles may be applicable to other materials as well, including thermosets. Grafted maleic anhydride groups have a versatile and high reactivity, which provides the possibility to perform a wide variety of modification and cross-linking reactions. Maleated poly(olefins) are specialty polymers produced on a commercial scale via reactive extrusion (around 150 kton/year) and are mainly used as interfacial agents. These new types of TPEs may be relatively cheap compared to common TPE block copolymers or blends, since they can ideally be produced in a one-step modification (grafting of maleic anhydride, followed by cross-linking) of a low-cost elastomer (EPM) on common compounding equipment.

The comparison is made between different methods, including ionic interactions, hydrogen bonding, covalent cross-links and combinations thereof, and is based on the determination of the structures, the rubber properties and the (re)processability. Structure-property and structure-processing relationships are established with the final goal to determine for which thermoreversible cross-linking method(s) a proper property-processing balance is obtained.

1.4. Outline of the thesis

First, the chemical structures, the morphology and the rubber properties are discussed for each thermoreversible cross-linking method separately in Chapters 2-6. All modification and cross-linking reactions are performed via a solution route, if possible, to ensure homogeneity of the reaction system and to obtain high conversions. The chemical structures and the anhydride conversions are determined using Fourier transform infrared (FTIR) spectroscopy. The morphology, as studied using SAXS and dynamic mechanical thermal analysis (DMTA), and the properties (hardness, tensile properties and compression set) of the cross-linked materials are also evaluated.

Ionomers with metal cations based on MAn-g-EPM are studied in Chapter 2. The effect of the degree of neutralization, the type of metal cation, either monovalent potassium or divalent zinc, and moisture uptake on the morphology and the mechanical properties is investigated and a comparison is made with MAn-g-EPM-based ionomers studied during previous work. The morphology is evaluated in more detail using an adapted Yarusso-Cooper model.

Chapter 3 describes a method to cross-link MAn-g-EPM with hydrogen bonds or with a combination of hydrogen bonds and ionic interactions, which is achieved via a reaction with equimolar amounts and an excess of N-alkylamines, respectively. The ability of these materials to undergo irreversible imide formation, which deteriorates the properties, is evaluated as a function of the processing times and temperatures. Finally, a method to prevent imide formation is discussed.
Different multiple hydrogen bonding arrays are compared in *Chapter 4*, including UPy, mono- and bisurea, ATA, and imidazolidone groups, which are attached as stable imides to the EPM backbone. Differences in the morphology, the properties and the (re)processability are related to differences in the number of hydrogen bonding donors and acceptors and their organization and directionality.

Reversible covalent cross-linking with diols is the subject of *Chapter 5*. The effects of the type and amount of diol and catalyst and the temperature on the reaction rate and the equilibrium anhydride conversion are determined using time-resolved FTIR spectroscopy, as well as their effect on the morphology and the properties. The (origin of the) thermoreversibility of the reactions and the (re)processability are studied using time-resolved FTIR measurements and flow-experiments in compression molding.

Covalent cross-linking with different combinations of alcohol and primary and secondary amine groups is discussed in *Chapter 6*. The effect of covalent cross-linking on the thermoreversibility and the (re)processability is studied using time-resolved FTIR measurements and flow-experiments in compression molding. Finally, combinations of these groups with tertiary amines, which form ionic interactions with ammonium cations instead of covalent bonds, are studied in a similar manner.

A detailed study of the rheological and time-dependent behavior for the different cross-linking methods is presented in *Chapter 7*. The (re)processability in thermoplastic equipment is evaluated using Mooney viscosity measurements, while the rheological behavior and the characteristic relaxation times for the different types of thermoreversible cross-links are studied in more detail.

The comparison of the different thermoreversible cross-linking methods is made in *Chapter 8*. The relevant rubber properties (tensile properties and elasticity) and the melt (re)processability are compared to obtain a selection of the most promising techniques with respect to the property-processing balance. An explanation for the observed differences is given based on the structure-property and structure-processing correlations.

*Chapter 9* describes two different approaches to improve the property-processing balance of these new types of TPEs. First, different amounts of standard EP(D)M processing oil are added prior cross-linking. Secondly, the anhydride content of MAn-g-EPM is lowered by converting defined fractions of the anhydride groups to apolar N-alkylimides via the reaction with N-decylamine. The effects of both methods on the morphology, the properties and the (re)processability are evaluated.

The *Technology Assessment* discusses the advantages and disadvantages of the newly-developed TPEs compared to (commercial) conventionally cross-linked elastomers and TPEs and discusses the possibilities for their commercial application. Finally, some suggestions for improvements and future research in this field are given.

### 1.5. References

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Chapter 2

Thermoreversible Cross-linking with Ionic Interactions*

Ionic thermoplastic elastomers with di-carboxylate functionalities were obtained via neutralization of hydrolyzed maleated EPM rubber (MAn-g-EPM) with potassium (K⁺) and zinc (Zn²⁺) acetate. The lower reactivity of the second of two adjacent carboxylic acid groups after neutralization of the first group prevents neutralization beyond 50% with monovalent K⁺ cations, while the remaining positive charge for the divalent Zn²⁺ cations enables further neutralization. Small-angle X-ray scattering (SAXS) showed the presence of microphase-separated aggregates for MAn-g-EPM that act as physical cross-links and increase the network density compared to the parent EPM. Neutralization with both K⁺ and Zn²⁺ cations results in significantly increased aggregate strength, which causes the ionic network to persist up to higher temperatures, while the network density remains unaffected. The type of cation has an important influence on the final morphology, because the particular coordination behavior of Zn²⁺ cations with di-carboxylates results in a poorly-defined aggregate structure. A very good fitting of the SAXS patterns is obtained by adapting the Yarusso-Cooper model to take into account a polydisperse aggregate size distribution and a non-constant matrix scattering. The necessity of the latter adaptation suggests the presence of small, isolated multiplets, randomly dispersed within the matrix. The tensile properties and elasticity improve with increasing degree of neutralization (DN) and are significantly better for the K-ionomers than for the Zn-ionomers, due to the stronger aggregates. All ionomers except the K-ionomers with high DN are repeatedly reprocessable via compression molding without affecting the properties. Finally, water absorption improves the properties of MAn-g-EPM and the Zn-ionomers, while it is detrimental for the properties of the K-ionomers.

2.1. Introduction

Ionomers are polymers that contain relatively small amounts (up to 15 mol%) of ionic groups pendant to or incorporated in the polymer backbone.\(^1\)\(^-\)\(^3\) The ionic groups are usually obtained via partial or full neutralization of acid groups, mainly carboxylic or sulfonic acids, with metal salts. It is well established that the ionic groups tend to form microphase-separated ionic aggregates within the non-ionic matrix, due to the large polarity difference between the ionic groups and the less polar backbone.\(^1\)\(^-\)\(^3\) The existence of these aggregates has been shown for many ionomers, mainly using small-angle X-ray and neutron scattering techniques (SAXS and SANS). A typical feature of the SAXS profile of ionomers is the so-called “ionic” peak, usually observed at q-values around 0.1-0.4 Å\(^{-1}\), where q is the modulus of the scattering vector (q=(4\(\pi/\lambda\))sin\(\theta\), where \(\lambda\) is the wavelength and \(2\theta\) is the scattering angle). Many structural models have been proposed to explain the morphology of ionomers,\(^4\)\(^-\)\(^9\) but there is still no general consensus on the correct model. The ionic aggregates act as physical cross-links and are responsible for the unique physical, mechanical and rheological properties of ionomers.

The melt processability of ionomers is related to the increased mobility of the ionic aggregates at elevated temperatures. Therefore, ionomers based on non-crystalline polymers with a low glass transition temperature (\(T_g\)) can be used as “ionic” thermoplastic elastomers (TPEs), if the ionic associations are sufficiently weakened at the processing temperatures.\(^10\)\(^-\)\(^12\) One example is metal-neutralized sulfonated EPDM, where EPDM is a terpolymer of ethylene, propylene and a diene monomer. The mechanical properties of EPDM are significantly improved upon the introduction of small amounts of zinc sulfonate groups and can even approach those of vulcanized EPDM.\(^13\)\(^-\)\(^15\) However, the ionic interactions are too strong even at conventional processing temperatures, resulting in very high melt viscosities. Polar plasticizers, such as zinc stearate, can be added to enhance the processability, but deteriorate the mechanical properties as well.\(^16\)\(^,\)\(^17\) Lundberg et al.\(^18\) showed that the ionic associations in sulfonated ionomers are much stronger than in their carboxylated analogues, resulting in melt viscosities that are two to three orders of magnitude higher. An additional disadvantage of sulfonated ionomers is that full neutralization is required, since residual sulfonic acid groups may thermally degrade at elevated temperatures. Therefore, carboxylated ionomers are preferred for practical applications.

Other attempts to prepare ionic TPEs resulted in ionomers with too high melt viscosities as well.\(^11\)\(^,\)\(^19\)\(^,\)\(^20\) In most cases, the ionomer precursor was an elastomer of relatively high molecular weight. During previous work in our group, the use of maleated ethylene/propylene copolymers (MAn-g-EPM) with a relatively low molecular weight as ionomer precursors was proposed to obtain ionomers with acceptable processing properties.\(^21\)\(^-\)\(^24\) The ionomers were prepared via hydrolysis of the grafted maleic anhydride (MAn) groups to the corresponding di-carboxylic acids, followed by neutralization with metal acetates, resulting in ionomers with di-carboxylate functionalities. The morphology of these ionomers was extensively studied using SAXS and solid-state NMR. An evaluation of several structural models showed that the Yaruss-Coooper (Y-C) model\(^8\) was the best model for the interpretation of the SAXS results.\(^21\)\(^,\)\(^22\) The size of the aggregates in MAn-g-EPM-based ionomers and, consequently, the number of ionic groups within an aggregate were significantly larger than for other types of ionomers, such as sodium- or zinc-neutralized ethylene-
Thermoreversible Cross-linking with Ionic Interactions

methacrylic acid copolymers (Surlyn®). The melt viscosities of these low-molecular-weight ionomers were still relatively high, most probably related to the high degrees of grafting (DG) that were necessary to obtain acceptable mechanical properties.

Therefore, in the current work, a different MAn-g-EPM precursor is studied with a higher, but still relatively low, molecular weight (M_n = 40 kg/mol) and a lower DG (2.1 wt%) compared to the low-molecular-weight precursor used in the previous studies, which had a M_n of 11 kg/mol and a DG of 7.3 wt%. Both precursors have a comparable average number of grafted MAn groups per EPM chain (Ω), which is calculated using:

\[
Ω = \frac{M_{EPM} \cdot DG \cdot 1000}{M_{MAn} \cdot 100}
\]  

(2.1)

where \(M_{EPM}\) is the molecular weight of the precursor (kg/mol) and \(M_{MAn}\) is the molecular weight of the grafted maleic anhydride (99 g/mol). This results in \(Ω = 8.1\) for the low-molecular-weight MAn-g-EPM and \(Ω = 8.5\) for the current MAn-g-EPM precursor.

Here, the MAn-g-EPM precursor is neutralized to various targeted degrees of neutralization (DN) with two different cations, namely monovalent potassium (K⁺) and divalent zinc (Zn^{2+}). The formation of the ionomers and the actual DN are studied using Fourier transform infrared (FTIR) spectroscopy. The effects of DN and the type of metal cation on the morphology are studied with SAXS and dynamic mechanical thermal analysis (DMTA), as well as their effects on the rubber properties, i.e., hardness, elasticity and tensile properties. The SAXS results are interpreted with a modified Y-C model to obtain a more quantitative insight in the aggregate structure. Additionally, a comparison of the morphology and the properties is made with the low-molecular-weight ionomers from the previous work. The reprocessability of the ionomers is studied via compression molding experiments, as well as the effect on the tensile properties. Finally, the effect of water absorption on the morphology and the tensile properties of the ionomers is determined.

2.2. Experimental section

2.2.1. Materials

Maleated ethylene/propylene copolymer (MAn-g-EPM, 49 wt% ethylene, 49 wt% propylene, 2.1 wt% maleic anhydride (MAn), M_n = 40 kg/mol, M_w = 90 kg/mol) and the parent EPM (50 wt% ethylene, 50 wt% propylene, M_n = 40 kg/mol, M_w = 90 kg/mol) were provided by DSM Elastomers. The MAn-g-EPM precursor was dried for 1 h at 170 °C under reduced pressure with a low N_2-flow prior to use to convert all carboxylic acid groups, formed upon hydrolysis, back to anhydride. Zinc acetate dihydrate (ZnAc_2, Fluka), potassium acetate (KAc, Aldrich), potassium hydroxide (KOH, Aldrich), toluene (Biosolve) and 2-propanol (Biosolve) were used as received.

2.2.2. Preparation of the ionomers

Typically, 25 g of MAn-g-EPM was dissolved in a mixture of 225 g of toluene and 25 g of 2-propanol at 80 °C. After complete dissolution of the precursor, 10 g of an aqueous solution containing the required amount of metal salt, i.e., ZnAc_2, KAc or KOH, was added and the two-phase mixture was stirred for 15 min
at 80 °C. Approximately 50 g of solvent was distilled off to remove the excess water. Then, 50 g of the toluene/2-propanol solvent mixture was added to the viscous system, followed by homogenization for 15 min at 80 °C. This cycle of evaporation and subsequent solvent addition was repeated as long as droplets of water were visible inside the toluene phase. The resulting gel was dried under a N₂-flow for several days at room temperature, followed by drying for 24 h at 100 °C.

The targeted degree of neutralization (DNₜ) is calculated using:

\[
DNₜ = \frac{\nu \cdot m_{M\text{Ac}} \cdot 1000}{M_{M\text{Ac}} \cdot \chi \cdot m_{\text{precursor}}} \times 100\%
\]

where \( \nu \) is the valency of the metal ion, \( m_{M\text{Ac}} \) is the mass of metal acetate added (g), \( M_{M\text{Ac}} \) is the molecular weight of the metal acetate (g/mol), \( m_{\text{precursor}} \) is the mass of MAn-g-EPM (g), and \( \chi \) is the acid content, which is calculated using:

\[
\chi = \frac{DG}{100} \cdot \frac{1000}{M_{M\text{An}}} \cdot 2 = 0.424 \, \text{equiv. acid/kg rubber}
\]

The samples are designated as \( M-DNₜ \), where \( M \) is the type of cation.

The materials were dried for 1 h at 170 °C under reduced pressure with a low N₂-flow prior to compression molding. Samples were compression molded between Teflon sheets for 20 min in a Collin press at 150 °C for EPM and MAn-g-EPM and at 200 °C for the ionomers.

### 2.2.3. Characterization techniques

**Fourier transform infrared (FTIR) spectroscopy.** Samples were measured on a BioRad Excalibur 3000 spectrometer equipped with a Specac Golden Gate attenuated total reflection (ATR) setup in a spectral range from 650 to 4000 cm⁻¹ at a resolution of 4 cm⁻¹, co-adding 35 scans. The experimental degree of neutralization (DNₑₓᵖ) is calculated from the absorbance of the anti-symmetric carbonyl (C=O) stretching vibration of the anhydride groups at 1785 cm⁻¹ \( (A_{1785}) \), using the absorbance of the methyl rocking vibration at 723 cm⁻¹ originating from the EPM backbone \( (A_{723}) \) as internal reference:

\[
DNₑₓᵖ = \left[ 1 - \left( \frac{A_{1785}}{A_{723}} \right)_{\text{ionomer}} \right] \cdot 100\%
\]

**Small-angle X-ray scattering (SAXS).** SAXS experiments were performed on (dried) compression-molded samples at the DUBBLE beamline (BM26B) at the European Synchrotron Radiation Facility (ESRF) in Grenoble (France). The data were collected using a 2D multiwire gas-filled detector with pixel array dimensions of 512 x 512. The detector was positioned at 2 m from the sample and the q-scale was calibrated using the positions of diffracted peaks from a standard silver behenate powder. The exposure time for each sample was 300 s and a wavelength of 1.2 Å was used. The experimental data were corrected for background scattering, i.e., subtraction of instrumental errors, and transformed into 1D-plots by azimuthal angle integration using the FIT2D program developed by Dr. Hammersley of ESRF. The resulting intensities were scaled to absolute intensity (in cm⁻¹) as a function of the scattering vector q using a Lupolen standard, which was measured via the same procedure. Finally, the data were converted to the normalized intensity per unit sample volume \( I(q)/[I(q)V] \) (in Å⁻³).
Dynamic mechanical thermal analysis (DMTA). Rectangular samples with dimensions of 10 x 3 x 1 mm were measured over a temperature range from -100 to 250 °C at a heating rate of 3 °C/min and a frequency of 1 Hz on a DMA Q800 (TA Instruments) with film tension clamps.

Hardness. The hardness was measured on 6 mm thick samples using a Shore A durometer according to ASTM D2240-91.

Tensile testing. Dumbbell-shaped tensile bars with dimensions of 35 x 2 x 1 mm and a parallel specimen length of 17.5 mm were punched from compression-molded films. Tensile tests were performed at room temperature with a constant speed of 0.5 mm/s on a Zwick Z010 tensile tester equipped with a force cell of 20 N using TestXpert v7.11 software. All materials were tested in at least five-fold.

Compression set (CS). Cylindrical samples with a diameter of 13 mm and a thickness of approx. 6 mm were compressed for 22 h between two parallel plates with a linear deformation of 25 % at room temperature (CS23) or at 70 °C (CS70). CS was determined after a relaxation time of 30 min at room temperature, using:

\[ CS = \left( \frac{t_n - t_i}{t_0 - t_i} \right) \times 100\% \]  

where \( t_n \) is the thickness of the spacer and \( t_0 \) and \( t_i \) are the initial and final sample thickness, respectively.

2.3. Results and discussion

2.3.1. Preparation of the ionomers

The MAn-g-EPM precursor is neutralized with KAc and ZnAc2 to different targeted degrees of neutralization (DNt). FTIR spectroscopy is a suitable technique to study the actual neutralization of MAn-g-EPM, since the position and the intensity of the carbonyl (C=O) stretching vibration bands change upon neutralization. The FTIR spectrum of the dried precursor MAn-g-EPM in Figure 2.1 shows two absorption bands characteristic for saturated, cyclic anhydrides at 1785 (strong) and 1865 cm\(^{-1}\) (weak), originating from the anti-symmetric and symmetric C=O stretching vibrations, respectively.\(^{26}\) No significant formation of intermolecular, acyclic anhydrides occurs during drying, since the characteristic bands around 1820 and 1750 cm\(^{-1}\) are not observed.\(^{26-28}\) The strong bands at 1460 and 1380 cm\(^{-1}\), which can be assigned to the overlapping anti-symmetric CH\(_3\)-bending and CH\(_2\)-scissoring and the symmetric CH\(_3\)-bending vibrations of the EPM backbone, respectively,\(^{26}\) remain unchanged upon neutralization. The absorption band at 723 cm\(^{-1}\), originating from the methyl rocking vibration of the EPM backbone, is used as internal reference. The anhydride bands decrease in intensity upon neutralization (Figure 2.1), while a new band at 1560 cm\(^{-1}\) appears for the K-ionomers and two overlapping bands around 1630 and 1560 cm\(^{-1}\) for the Zn-ionomers. These new bands are attributed to the C=O stretching vibration(s) of the metal-carboxylates.\(^{19,26,29}\) The difference in the (number of) carboxylate bands between the K- and Zn-ionomers is related to differences in the coordination around the metal cations.\(^{29}\)

Figure 2.2 shows the experimental DN (DN exp), which was determined from the FTIR spectra using Equation 2.4, as a function of DN t. All ionomers were dried for 1 h at 170 °C prior to the FTIR experiments to convert all remaining carboxylic acid groups, which were formed upon water addition during the neutralization step, back to anhydride groups. For the K-ionomers, DN exp is equal to DN t for DN t < 50 %, while a plateau value in DN exp around 50 % is observed for higher
DN<sub>t</sub>. Initially, the monovalent K<sup+</sup> cation neutralizes the first of the two adjacent carboxylic acid groups from the hydrolyzed anhydride groups. The formation of the K-carboxylate significantly decreases the reactivity of the second carboxylic acid group towards the weak base KAc<sup></sup>. Therefore, only one of the two adjacent carboxylic acid groups is neutralized with KAc, which explains the plateau in DN<sub>exp</sub> around 50 %. The further increase in the intensity of the carboxylate band at 1560 cm<sup>-1</sup> (Figure 2.1) for higher DN<sub>t</sub> is simply due to the presence of excess KAc, since KAc gives an absorption band around the same position. Almost full neutralization (DN<sub>exp</sub> > 90 %) is achieved upon neutralization with a stronger base (KOH), which supports this hypothesis.

![FTIR spectra for MAn-g-EPM and (a) K-ionomers and (b) Zn-ionomers with various DN<sub>t</sub> after drying for 1 h at 170 °C. The spectra are shifted vertically for clarity.](image)

During neutralization, each di-carboxylic acid moiety is converted to a combination of a carboxylate and a carboxylic acid, so no anhydride bands are observed in the FTIR spectra of the ionomers before drying (not shown here). After drying, anhydride bands are present at 1785 cm<sup>-1</sup> for the ionomers (Figure 2.1), which indicates that only intramolecular, cyclic anhydrides are formed and no intermolecular, acyclic anhydrides, since no absorption band at 1750 cm<sup>-1</sup> is observed.<sup>26-28</sup> These results show that a reorganization of ionic groups occurs, since only acyclic anhydrides can be formed from the carboxylate-carboxylic acid moieties. The formation of cyclic anhydrides requires the conversion of two carboxylate-carboxylic acid moieties into a di-carboxylate and a di-carboxylic acid, which subsequently ring-closes to anhydride. The removal of water from the system via the applied vacuum is the driving force for anhydride and, hence, di-carboxylate formation. This is supported by observations that no anhydride bands are present in the FTIR spectra (not shown here) after drying at 170 °C without vacuum. This demonstrates that dicarboxylates cannot be formed with weak bases with K<sup+</sup> cations without a proper driving force.

The situation is completely different for the Zn-ionomers. DN<sub>exp</sub> increases continuously, but remains significantly lower than DN<sub>t</sub>. A possible explanation for this behavior is that not all ZnAc<sub>2</sub> molecules are fully dissociated to Zn<sup>2+</sup>, but that ZnAc<sup><sup>+</sup></sup> complexes are formed as well.<sup>31</sup> Therefore, a fraction of the Zn-atoms may be present as ZnAc<sup>+</sup> cations inside the ionic aggregates, which coordinate with one carboxylate group only, resulting in a lower DN<sub>exp</sub> than DN<sub>t</sub>. The use of the weak base ZnAc<sub>2</sub> does not result in a plateau in DN<sub>exp</sub>, because the remaining positive charge on the
divalent Zn\textsuperscript{2+} cation after neutralization of the first carboxylic acid group repels the proton of the second carboxylic acid group, so a driving force for further neutralization exists. This is supported by the observation that drying of the Zn-ionomers for prolonged time at 100 °C under vacuum is already sufficient to convert all residual carboxylic acid groups to cyclic anhydrides.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure2.png}
\caption{The experimental degree of neutralization (DN\textsubscript{exp}) as a function of the targeted degree of neutralization (DN\textsubscript{th}) for the K- and Zn-ionomers. The dashed line indicates full neutralization.}
\end{figure}

### 2.3.2. Morphology of the ionomers

\textit{Small-angle X-ray scattering (SAXS).} The SAXS profile of the MAn-g-EPM precursor in Figure 2.3 shows a broad scattering peak around q = 0.06 Å\textsuperscript{-1}, which indicates the presence of microphase-separated aggregates. The driving force for this is the large polarity difference between the polar anhydride groups and the apolar EPM chain segments. A distinct scattering peak at comparable q-values was also observed for the low-molecular-weight MAn-g-EPM precursors from the previous studies, but only above a threshold value in DG of around 3 wt\%.\textsuperscript{21-23} The higher molecular weight for the current precursor may explain the distinct peak despite its lower DG (2.1 wt%).

A sharp scattering peak is observed in the SAXS profiles of the K-ionomers, while this peak is only evident as a shoulder for the Zn-ionomers (Figure 2.3). These results demonstrate that the aggregates remain intact upon neutralization with either cation and that the type of cation has a significant influence on the aggregate structure. The microphase separation is well defined for the monovalent K\textsuperscript{+}-cations, resulting in a sharp scattering peak. The use of the divalent Zn\textsuperscript{2+} cations results in a rather ill-defined aggregate structure, especially at lower DN, which is most probably related to the specific coordination behavior of Zn\textsuperscript{2+} cations with the di-carboxylate moieties of MAn-g-EPM. Grady et al. showed that Zn\textsuperscript{2+} cations do not coordinate to two carboxylates originating from the same hydrolyzed anhydride, because the resulting bond angles and distances would be too distorted.\textsuperscript{24} Therefore, the coordination around the Zn\textsuperscript{2+} cations requires two carboxylate groups from two different anhydrides, which may hinder the proximity of other Zn\textsuperscript{2+} cations and the process of aggregation to a certain extent, especially in view of the low DG of the MAn-g-EPM precursor. The absolute intensity of the scattering peak increases with increasing DN\textsubscript{th} for both the K- and Zn-ionomers, which is related to the higher electron density difference between the EPM matrix and the aggregates upon the introduction of ionic interactions.
Initially, the SAXS profiles were fitted with the Yarusso-Cooper (Y-C) model, which describes the ionic aggregates as spherical particles with radius $R_1$, surrounded by a restricted-mobility layer with radius $R_{CA}$. The particles are arranged in a liquid-like order with a distance of closest approach of $2R_{CA}$. The model uses four adaptable fitting parameters, namely $R_1$, $R_{CA}$, $V_p$ and $\Delta \rho$. $V_p$ is the average volume of a volume element containing one scattering particle, so $1/V_p$ is a measure for the number of aggregates per volume element. Finally, $\Delta \rho$ is the electron density difference between the scattering particles and the EPM matrix. This model was able to fit the SAXS patterns of the previously studied low-molecular-weight ionomers very well. Figure 2.4 shows that the Y-C model is not capable of fitting the SAXS profiles of the current ionomers appropriately, especially at higher $q$-values. Furthermore, the model does not fit the scattering peaks of the Zn-ionomers very well, which are present as a shoulder.

In order to improve the fits, polydispersity of the aggregate size was taken into account. The SAXS profiles of aggregates with polydisperse size distribution can be described by a model of spherical domains with a liquid-like order, as demonstrated in a previous paper by one of the authors. This model uses the analytical Percus-Yevick equation for the structure factor to represent the effect of interference of neighboring scattering centers. This adjustment improves the quality of the fits significantly, but the model still cannot describe the scattering at large $q$-values correctly (not shown here). The most probable explanation for this behavior is the presence of small scattering entities with sizes of a few Å randomly dispersed within the matrix, resulting in a non-constant background scattering from the matrix. In order to test this hypothesis, the anhydride groups of MAn-g-EPM were fully converted to N-alkylimide groups. The small difference in polarity of these groups with the EPM matrix prevents aggregate formation, as observed by the disappearance of the ionic peak. The SAXS profile of this material demonstrated a dependency of the intensity on $q^\alpha$ with $\alpha$ very close to unity, which suggests that some small structures are indeed present inside the matrix. It is reasonable to assume that the relatively apolar N-alkylimide groups can form small multiplets, due to the (small) polarity difference with the matrix. Therefore, a similar background shape is introduced in our model.
These adjustments result in the following equation for the scattered intensity, assuming a distribution of aggregate sizes and a non-constant matrix scattering:

$$\frac{I(q)}{I_{s}(q)V} = I_{\text{ionic}} + I_{\text{background}} = \Delta \rho^{2} \int_{0}^{\infty} V_{p}^2 \Phi(qR_{1}) \frac{1}{1 + \frac{24\eta G(2qR_{CA})}{2qR_{CA}}} N(R_{1})dR_{1} + Cq^{-\alpha}$$

where $V_{1}$ is $\frac{4}{3}\pi R_{1}^{3}$, $V_{CA}$ is $\frac{4}{3}\pi R_{CA}^{3}$, $\eta$ is the sphere volume fraction, $G(2qR_{CA})$ is a function of $q$, $R_{CA}$ and $\eta$, and $N(R_{1})$ is the aggregate size distribution. $C$ is a scaling constant for the background scattering and $\alpha$ is a factor close to unity in all cases. Finally, $\Phi(x)$ is a mathematical function:

$$\Phi(x) = 3 \frac{\sin x - x \cos x}{x^{3}}$$

This model provides excellent fits for the scattering profiles of the ionomers over the whole $q$-range (Figure 2.4), thereby confirming the presence of small scattering structures within the matrix, i.e., multiplets containing a few ionic groups, in addition to the (large) aggregates. The necessity of these adjustments of the Y-C model for the current ionomers and not for the previously studied low-molecular-weight ionomers is related to the lower number of ionic groups and the larger molecular weight between them for the current ionomers. This increases the probability that ionic groups cannot find an aggregate and that small multiplets are formed. It was shown for ionomers that the probability of completely-isolated ionic groups is almost zero, so the assumption of the presence of multiplets for the current ionomers seems reasonable.

The values of the relevant fitting parameters, i.e., $R_{1}$, $R_{CA}$, $V_{p}$ and $\Delta \rho$, are given in Table 2.1. For both the K- and Zn-ionomers, $R_{1}$ and $R_{CA}$ increase initially as a function of DN, followed by a decrease at higher DN. These effects are much larger for the K-ionomers, which is related to the better-defined aggregate structure and the different coordination mechanism. The neutralization of the carboxylic acid groups and the coordination around the metal cations causes the size of the aggregates ($R_{1}$) to increase, whereas tightening of the aggregates at higher DN explains the
subsequent decrease in size. The large increase in $R_{CA}$ for the K-ionomers compared to MAn-g-EPM is due to the strong aggregation, which anchors the corresponding chain segments tightly to the aggregates. This also explains the shift in the peak maximum to lower q-values (Figure 2.3), since it was shown that $R_{CA}$ is the main factor determining the peak position.\(^8,21\) The poorly-defined and, consequently, relatively weak aggregate structure for the Zn-ionomers explains the smaller increase in $R_{CA}$ and the small shift of the peak maximum (Figure 2.3). Note that the sizes of the aggregates are comparable to those of the low-molecular-weight ionomers from the previous work\(^23\) and that they are much larger than for other ionomers, such as sodium- or zinc-neutralized ethylene-methacrylic acid copolymers.

Table 2.1. Parameters from the best fit of Equation 2.6 for MAn-g-EPM and the K- and Zn-ionomers.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$R_1$ (Å)</th>
<th>$R_{CA}$ (Å)</th>
<th>$R_{CA}-R_1$ (Å)</th>
<th>$V_p$ (Å³)</th>
<th>$\Delta\rho$ ($e^-\cdotÅ^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MAn-g-EPM</td>
<td>17.3</td>
<td>44.9</td>
<td>27.6</td>
<td>3.9\cdot10^6</td>
<td>0.04</td>
</tr>
<tr>
<td>K-25</td>
<td>26.1</td>
<td>63.3</td>
<td>37.2</td>
<td>5.3\cdot10^6</td>
<td>0.08</td>
</tr>
<tr>
<td>K-50</td>
<td>23.4</td>
<td>56.1</td>
<td>32.7</td>
<td>3.3\cdot10^6</td>
<td>0.13</td>
</tr>
<tr>
<td>K-100</td>
<td>24.8</td>
<td>58.2</td>
<td>32.4</td>
<td>3.4\cdot10^6</td>
<td>0.33</td>
</tr>
<tr>
<td>Zn-25</td>
<td>20.0</td>
<td>47.9</td>
<td>27.9</td>
<td>2.7\cdot10^6</td>
<td>0.14</td>
</tr>
<tr>
<td>Zn-50</td>
<td>18.8</td>
<td>50.3</td>
<td>31.5</td>
<td>3.8\cdot10^6</td>
<td>0.16</td>
</tr>
<tr>
<td>Zn-100</td>
<td>16.9</td>
<td>49.6</td>
<td>32.7</td>
<td>3.3\cdot10^6</td>
<td>0.29</td>
</tr>
</tbody>
</table>

$V_p$ and, hence, the estimate of the number of aggregates per volume element ($1/V_p$) are prone to errors, because the presence of multiplets is not taken into account in the definition. However, their values remain more or less similar, indicating that the number of aggregates is not affected upon neutralization. The experimental values of $\Delta\rho$ are also not entirely correct, since $\Delta\rho$ is defined as the electron density difference between the matrix and the aggregates. The actual electron density of the matrix is increased due to the presence of the electron-dense multiplets, resulting in lower apparent values of $\Delta\rho$ than the true values. Despite these errors, $\Delta\rho$ increases with increasing DN compared to MAn-g-EPM, which indicates that the majority of the ionic groups are located inside the aggregates and not in the multiplets.

In conclusion, the current, adjusted Y-C model is capable of fitting the experimental SAXS results very well, as it assumes the presence of small scattering entities, i.e., multiplets, within the matrix in addition to the large aggregates. The current ionomers behave differently than the previously-studied low-molecular-weight ionomers, for which the original Y-C model could describe the SAXS patterns satisfactory. The model gives quantitative information about the sizes of the large aggregates, but unfortunately not for the multiplets, while some errors are made in the values of $\Delta\rho$ and $V_p$. However, this model can be used to explain certain trends, as will be shown for the effect of water absorption in the final section of this chapter.
Dynamic mechanical thermal analysis (DMTA). Figure 2.5 shows the storage moduli as a function of the temperature for EPM, MAn-g-EPM and the ionomers. The glass and rubber moduli and $T_g$ (around -50 °C) increase for MAn-g-EPM compared to the parent EPM, due to the presence of the microphase-aggregates. The higher rubber plateau modulus for MAn-g-EPM suggests that the aggregates act as multi-functional physical cross-links that increase the network density compared to the parent EPM. The rubber plateau is extended to higher temperatures, indicating that MAn-g-EPM starts to flow at higher temperatures than EPM.

Neutralization of MAn-g-EPM with either K$^+$ or Zn$^{2+}$ cations does not result in significant changes of the rubber plateau modulus, which indicates that the network density remains approximately constant. The SAXS experiments showed the presence of both large aggregates and small multiplets, with possibly different ratios depending on DN and the type of cation. However, the multiplets still contain several ionic groups (sizes in the order of a few Å) and act as multi-functional cross-links similar to the aggregates. The network density is unaffected by the type and the ratio of microphase-separated structures, most probably due to the fixed molecular weight between the functional groups, which governs the distance between the aggregates and/or the multiplets. This agrees with the more or less unaffected number of aggregates per volume element ($1/V_p$). The aggregates become stronger upon replacing the relatively weak polar interactions between the anhydride groups with ionic interactions and persist to higher temperatures, as indicated by the extended rubber plateau. The K-ionomers have a broader plateau than the Zn-ionomers, especially at lower DN, which confirms that the ionic associations are stronger for the K-ionomers. Finally, neutralization does not affect $T_g$, which may be due to the fact that only the aggregate strength is changed upon neutralization and that the network structure remains similar.

### 2.3.3. Mechanical properties of the ionomers

The previous section showed that microphase-separated aggregates are formed for the MAn-g-EPM precursor and the ionomers and that the aggregate strength is influenced by DN and the type of cation. This section presents the effects of these parameters on the mechanical properties. Figure 2.6 shows representative tensile curves for MAn-g-EPM and the ionomers, while Table 2.2 gives
average values of the hardness, the tensile strength (TS), the elongation at break (EB), the modulus at 200 % strain ($M_{200}$) and the compression sets (CS) at room temperature (CS$_{23}$) and at 70 °C (CS$_{70}$). CS is a measure for the elasticity and has a value of 0 % for an ideally elastic material and of 100 % for a fully plastic material.

![Figure 2.6. Representative tensile curves for MAn-g-EPM and the K- and Zn-ionomers.](image)

**Table 2.2. Mechanical properties of MAn-g-EPM and the K- and Zn-ionomers.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>$DN_t$ (%)</th>
<th>$DN_{exp}$ (%)</th>
<th>Hardness (Shore A)</th>
<th>TS (MPa)</th>
<th>EB (%)</th>
<th>$M_{200}$ (MPa)</th>
<th>CS$_{23}$ (%)</th>
<th>CS$_{70}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MAn-g-EPM</td>
<td>0</td>
<td>0</td>
<td>38</td>
<td>0.4</td>
<td>560</td>
<td>0.4</td>
<td>88</td>
<td>100</td>
</tr>
<tr>
<td>K-25</td>
<td>25</td>
<td>26</td>
<td>53</td>
<td>2.7</td>
<td>760</td>
<td>1.0</td>
<td>36</td>
<td>78</td>
</tr>
<tr>
<td>K-50</td>
<td>50</td>
<td>48</td>
<td>56</td>
<td>5.5</td>
<td>680</td>
<td>1.8</td>
<td>30</td>
<td>64</td>
</tr>
<tr>
<td>K-100</td>
<td>100</td>
<td>52</td>
<td>56</td>
<td>9.9</td>
<td>820</td>
<td>2.1</td>
<td>15</td>
<td>39</td>
</tr>
<tr>
<td>Zn-50</td>
<td>50</td>
<td>43</td>
<td>45</td>
<td>1.0</td>
<td>660</td>
<td>0.5</td>
<td>51</td>
<td>83</td>
</tr>
<tr>
<td>Zn-100</td>
<td>100</td>
<td>78</td>
<td>57</td>
<td>4.5</td>
<td>680</td>
<td>1.3</td>
<td>22</td>
<td>54</td>
</tr>
</tbody>
</table>

The properties of the ionomers are significantly affected upon neutralization. The hardness, TS and $M_{200}$ increase significantly for higher DN, while EB remains more or less constant and CS$_{23}$ and CS$_{70}$ decrease, indicating an improved elasticity. The K-ionomers have a higher hardness and $M_{200}$ and superior tensile properties and elasticity compared to the Zn-ionomers at similar $DN_t$. The properties of the K-100 ionomer are significantly improved compared to K-50, while FTIR experiments showed that both materials have a similar $DN_{exp}$ (Figure 2.2). This suggests that the excess (polar) KAc strengthens the ionic aggregates even further. Other studies also demonstrated a positive effect of an excess metal salt on the properties of ionomers.$^{36,37}$

Table 2.3 shows the mechanical properties of the Zn-ionomers based on the low-molecular-weight MAn-g-EPM precursor from the previous work with a comparable number of MAn-groups per chain.$^{21,23}$ Unfortunately, no K-ionomers based on this precursor were studied. The current K- and Zn-ionomers have a significantly higher TS and EB compared to the low-molecular-weight Zn-ionomers, except TS for the Zn-50 ionomer, while CS$_{23}$ and CS$_{70}$ are higher. For conventionally
cross-linked elastomers, an increase in the cross-link density generally results in a decrease of EB and CS and a maximum in TS.\textsuperscript{38,39} For the current ionomers, the network density is lower compared to the low-molecular-weight ionomers, since the molecular weight between the functional groups is larger, which explains the higher EB and CS for the current ionomers. A too high network density (beyond the aforementioned maximum) for the low-molecular-weight ionomers may explain the lower TS than for the current ionomers. The low-molecular-weight MAN-g-EPM precursor also has a higher hardness and lower CS\textsubscript{23} than the current precursor for the same reasons (Table 2.3).

Table 2.3. Mechanical properties of Zn-ionomers based on a MAN-g-EPM precursor with a M\textsubscript{n} of 11 kg/mol and a DG of 7.3 wt\%.\textsuperscript{21,23}

<table>
<thead>
<tr>
<th>DN (%)</th>
<th>Hardness (Shore A)</th>
<th>TS (MPa)</th>
<th>EB (%)</th>
<th>M\textsubscript{100} (MPa)</th>
<th>CS\textsubscript{23} (%)</th>
<th>CS\textsubscript{70} (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>42</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>48</td>
<td>100</td>
</tr>
<tr>
<td>10</td>
<td>44</td>
<td>1.2</td>
<td>270</td>
<td>0.5</td>
<td>44</td>
<td>92</td>
</tr>
<tr>
<td>25</td>
<td>45</td>
<td>1.9</td>
<td>270</td>
<td>0.6</td>
<td>37</td>
<td>65</td>
</tr>
<tr>
<td>50</td>
<td>47</td>
<td>1.2</td>
<td>170</td>
<td>0.6</td>
<td>26</td>
<td>43</td>
</tr>
<tr>
<td>75</td>
<td>50</td>
<td>1.4</td>
<td>150</td>
<td>0.8</td>
<td>21</td>
<td>35</td>
</tr>
<tr>
<td>100</td>
<td>52</td>
<td>1.7</td>
<td>140</td>
<td>1.2</td>
<td>16</td>
<td>31</td>
</tr>
</tbody>
</table>

*Only M\textsubscript{100} values were reported for this series of Zn-ionomers.*

It was concluded for the low-molecular-weight Zn-ionomers that the strength of the aggregates is the determining factor for the mechanical properties\textsuperscript{23}, which resulted in an increase in TS and modulus with increasing DN, while CS is improved. EB decreases with increasing DN for the low-molecular-weight ionomers, whereas it remains approximately constant for the current ionomers. It has been shown that higher EB and TS are obtained for ionomers compared to covalently cross-linked materials, due to the occurrence of “ion hopping”.\textsuperscript{40} Ionic groups are pulled out of the aggregates under deformation, which allows stress relaxation of the chain segments containing the ionic groups. The ionic groups can re-form ionic interactions upon entering another aggregate and bear stress again. This prevents premature failure of the material and results in higher EB and TS. If the ionic aggregates are extremely strong, as may be expected for the low-molecular-weight ionomers with relatively high DG, this hopping process hardly occurs. Instead, cavities are formed within the matrix once the stress level becomes too high, leading to macroscopic failure. This effect is more pronounced for stronger aggregates, i.e., higher DN, resulting in a decrease in EB with increasing DN. For the current ionomers, the aggregates are weaker than the extremely strong aggregates for the low-molecular-weight ionomers, thereby allowing hopping at any DN. The molecular weight between the functional groups is the same for the current ionomers, which may explain the constant EB with increasing DN for the current ionomers and the different trends than for the previous low-molecular-weight ionomers.

The effect of the type of cation on the mechanical properties was also studied during previous work, albeit for ionomers based on yet another MAN-g-EPM precursor.\textsuperscript{21} It was observed that the tensile
properties were better for monovalent cations, such as $K^+$, than for divalent cations, such as $Zn^{2+}$, although the differences were much smaller. The behavior of the MAN-g-EPM-based ionomers is different from general observations that Zn-ionomers have superior mechanical properties compared to ionomers with monovalent cations.\textsuperscript{37,41,42} For the current ionomers, the SAXS results demonstrated that a weaker aggregate structure is obtained for the Zn-ionomers than for the K-ionomers (Figure 2.3), which explains their poorer mechanical properties.

### 2.3.4. (Re)processability of the ionomers

SAXS experiments have consistently shown that ionic aggregates persist to temperatures as high as 300 °C.\textsuperscript{43-45} Indeed, the DMTA experiments (Figure 2.5) showed for the current ionomers that the rubber plateau and, hence, the ionic network persist to temperatures above 250 °C. However, ionomers can usually be melt processed at temperatures far below 300 °C under low-shear processing conditions, such as in compression molding.\textsuperscript{46,47} The current K- and Zn-ionomers can indeed be easily compression molded into smooth and homogeneous films at 200 °C, with the exception of the K-75 and K-100 ionomers, for which the extremely strong ionic interactions prevent sufficient flow. It is generally accepted that flow in ionomers proceeds via the aforementioned “ion-hopping” process, as originally proposed by Cooper.\textsuperscript{40} Ionic associations have a characteristic lifetime, which is the average time an ionic group resides within an ionic aggregate. After this average lifetime, the ionic group can leave the aggregate and “hop” between aggregates, thereby allowing stress relaxation of the chain segment containing the ionic group. Ionomers can flow via this mechanism without breaking all their ionic associations simultaneously.\textsuperscript{47}

The Zn-50 and K-50 ionomers were subjected to repeated cycles of cutting the samples into pieces and compression molding the pieces at 200 °C. Fully “healed” films are obtained after each cycle, up to four times, which demonstrates that the ionic cross-links are indeed thermoreversible. The FTIR spectra of the ionomers do not change upon reprocessing, indicating that no undesired side reactions occur. Figure 2.7 shows the effect of the number of reprocessing cycles on the tensile properties for the K-50 ionomer. The trends for Zn-50 are similar and are not shown here.

![Figure 2.7](image-url)  
**Figure 2.7.** The tensile properties (TS, $M_{200}$ and EB) for the K-50 ionomer as a function of the number of processing cycles.
TS, EB and M$_{200}$ do not change significantly within experimental reproducibility, which demonstrates that these ionomers are repeatedly processable via compression molding without changes in the mechanical properties. Reprocessing may be a problem for the K-75 and K-100 ionomers, since it is difficult to obtain homogeneous films for these materials.

### 2.3.5. Effect of water absorption

Ionomers are generally sensitive to water absorption, since the hydrophilic ionic groups tend to attract polar species, such as water molecules. Water is preferentially absorbed within the ionic aggregates and will mainly affect the aggregate structure.$^{42,48,49}$ Therefore, water absorption is expected to have a strong influence on the macroscopic properties of the ionomers, which is of great importance for practical applications. The general observation in ionomer literature is that high levels of water absorption have a plasticizing or even disruptive effect on the ionic aggregates and negatively influence the ionomer properties.$^{50,51}$

The current MAn-g-EPM precursor and some of the ionomers were immersed in water for several days, after which the changes in the SAXS profiles and the tensile properties were determined. The scattering peaks in the SAXS profiles of the K-25 and Zn-50 ionomers (Figure 2.8) increase in intensity after water absorption (‘wet’), but significant changes in the shape or position of the peak are not observed. The increase in intensity is related to the higher electron density difference with the EPM matrix upon incorporation of the polar water inside the aggregates. Fitting of the SAXS profiles with the adjusted Y-C model (not shown here) shows that the aggregate structures do not change significantly upon water absorption and that the aggregates do not swell (comparable values of R$_1$ and R$_{CA}$). A larger fraction of the background scattering (higher C in Equation 2.6) was necessary for the wet precursor and ionomers than for the dry materials to obtain the best fits. This indicates that the water mainly affects the multiplets and not the aggregates, which explains why the aggregate structure does not change a lot. This is not completely surprising, since the small multiplets are expected to be better accessible for water than the aggregates with their relatively large restricted mobility layer. Water absorption did significantly swell the aggregates for the low-molecular-weight ionomers from the previous work,$^{21}$ since the absence of multiplets forced water uptake by the aggregates themselves.

Figures 2.9 and 2.10 compare representative tensile curves for MAn-g-EPM and selected K- and Zn-ionomers, respectively, before and after water absorption, while the average values of TS, M$_{200}$ and EB are given in Table 2.4. The “wet” MAn-g-EPM has a higher TS and M$_{200}$, and a lower EB than the “dry” material (Figure 2.9). The anhydride groups open upon reaction with water to form two carboxylic acid groups, which are able to form hydrogen bonds. These hydrogen bonds strengthen the aggregates in MAn-g-EPM, resulting in substantially-changed mechanical properties. It can be assumed that hopping-like processes are possible for other types of physical interactions as well, such as polar interactions and hydrogen bonds. Hopping of hydrogen bonds may be more difficult compared to the relatively weak polar interactions between aggregates, which may explain the decreased EB compared to the dry material. The effects of water absorption are fully reversible, since the anhydride groups are formed again upon drying at 170 °C, resulting in properties similar to those of the “dry” MAn-g-EPM.
The effect of water absorption on the tensile properties is different for the K-ionomers than for the Zn-ionomers. The tensile properties of the K-ionomers do not change significantly (K-25) or even deteriorate (K-50) upon water saturation. For the Zn-ionomers on the other hand, the tensile properties are improved upon water absorption, as TS increases without significant changes in EB. Part of the absorbed water opens the residual anhydride rings of the ionomers to yield two carboxylic acid groups, similarly to the MAn-g-EPM precursor, which gives these non-neutralized groups the capability to form hydrogen bonds, especially at low DN. This explains the larger changes in the tensile properties for Zn-50 than for Zn-100 and the unaffected properties for K-25 compared to the deterioration for K-50.

The water resides within the polar multiplets and aggregates, where it participates in the coordination around the cations. The different effects of water on the K- and Zn-ionomers cannot be explained with the help of SAXS. Rather, changes in the local coordination around the metal
cations and, concomitantly, changes in the strength of the aggregates may be responsible for the observed differences. The excess of water can have two different effects, i.e., it improves the coordination around the cations or replaces carboxylate groups as ligand to plasticize the aggregates.\textsuperscript{48,50} The former effect may explain the improved properties of the Zn-ionomers upon water absorption, whereas the latter effect for the K-ionomers may overrule the positive effect of hydrogen bonding for K-25 and deteriorate the properties for K-50.

Table 2.4. Tensile properties of MAn-g-EPM and K- and Zn-ionomers before (“dry”) and after (“wet”) water absorption.

<table>
<thead>
<tr>
<th></th>
<th>“Dry” materials</th>
<th></th>
<th>“Wet” materials</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>TS (MPa)</td>
<td>EB (%)</td>
<td>$M_{200}$ (MPa)</td>
</tr>
<tr>
<td>MAn-g-EPM</td>
<td>0.4</td>
<td>560</td>
<td>0.4</td>
</tr>
<tr>
<td>K-25</td>
<td>2.7</td>
<td>760</td>
<td>1.0</td>
</tr>
<tr>
<td>K-50</td>
<td>5.5</td>
<td>680</td>
<td>1.8</td>
</tr>
<tr>
<td>Zn-50</td>
<td>1.0</td>
<td>660</td>
<td>0.5</td>
</tr>
<tr>
<td>Zn-100</td>
<td>4.5</td>
<td>680</td>
<td>1.3</td>
</tr>
</tbody>
</table>

2.4. Conclusions

In this work, ionic TPEs were obtained via the neutralization of hydrolyzed MAn-g-EPM to various DN and with K\textsuperscript{+} and Zn\textsuperscript{2+} cations, resulting in ionomers with di-carboxylate functionalities. The weak KAc base can only neutralize one of the two adjacent carboxylic acid groups, resulting in a plateau in DN\textsubscript{exp} around 50 \% neutralization, due to the lowered reactivity of the second carboxylic acid after neutralization of the first group. Neutralization of the second carboxylic acid is possible for the Zn-ionomers, due to the remaining positive charge on the Zn\textsuperscript{2+} cations, although the presence of some ZnAc\textsuperscript{+} cations prevents full neutralization.

Microphase-separated aggregates that act as physical cross-links are already present in the MAn-g-EPM precursor, resulting in an increased network density compared to the parent EPM. Neutralization with both cations increases the strength of the aggregates significantly compared to the precursor, which allows the ionic network to persist to higher temperatures, but does not affect the network density. The type of cation used for neutralization has an important influence on the morphology. A well-defined aggregate structure is formed for the K-ionomers, while the particular coordination behavior of Zn\textsuperscript{2+} cations with di-carboxylate moieties seems to disturb aggregate formation to a certain extent. The original Y-C model was adjusted to take into account both a polydisperse aggregate size distribution and a non-constant matrix scattering, which results in excellent fitting of the SAXS results. The necessity of the latter adjustment indicates that the microphase-separated structure not only contains the (large) aggregates, but also small, isolated multiplets, randomly dispersed within the EPM matrix, due to the relatively large molecular weight between functional groups. The model does not give quantitative information on the multiplets, while systematic errors are made in some of the fitting parameters ($V_p$ and $\Delta p$).
The hardness, tensile properties and elasticity change dramatically upon neutralization of the MAn-g-EPM precursor with increasing DN, with the larger changes for the K-ionomers than for the Zn-ionomers, due to the relatively weak microphase separation for the latter ionomers. The tensile properties of the current ionomers are significantly better than for the previously-studied low-molecular-weight ionomers, while the elasticity is somewhat less favorable. The K- and Zn-ionomers can be repeatedly compression molded into homogeneous films without affecting properties, which demonstrates that the ionic cross-links are truly thermoreversible. Exceptions are the K-ionomers with high DN, due to their extremely strong ionic associations. Water absorption improves the tensile properties of the MAn-g-EPM precursor and the Zn-ionomers, which may be advantageous in certain (outdoor) applications, but deteriorates the properties of the K-ionomers.

2.5. References

6 Marx, C. L.; Caulfield, D. F.; Cooper, S. L. Macromolecules 1973, 6, 344-353.
8 Yarusso, D. J.; Cooper, S. L. Macromolecules 1983, 16, 1871-1880.
25 It can be calculated from Equation 2.1 that the average number of MAn groups per EPM chain of this MAn-g-EPM (DG of 2.1 wt\% and $M_n$ of 40 kg/mol) is 8.5, which corresponds to an average molecular weight between functional groups of 4.7 kg/mol. In view of the molecular weight between entanglements ($M_e$) of EPM of around 2 kg/mol (Litvinov, V. Macromolecules 2006, 39, 8727-8741), it is expected that mostly free entanglements are present. Another important characteristic is that the anhydride groups are not fully randomly distributed onto the EPM backbone (Vangani, V.; Drage, J.; Mehta, J.; Mathew, A. K.; Duhamel, J. J. Phys. Chem. B 2001, 105, 4827-4839). These structural features will have a certain influence on the resulting morphologies and properties, but are not taken into account in this work, since the same starting material is used for all thermoreversible cross-linking methods and because these effects are difficult to quantify for only one MAn-g-EPM grade.


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44 Yarusso, D. J.; Cooper, S. L. Polymer 1985, 18, 371-378.


Chapter 3

Thermoreversible Cross-linking with Hydrogen Bonds (Combined with Ionic Interactions)*

The objective of this chapter was to thermoreversibly cross-link maleated ethylene/propylene copolymer (MAn-g-EPM) via a reaction with primary N-alkylamines of different length, either with an equimolar amount to obtain amide-acids, which form hydrogen bonds, or with an excess to obtain amide-salts, which form both hydrogen bonds and ionic interactions. Small-angle X-ray scattering (SAXS) experiments showed the presence of microphase-separated aggregates that act as physical cross-links for both the MAn-g-EPM precursor and all alkylamide-acids and -salts. The cross-linked materials can be repeatedly compression molded at 80 °C into homogeneous films without changes in the FTIR spectra, indicating that the (physical) cross-links are truly reversible. The tensile properties and elasticity are improved by converting MAn-g-EPM to the amide-acids, due to hydrogen bonding, and even further by converting the amide-acids to the amide-salts, because of the additional ionic interactions. Better tensile properties and elasticity are obtained for the octadecylamide-salts than for hexylamide-salts, which is explained by packing of the long alkyl-tails in a crystalline-like order for the former materials. This packing is rather ill-defined, since a scattering peak is only observed in the SAXS patterns for amide-salts with an excess of N-octadecylamine after compression molding at highly elevated temperatures. Irreversible imide formation occurs at high temperatures for all amide-acids and -salts, resulting in disappearance of the aggregates and, hence, in a dramatic decrease in the properties. Therefore, these temperatures should be avoided during (re)processing. Replacement of the excess of N-alkylamine with potassium hydroxide prevents imide formation at high temperatures and yields a further improvement in properties, but unfortunately also results in materials that are difficult to compression mold.

* This chapter is partly reproduced from: Sun, C. X.; van der Mee, M. A. J.; Goossens, J. G. P.; van Duin, M. Macromolecules 2006, 39, 3441-3449.
3.1. Introduction

Ionomers are a class of materials with thermoreversible cross-links. These are polymers that contain relatively small amounts (up to 15 mol percent) of ionic groups pendant to or incorporated in the polymer backbone. It is well established that the ionic groups tend to form microphase-separated ionic aggregates, dispersed in a non-ionic matrix, due to the large polarity difference between the ionic groups and the less polar backbone. The existence of these aggregates has been shown for many ionomers, mainly using small-angle X-ray scattering (SAXS). The melt processability of ionomers is related to the increased mobility of the ionic aggregates at elevated temperatures.

Hydrogen bonds can also be used for thermoreversible cross-linking, since they weaken significantly at elevated temperatures. The strength of a single hydrogen bonding donor and acceptor pair is limited, but it is quite simple to improve the strength of hydrogen bonds by combining them in multiple hydrogen bonding arrays. Several multiple hydrogen bonding arrays have been discussed in literature, including imide-diaminopyridine (DAD-ADA) arrays between melamine and three imide groups and the self-complementary phenylurazole, 2-ureido-4-pyrimidinone (UPy), (bis)urea, triazole and imidazolidone arrays.

This chapter presents our work on the thermoreversible cross-linking of maleated ethylene/propylene copolymer (MAn-g-EPM), using either hydrogen bonds or a combination of hydrogen bonds and ionic interactions with ammonium cations. MAn-g-EPM itself is unable to form hydrogen bonds, since the grafted maleic anhydride groups do not possess a hydrogen bonding donor. An equimolar amount of a primary N-alkyl amine is used to open the anhydride rings, thereby forming amide-acids which can form intermolecular hydrogen bonds to cross-link the rubber. Primary aliphatic amines are used for this purpose because of their fast reaction with cyclic anhydride groups in solution at low temperatures without the need for a catalyst. The reaction of cyclic anhydrides with amines has been extensively used for maleic anhydride copolymers, mainly poly(styrene-co-maleic anhydride), usually with the purpose to obtain maleimide copolymers. It is well known that amide-acids can undergo ring closure to form imides at elevated temperatures. In the current work, imide formation results in a loss of hydrogen bonding capability and, hence, a deterioration of properties is expected. This would severely limit the processing temperature window for these materials.

Amide-acids have a carboxylic acid functionality that can be neutralized to introduce additional ionic interactions. Primary amines are capable of neutralizing carboxylic acid groups, so the addition of an excess of primary amine to MAn-g-EPM results in the formation of amide-salts with ammonium cations, which form both hydrogen bonds and ionic interactions. Additionally, the presence of ionic interactions for the amide-salts may prevent imide formation.

Fourier transform infrared (FTIR) spectroscopy is used to study the conversion of MAn-g-EPM with N-alkylamines in the polar solvent tetrahydrofuran and to determine the chemical structures of the reaction products. The effects of the type and amount of primary amine on the morphology, as studied by SAXS, and the mechanical properties, i.e., hardness, tensile properties and compression set (CS), are investigated to obtain more insight in the cross-linking mechanism(s). The effect of the processing conditions on the possible imide formation is studied for the amide-acids and -salts, as
well as the effects on the morphology and mechanical properties. Finally, a different base for the conversion of amide-acid to amide-salt, namely potassium hydroxide, is used to explore the effect on the imide formation and the mechanical properties.

Scheme 3.1. Reaction scheme for the modification of MAn-g-EPM with N-alkylamines.

3.2. Experimental section

3.2.1. Materials

Maleated ethylene/propylene copolymer (MAn-g-EPM, 49 wt% ethylene, 49 wt% propylene, 2.1 wt% maleic anhydride (MAn), $M_n = 40$ kg/mol, $M_w = 90$ kg/mol) was provided by DSM Elastomers. It was dried for 1 h at 170 $^\circ$C under reduced pressure with a low N$_2$-flow prior to use to convert all carboxylic acid groups, formed upon hydrolysis, back to anhydride. N-propylamine (C$_3$, Aldrich), N-hexylamine (C$_6$, Aldrich), N-decylamine (C$_{10}$, Aldrich), N-tetradecylamine (C$_{14}$, Aldrich), N-octadecylamine (C$_{18}$, Aldrich), ammonia (NH$_4$OH in water, Aldrich), tetrahydrofuran (THF, Biosolve), acetone (Biosolve) and potassium hydroxide (KOH, Merck) were used as received.

3.2.2. Modification reactions

Typically, 10 g of MAn-g-EPM was dissolved in 100 g of THF at 60 $^\circ$C, after which the solution was cooled down to room temperature. In parallel, the required amount of N-alkylamine, calculated from the grafted maleic anhydride content, was dissolved in THF at room temperature. The N-alkylamine solution was added to the MAn-g-EPM solution and stirred for at least 1 h. The reaction products were precipitated in acetone and dried at 40 $^\circ$C under vacuum. NH$_3$-saturated MAn-g-EPM was obtained by exposing compression-molded films of MAn-g-EPM to a NH$_3$-atmosphere for several days at room temperature. For the modification with KOH, typically 5 g of hexylamide-acid, obtained via the modification of MAn-g-EPM with one equivalent of N-hexylamine, was dissolved in 50 g of a toluene/isopropanol mixture (90:10 w/w) at 60 $^\circ$C, after which the solution was cooled down to room temperature. In parallel, the required amount of
KOH was dissolved in isopropanol at room temperature. The KOH solution was added to the hexylamide-acid solution and stirred for at least 1 h. The materials were dried for several days at 40 °C under a N₂-flow.

The modified materials were compression molded between Teflon sheets for 20 min in a Collin press at 80 °C to avoid imide formation or at different temperatures and times to observe the effect on imide formation. The KOH-neutralized hexylamide-acids were compression molded for 20 min at 180 °C.

3.2.3. Nomenclature

The materials, to which one equivalent of N-alkylamine, based on the anhydride groups, was added, are named alkylamide-acids. The materials to which two or more equivalents of amine were added are named alkylamide-salts. The products of the alkylamide-acids and the NH₃-saturated MAn-g-EPM after compression molding at 180 °C are referred to as alkylimides and NH₃-imide, respectively.

3.2.4. Characterization techniques

Fourier transform infrared (FTIR) spectroscopy. Samples were analyzed on a BioRad Excalibur 3000 spectrometer equipped with a Specac Golden Gate attenuated total reflection (ATR) setup over a spectral range from 650 to 4000 cm⁻¹ at a resolution of 4 cm⁻¹, co-adding 35 scans.

Small-angle X-ray scattering (SAXS). SAXS experiments were performed on compression-molded samples at the DUBBLE beamline (BM26) at the European Synchrotron Radiation Facility (ESRF) in Grenoble (France). The data were collected using a 2D multiwire gas-filled detector with pixel array dimensions of 512 x 512. The detector was positioned at 2.5 m from the sample and the q-scale was calibrated using the positions of diffracted peaks from collagen of a rat-tail. The exposure time for each sample was 100 s and a wavelength of 1.2 Å was used. The experimental data were corrected for background scattering, i.e., subtraction of instrumental errors, and transformed into 1D-plots by azimuthal angle integration using the FIT2D program developed by Dr. Hammersley of ESRF.

Dynamic mechanical thermal analysis (DMTA). Rectangular samples with dimensions of 10 x 3 x 1 mm were measured over a temperature range from -100 to 200 °C at a heating rate of 3 °C/min and a frequency of 1 Hz on a DMA Q800 (TA Instruments) with film tension clamps.

Tensile testing. Dumbbell-shaped tensile bars with dimensions of 35 x 2 x 1 mm and a parallel specimen length of 17.5 mm were punched from compression-molded films. Tensile tests were performed with a constant speed of 0.5 mm/s at room temperature on a Zwick Z010 tensile tester equipped with a 20 N force cell using TestXpert v7.11 software. All materials were tested in at least five-fold.

Hardness. The hardness was measured on 6 mm thick samples using a Shore A durometer according to ASTM D2240-91.

Compression set (CS). Cylindrical samples with a diameter of 13 mm and a thickness of approx. 6 mm were compressed for 22 h between two parallel plates with a linear deformation of 25 % at room temperature (CS₂₅) or at 70 °C (CS₇₀). CS was determined after a relaxation time of 30 min at room temperature using:

\[ CS = \left( t_0 - t_i \right) / \left( t_0 - t_n \right) \times 100% \]  

(3.1)

where \( t_n \) is the thickness of the spacer and \( t_0 \) and \( t_i \) are the initial and final sample thickness, respectively.
3.3. Results and Discussion

3.3.1. Formation of the amide-acids and -salts

The amount of N-alkylamine added to MANg-EPM has an important influence on the structure of the functional groups, as it determines whether amide-acids or amide-salts are formed (Scheme 3.1). FTIR spectroscopy is a suitable technique to study these structures, since the position and the intensity of the carbonyl (C=O) stretching vibration bands of the grafted MAN groups change upon reaction. An overview of the assignment of the characteristic FTIR bands is given in Table 3.1. The FTIR spectrum of the dried MANg-EPM precursor in Figure 3.1 shows two absorption bands characteristic for saturated, cyclic anhydrides at 1785 cm\(^{-1}\) (strong) and 1865 cm\(^{-1}\) (weak), originating from the anti-symmetric and symmetric C=O stretching vibrations, respectively.\(^{19,21,28}\) The large bands at 1460 and 1380 cm\(^{-1}\), which are assigned to the overlapping anti-symmetric CH\(_3\)-bending and CH\(_2\)-scissoring and the symmetric CH\(_3\)-bending vibrations of the EPM backbone respectively,\(^{29}\) remain unchanged upon reaction and are used as internal reference.

<table>
<thead>
<tr>
<th>Wavenumber (cm(^{-1}))</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1865</td>
<td>(symmetric) anhydride C=O</td>
</tr>
<tr>
<td>1785</td>
<td>(anti-symmetric) anhydride C=O</td>
</tr>
<tr>
<td>1770</td>
<td>(symmetric) imide C=O</td>
</tr>
<tr>
<td>1710</td>
<td>carboxylic acid C=O</td>
</tr>
<tr>
<td>1705 (1715)(^*)</td>
<td>(anti-symmetric) imide C=O</td>
</tr>
<tr>
<td>1640 (1665)(^*)</td>
<td>amide C=O (amide-I)</td>
</tr>
<tr>
<td>1560</td>
<td>carboxylate C=O</td>
</tr>
<tr>
<td>1555</td>
<td>amide N-H (amide-II)</td>
</tr>
</tbody>
</table>

* Band positions are slightly shifted for the NH\(_3\)-saturated materials and are given in parentheses.

Three new absorption bands appear upon the addition of one equivalent of N-hexylamine to MANg-EPM, while the intensity of the anhydride bands decreases. The band at 1710 cm\(^{-1}\) is assigned to the C=O stretching vibration of the carboxylic acid and the bands at 1640 and 1555 cm\(^{-1}\) to the C=O (amide-I) and NH (amide-II) stretching vibrations of the amide, respectively,\(^{18,20,28}\) indicating that the hexylamide-acid is indeed formed. The FTIR spectra of the propyl-, decyl-, tetradecyl- and octadecylamide-acids are not shown here, because they are very similar in this spectral region.

The intensity of the band at 1710 cm\(^{-1}\), originating from the carboxylic acid, decreases upon addition of two equivalents of N-hexylamine, indicating the successful neutralization of the carboxylic acid groups and the formation of the amide-salt. The FTIR spectra do not change significantly upon addition of an excess of N-hexylamine (5 equivalents). The FTIR spectra for the octadecylamide-salts are similar in this spectral region and are not shown here. The spectrum of the NH\(_3\)-saturated MANg-EPM is comparable to that of the hexylamide-salts, except that the amide-I band is shifted to 1665 cm\(^{-1}\), due to the substitution of the alkyl-tail with a hydrogen atom.
3.3.2. Morphology of the amide-acids and -salts

The morphology has a significant influence on the final properties of the materials and is studied using small-angle X-ray scattering (SAXS). It was shown in Chapter 2 that microphase-separated anhydride-rich aggregates are already formed for the MAn-g-EPM precursor, due to the large polarity difference between the polar anhydride groups and the apolar EPM chains. Fitting of the SAXS profiles with the Yarusso-Cooper model\textsuperscript{30}, which proved to be the best model for ionomers based on other MAn-g-EPM grades\textsuperscript{31}, was shown to be far from straightforward (Chapter 2). Therefore, in the context of this chapter, no detailed evaluation of structural models for description of the SAXS profiles is performed, but the qualitative changes in the profiles are discussed.

Figure 3.2a shows that the SAXS patterns of the alkylamide-acids have a broad scattering peak around the same position as MAn-g-EPM. The intensity of the scattering peak increases for the propylamide-acid and subsequently decreases for the hexyl-, decyl- and octadecylamide-acids, while the position of the peak remains more or less the same. The introduction of longer apolar alkyl-tails into the aggregates decreases the electron density difference between the (initially) polar aggregates and the apolar EPM matrix, resulting in a decrease in scattered intensity. The restricted mobility layer surrounding the aggregates, which is the main parameter affecting the peak position\textsuperscript{30,31}, is not expected to increase in size in view of the relative weakness of the hydrogen bonds, resulting in an unaffected peak position.

Figure 3.2b shows that the scattered intensity increases upon the addition of a larger amount of N-hexylamine (two or five equivalents) to MAn-g-EPM, while the peak position remains constant. The same trends occur for the SAXS patterns of the octadecylamide-salts, which are not shown here. The increase in intensity is related to the increased electron density difference upon the introduction of ionic interactions to the aggregates. Again, the relative weakness of the current interactions, i.e., hydrogen bonds and ionic interactions with ammonium cations\textsuperscript{26}, may explain the unaffected position of the peak maximum.
3.3.3. Mechanical properties of the amide-acids and -salts

It was shown in the previous section that microphase-separated aggregates that act as physical cross-links are present for the MAn-g-EPM precursor. The aggregates prevail upon modification to amide-acid or -salt with an increased strength, which will significantly influence the properties. All amide-acids and amide-salts can be easily compression molded into homogeneous films at 80 °C. The octadecylamide-acid and octadecylamide-salt with 5 equivalents were subjected to repeated cycles of cutting the samples in small pieces followed by compression molding at 80 °C. After each cycle, up to four times, fully “healed” films were obtained, for which the FTIR spectra did not change, indicating that the cross-links for these materials are indeed thermoreversible.

Figure 3.3 shows representative tensile curves for the alkylamide-acids, while Table 3.2 shows average values of the hardness, the tensile strength (TS), the elongation at break (EB) and the modulus at 200% strain (M200) and the compression sets (CS) at room temperature (CS23) and at 70 °C (CS70) for all materials. All alkylamide-acids have significantly increased hardness and somewhat improved tensile properties compared to MAn-g-EPM, due to the additional hydrogen bonding. For materials containing (thermo)reversible interactions, CS is dependent on two (relaxation) processes, namely plastic deformation during compression, which does not occur for an ideal cross-linked rubber, and elastic recovery after removal of the compression. CS23 is rather poor for the amide-acids due to significant plastic deformation during compression, although it is somewhat improved compared to MAn-g-EPM, due to the introduction of hydrogen bonds. Plastic deformation becomes more prominent at elevated temperatures, which explains the CS70 values of approximately 100% for MAn-g-EPM and all amide-acids.

The length of the alkyl-tail of the primary amine has a significant influence on the tensile properties, as shown in Figure 3.3. However, the trends in tensile properties, i.e., C18 > C3 ≈ C14 > C10 > C6, do not simply follow the tail length of the primary amines, which is explained by the occurrence of two competing effects. The first effect is that longer apolar tails disturb the aggregate...
formation, resulting in poorer properties. This explains the decrease in properties for the hexylamide-acid compared to the propylamide-acid. Secondly, the longer tails may organize themselves in a crystalline-like order, which may result in improved properties. A better and stronger packing is expected for the longest alkyl-tails, which may explain the trend \( C_{18} > C_{14} > C_{10} > C_6 \). No sign of this ‘crystallization’ was observed in the SAXS patterns of the decyl- or octadecylamide-acid (Figure 3.2). Possible reasons could be that the packing of the tails is rather ill-defined, since the materials were never at high temperatures, or that the amount of amine added is too low to be visible in the SAXS pattern. Another possible explanation for the improved properties for longer alkyl-tails is that simply a higher force is required to pull longer alkyl-tails out of the aggregates. Similar trends occur for \( CS_{23} \) due to these competing effects, resulting in an initially poorer elasticity for increasing tail length, followed by an improvement for the longest amines.

![Figure 3.3. Tensile curves of MAn-g-EPM and different alkylamide-acids, viz. propyl- (C3), hexyl- (C6), decyl- (C10), tetradecyl- (C14) and octadecylamide-acid (C18).](image)

Figure 3.4 and Table 3.2 show that the tensile properties are improved for the hexyl- and octadecylamide-salts with two and five equivalents compared to the respective amide-acids, which is related to the introduction of ionic interactions besides the hydrogen bonds (Scheme 3.1), resulting in stronger and more stable cross-linking units. A further excess of amine is incorporated in the aggregates as well, where it may strengthen the aggregates via polar interactions to yield even better properties for the amide-salts with five equivalents.

A comparison of the hexyl- and octadecylamide-salts in Figure 3.4 shows that the tensile properties are significantly better for the octadecylamide-salts. The minor improvement in tensile properties and the unaffected \( CS_{23} \) (Table 3.2) for the hexylamide-salts compared to the hexylamide-acid is related to the disturbing effect of the apolar hexyl-tails on the aggregate formation, which overrules the positive effect of the additional ionic interactions to a large extent. The larger improvement in tensile properties and \( CS_{23} \) for the octadecylamide-salts may be related to the packing of the long octadecyl-tails in a crystalline-like fashion within the aggregates, which may strengthen the aggregates. Again, no sign of this organization is visible in the SAXS patterns for the octadecylamide-salts (Figure 3.2). \( CS_{70} \) is (almost) 100% for all alkylamide-salts, which is related to the relative weakness of ionic interactions with (alkyl)ammonium cations. The aforementioned
packing of octadecyl-tails cannot have a positive influence on CS\textsubscript{70} for the octadecylamide-salts, since the experimental temperature exceeds the melting point of N-octadecylamine (50-54 °C).

**Table 3.2.** Mechanical properties of N-alkylamine-modified MAn-g-EPM.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Hardness (Shore A)</th>
<th>TS (MPa)</th>
<th>EB (%)</th>
<th>$M_{200}$ (MPa)</th>
<th>CS\textsubscript{23} (%)</th>
<th>CS\textsubscript{70} (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MAn-g-EPM (dried)</td>
<td>38</td>
<td>0.4</td>
<td>560</td>
<td>0.4</td>
<td>88</td>
<td>100</td>
</tr>
<tr>
<td>propylamide-acid</td>
<td>55</td>
<td>1.3</td>
<td>610</td>
<td>1.0</td>
<td>56</td>
<td>99</td>
</tr>
<tr>
<td>hexylamide-acid</td>
<td>56</td>
<td>1.1</td>
<td>790</td>
<td>0.8</td>
<td>65</td>
<td>100</td>
</tr>
<tr>
<td>decylamide-acid</td>
<td>54</td>
<td>1.3</td>
<td>890</td>
<td>0.9</td>
<td>68</td>
<td>100</td>
</tr>
<tr>
<td>tetradecylamide-acid</td>
<td>56</td>
<td>1.4</td>
<td>800</td>
<td>1.0</td>
<td>67</td>
<td>100</td>
</tr>
<tr>
<td>octadecylamide-acid</td>
<td>56</td>
<td>1.7</td>
<td>760</td>
<td>1.1</td>
<td>60</td>
<td>98</td>
</tr>
<tr>
<td>hexylamide-salt (2 eq.)</td>
<td>56</td>
<td>1.4</td>
<td>760</td>
<td>0.9</td>
<td>65</td>
<td>100</td>
</tr>
<tr>
<td>hexylamide-salt (5 eq.)</td>
<td>58</td>
<td>2.0</td>
<td>870</td>
<td>1.0</td>
<td>64</td>
<td>100</td>
</tr>
<tr>
<td>octadecylamide-salt (2 eq.)</td>
<td>56</td>
<td>2.9</td>
<td>490</td>
<td>1.8</td>
<td>33</td>
<td>100</td>
</tr>
<tr>
<td>octadecylamide-salt (5 eq.)</td>
<td>61</td>
<td>4.8</td>
<td>620</td>
<td>2.1</td>
<td>25</td>
<td>95</td>
</tr>
<tr>
<td>NH\textsubscript{3}-saturated MAn-g-EPM</td>
<td>54</td>
<td>4.6</td>
<td>480</td>
<td>2.0</td>
<td>24</td>
<td>60</td>
</tr>
<tr>
<td>NH\textsubscript{3}-saturated MAn-g-EPM\textsuperscript{*}</td>
<td>-</td>
<td>3.7</td>
<td>520</td>
<td>1.7</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>propylimide</td>
<td>35</td>
<td>0.1</td>
<td>410</td>
<td>0.2</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>octadecylimide</td>
<td>37</td>
<td>0.1</td>
<td>370</td>
<td>0.2</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>NH\textsubscript{3}-imide</td>
<td>49</td>
<td>0.7</td>
<td>440</td>
<td>0.7</td>
<td>76</td>
<td>100</td>
</tr>
</tbody>
</table>

\textsuperscript{*} Sample exposed to normal atmosphere for 5 days.

The explanation above is supported by results obtained from DMTA. Figure 3.5 shows the storage modulus as a function of the temperature for MAn-g-EPM, the octadecylamide-acid and -salts and the octadecylimide. The large transition around -50 °C for all materials is the glass transition temperature of the EPM backbone. The transition around 55 °C for the octadecylamide-salts is attributed to disordering of the packed octadecyl-tails (i.e., melting), since this is close to the melting point of pure N-octadecylamine, while obviously no such transition is observed for the hexylamide-salts (not shown here). The transition at 0 °C is caused by melting of traces of absorbed water. The increase in modulus for the octadecylamide-salt with five equivalents around 120 °C may be related to reorganization within the aggregates.

Figure 3.5 further shows that the rubber plateau modulus, which is a direct measure for the network density, is slightly increased for the octadecylamide-acid and the -salts compared to MAn-g-EPM, indicating only a small increase in the network density upon cross-linking, whereas the tensile and elastic properties are significantly different. This suggests that the properties of these materials are not determined by the network density, as is the case for conventionally cross-linked rubbers,\textsuperscript{32,33} but by the aggregate strength, which is increased due to hydrogen bonding and ionic interactions.
Figure 3.4. Tensile curves of MAn-g-EPM (a) modified with different amounts of N-hexylamine (C₆) and saturated with NH₃ (directly out of NH₃-atmosphere and after exposure to normal atmosphere for 5 days) and (b) modified with different amounts of N-octadecylamine (C₁₈).

Figure 3.5. Storage modulus as a function of the temperature for MAn-g-EPM, MAn-g-EPM modified with different amounts of N-octadecylamine (C₁₈) and octadecylimide.

NH₃-saturated MAn-g-EPM has better tensile properties and CS compared to the alkylamide-salts, due to the larger extent of hydrogen bonding and the higher polarity of NH₃ compared to N-alkylamines. However, a main concern is the high volatility of (the excess of) NH₃, which evaporates out of the rubber over time. Figure 3.4 shows that the tensile properties are already significantly decreased after five days in normal atmosphere.

At this point, it is concluded that the tensile properties are significantly improved when MAn-g-EPM is modified with primary amines, especially in the case of large amounts of N-octadecylamine and NH₃. However, imide formation may occur for the amide-acids and possibly the amide-salts at elevated temperatures. The next sections deal with the influence of (high temperature) compression molding on the structure and the properties of both the amide-acids and the amide-salts.
3.3.4. Imide formation for the amide-acids

Figure 3.6 shows the FTIR spectra for the hexylamide-acid after compression molding for 20 min at temperatures varying from 80 to 160 °C. The spectra do not change significantly up to 120 °C, indicating that the amide-acid is still present. A sharp band at 1705 cm⁻¹ appears at 140 °C and higher, which is assigned to the anti-symmetric C=O stretching vibration of the imide, while the amide bands at 1640 and 1555 cm⁻¹ decrease in intensity. This indicates that significant imide formation (according to Scheme 3.1) occurs at temperatures of 140 °C and higher for the hexylamide-acid, which is more or less complete at 160 and 180 °C. Unfortunately, a quantitative analysis of the imide formation is difficult, due to the significant overlap of the bands for the carboxylic acid around 1710 cm⁻¹ and the imide around 1705 cm⁻¹. The (weak) symmetric C=O stretching vibration band of the imide, usually present at 1770 cm⁻¹, is not observed here due to overlap with the anti-symmetric C=O stretching vibration of the residual anhydride groups at 1785 cm⁻¹. Formation of intermolecular, acyclic imides does not occur significantly, since no additional band around 1670-1690 cm⁻¹ is observed. In addition, the materials are fully soluble in THF after imide formation, indicating the absence of intermolecular linkages. A new band appears at 1400 cm⁻¹ for the alkylimides, which is most probably originating from the C-N stretch of the imide ring. Full imide formation occurs also for the propyl- and octadecylamide-acids after compression molding at 180 °C (not shown here).

Additional experiments showed that the FTIR spectra remain unchanged for the hexylamide-acid after compression molding at 80 and 100 °C, even after 4 h, indicating that no imide formation takes place at these temperatures. However, some imide formation occurs after compression molding for 1 h at 120 °C, which becomes more extensive after longer times. Therefore, temperatures of 120 °C and higher should be avoided during processing of the amide-acids to avoid imide formation.

The SAXS patterns of the imides in Figure 3.7 show that no aggregates exist in the propyl- and octadecylamide materials. The formation of the alkylimide drastically decreases the polarity of the functional groups compared to the amide-acid and, hence, the tendency for microphase separation, resulting in the disappearance of the aggregates for the alkylimides. As a consequence, the network

![Figure 3.6. FTIR spectra of hexylamide-acid after compression molding for 20 min at different temperatures. The spectra are shifted vertically for clarity.](image-url)
density is significantly decreased, resulting in a significant drop in rubbery plateau modulus for the octadecylimide compared to the octadecylamide-acid, as shown in Figure 3.5. The tensile properties of the imides (Figure 3.8 and Table 3.2) decrease to a level even below the MAn-g-EPM precursor, due to the disappearance of the aggregates and the absence of cross-linking mechanisms. CS$_{23}$ is 100 % for the alkylimides, indicating that the materials do not behave elastically anymore.

![Figure 3.7](chart.png) **Figure 3.7.** SAXS patterns of MAn-g-EPM and propyl- (C$_3$) and octadecylimide (C$_{18}$). The patterns are shifted vertically in steps of 0.2 a.u. for clarity.

![Figure 3.8](chart.png) **Figure 3.8.** Tensile curves of MAn-g-EPM and different imides, viz. NH$_3$-, propyl- (C$_3$) and octadecylimide (C$_{18}$), after compression molding at 180 °C.

### 3.3.5. Imide formation for the amide-salts

Figure 3.9 shows the FTIR spectra of the hexyl- and octadecylamide-salts with two and five equivalents and the NH$_3$-saturated MAn-g-EPM after compression molding at 180 °C. The disappearance of the amide-I and amide-II bands at 1645 and 1555 cm$^{-1}$, respectively, and the appearance of a new sharp band at 1705 cm$^{-1}$ indicate that full imide formation occurs for the hexylamide-salts and the NH$_3$-saturated MAn-g-EPM, which is further referred to as NH$_3$-imide. The (imide) band for the NH$_3$-imide is observed at a higher wavenumber (1715 cm$^{-1}$) than for the alkylimides, due to the higher polarity of the hydrogen-imide. These results indicate that the ionic interactions for the amide-salts are not strong enough to prevent imide formation at elevated temperatures, which agrees with the CS$_{70}$ of around 100 % for these materials.

Three new bands appear at 1645, 1590 and 1565 cm$^{-1}$ for the octadecylamide-salts, while the band at 1460 cm$^{-1}$, which originates from the CH$_3$-bending and CH$_2$-scissoring vibrations of the aliphatic EPM chains and octadecyl-tails, splits up into multiple bands. The intensity of the imide band is significantly lower for the octadecylamide-salt with five equivalents than for the other materials.

Figure 3.10 shows the FTIR spectra for samples of the octadecylamide-salt with five equivalents after compression molding at various temperatures. The spectra do not change significantly after compression molding at temperatures up to 120 °C, indicating that the amide-salt prevails. The appearance of the new bands, the splitting of the band at 1460 cm$^{-1}$ and the imide formation start to occur after compression molding at temperatures of 140 °C and higher.
The splitting of the band at 1460 cm\(^{-1}\) is attributed to the packing of the octadecyl-tails in a crystalline-like order having an all-trans conformation, such as observed for e.g., polyethylene.\(^{37-39}\) The bands at 1645, 1590 and 1565 cm\(^{-1}\) also appear for the pure N-octadecylamine after heating to 60 °C (solid-solid transition), while they disappear again upon melting after heating to 80 °C. Heating to 80 °C of the octadecylamide-salt with five equivalents that was compression molded at 160 °C results in the disappearance of these bands as well. This suggests that these bands originate from the excess of N-octadecylamine with an ordered, crystalline-like structure. Additionally, the band at 1460 cm\(^{-1}\) regains its original shape after heating at 80 °C, which is related to the disappearance of the ordered structure. The intensity of the imide band at 1705 cm\(^{-1}\) increases after heating to the same level as for the hexylamide-salts compression molded at 180 °C, indicating that full imide formation occurs for the octadecylamide-salts as well. The FTIR spectra are scaled using the band at 1460 cm\(^{-1}\), which is prone to changes. The scaling is therefore not correct for the octadecylamide-salts, resulting in a lower observed intensity of the imide band than it actually is.

![Figure 3.9](image1.png)

**Figure 3.9.** FTIR spectra of the hexyl- (C\(_6\)) and octadecylamide-salts (C\(_{18}\)) and NH\(_3\)-saturated MAn-g-EPM after compression molding at 180 °C. Spectra are shifted vertically for clarity.

![Figure 3.10](image2.png)

**Figure 3.10.** FTIR spectra of the octadecylamide-salt with five equivalents after compression molding at different temperatures. The spectra are shifted vertically for clarity.

The SAXS patterns of the amide-salts after compression molding at 180 °C in Figure 3.11 show that the aggregates disappear for all alkylamide-salts due to the imide formation, but that aggregates are still present for the NH\(_3\)-imide. The higher polarity of the NH\(_3\)-imide groups compared to the alkylimides and its ability to form hydrogen bonds enable aggregate formation similar to MAn-g-EPM. The NH\(_3\)-imide has somewhat better mechanical properties than MAn-g-EPM, as shown in Figure 3.8 and Table 3.2, due to the presence of hydrogen bonds. However, the properties of the NH\(_3\)-imide are significantly decreased compared to the NH\(_3\)-saturated MAn-g-EPM.

Figure 3.11 further shows that a new sharp peak appears for the octadecylamide-salt with five equivalents around q = 0.12 Å\(^{-1}\), corresponding to a d-spacing of 54 Å. This suggests that the octadecyl-tails pack together in a bi-layered structure. This peak is not observed for the hexylamide-salts, for which no packing of the chains is expected, and the octadecylamide-salt with two equivalents, for which the amount of octadecyl-tails is probably too low to be visible. The SAXS
patterns of samples of the octadecylamide-salt with five equivalents after compression molding at various temperatures in Figure 3.12 show that the broad peak centered around at $q = 0.06 \text{ Å}^{-1}$ shifts to lower $q$-values for increasing temperatures, indicating changes in the aggregate structure. The aggregates disappear for the samples compression-molded at 160 and 180 ºC, due to imide formation. The sharp peak at $q = 0.12 \text{ Å}^{-1}$ appears after compression molding at 140 ºC or higher. These results suggest that both a certain amount of octadecyl-tails and high temperatures are required for a well-ordered packing of the long alkyl-tails. The bi-layered packing of the octadecyl-tails implies that the NH$_2$-end groups are directed towards each other. The bands at 1645, 1590 and 1560 cm$^{-1}$ are believed to originate from interactions or even (reversible) reactions between NH$_2$-groups within this structure, such as carbamic acid formation with CO$_2$.

**Figure 3.11.** SAXS patterns of the hexyl- (C$_6$) and octadecylamide-salts (C$_{18}$) and the NH$_3$-saturated MAn-g-EPM (NH$_3$-imide) after compression molding at 180 ºC. Patterns are shifted vertically in steps of 0.2 a.u. for clarity.

**Figure 3.12.** SAXS patterns of the octadecylamide-salt with five equivalents after compression molding at different temperatures. The patterns are shifted vertically in steps of 0.2 a.u. for clarity.

**Figure 3.13.** Tensile curves of the octadecylamide-salt with five equivalents after compression molding at different temperatures.
Figure 3.13 shows the tensile properties of the octadecylamide-salt with five equivalents after compression molding at various temperatures. The properties deteriorate slightly for the samples compression-molded at 100 and 120 °C, for which the amide-salt is still present. This decrease is most probably related to changes in the aggregate structure. A significant decrease in properties occurs for the sample compression-molded at 140 °C, for which some imide formation occurs. The properties of the samples compression-molded at 160 and 180 °C are even poorer than for the MAng-EPM precursor, because the aggregates disappear completely, similarly to the octadecylimide (Figure 3.8). The packing of the octadecyl-tails still occurs, as shown with SAXS (Figure 3.12), but does not have a positive influence on the properties.

3.3.6. Prevention of imide formation

It was shown that imide formation at elevated temperatures results in a dramatic decrease in properties (Figure 3.8). The introduction of additional ionic interactions for the alkylamide-salts could not prevent the imide formation, since the ionic interactions in the amide-salts are not strong enough. Weiss et al.26 showed for sulfonated polystyrene ionomers that ionic interactions are significantly stronger for metal cations than for primary (alkyl)ammonium cations, while Xie et al.27 demonstrated the same for sulfonated butyl rubbers. Therefore, potassium hydroxide (KOH) was used for the neutralization of the carboxylic acid group of the hexylamide-acid, instead of a second (or higher) equivalent of N-hexylamine, to study whether stronger ionic interactions with potassium cations can prevent imide formation. Two different amounts of KOH were added: one equivalent, i.e., the stoichiometric amount to neutralize all carboxylic acid groups of the hexylamide-acid, and two equivalents.

Figure 3.14 shows that the carboxylic acid band at 1710 cm⁻¹ does not completely disappear for the material with one equivalent of KOH after drying, indicating that some residual hexylamide-acid groups are present. A new band appears at 1560 cm⁻¹, which is assigned to the carboxylate.29,40,41 A small band at 1705 cm⁻¹ is visible after compression molding at 180 °C, indicating that (only) a limited amount of imide is formed. The dried material contains some residual hexylamide-acid groups, which are easily converted to imides upon heating (Figure 3.6). The carboxylic acid band is even lower in intensity for the material modified with two equivalents of KOH after drying, which shows that almost all amide-acid groups are converted to amide-salt. The FTIR spectrum remains unaffected after compression molding, indicating that imide formation is fully suppressed.

The tensile properties of the KOH-neutralized hexylamide-acids in Figure 3.15 are significantly better than for the hexylamide-salt with five equivalents. The material with two equivalents of KOH has better properties than the material with one equivalent, which indicates that the excess of KOH further strengthens the aggregates. The ionic interactions with potassium are indeed much stronger than those with ammonium cations,26,27 resulting in both prevention of imide formation and better mechanical properties. A main disadvantage with this approach is that is becomes rather difficult to obtain homogeneous films of these materials after compression molding, even at temperatures of 200 °C, which gives these materials a processing disadvantage.
Figure 3.14. FTIR spectra of KOH-neutralized hexylamide-salt after drying (RT) and after compression molding at 180 °C (CM). The spectra are shifted vertically for clarity.

Figure 3.15. Tensile curves of hexylamide-acid neutralized with KOH and the hexylamide-salt with five equivalents.

3.4. Conclusions

In this work, MAn-g-EPM was thermoreversibly cross-linked using various amounts of different N-alkylamines. The addition of one equivalent of N-alkylamine results in the formation of amide-acids, which form hydrogen bonds. An excess of amine (two equivalents or more) neutralizes the carboxylic acid groups of the amide-acids, thereby forming amide-salts, which combine hydrogen bonds and ionic interactions. Microphase-separated aggregates that act as physical cross-links are formed for the MAn-g-EPM precursor and the amide-acids and -salts. The materials can be repeatedly compression molded at 80 °C into homogeneous films without changes in the FTIR spectra, which indicates that the physical cross-links are indeed reversible.

The tensile properties and the elasticity of the amide-acids are improved compared to MAn-g-EPM, due to the presence of hydrogen bonds within the aggregates. The trend of an initial small deterioration for longer N-alkylamines, followed by an improvement for the longest ones is explained by two competing effects, namely disruption of the aggregates by longer apolar alkyl-tails and packing of long tails in a crystalline-like order. This packing is apparently rather ill-defined, since no sign of this packing is visible in the SAXS patterns. The properties improve significantly for the amide-salts, due to the presence of additional ionic interactions, with better properties for the octadecylamide-salts compared to the hexylamide-salts. The alkylamide-acids and -salts do not behave elastically anymore at 70 °C, indicating that the hydrogen bonds and/or ionic interactions are relatively weak at elevated temperatures. The best properties are obtained for the NH₃-saturated MAn-g-EPM, but a major problem is the high volatility of NH₃, which results in a significant drop in tensile properties already after 5 days in normal atmosphere.

A major concern is the occurrence of imide formation for all amide-acids and amide-salts after compression molding at temperatures of 120 °C and higher, resulting in the disappearance of the aggregates and poor mechanical properties. The relatively weak ionic interactions with ammonium
cations could not prevent imide formation for the amide-salts. Therefore, these temperatures should be avoided during (re)processing. A new sharp scattering peak is observed in the SAXS patterns of the octadecylamide-salt with five equivalents after compression molding at temperatures of 140 °C and higher, which indicates packing of octadecyl-tails in a bi-layered structure. Imide formation can be prevented by using a different base, i.e., KOH, for the neutralization of the carboxylic acid group of the hexylamide-acid. The mechanical properties are significantly improved for the KOH-neutralized materials compared to the hexylamide-salts, due to the stronger ionic interactions with metal cations, which also make these materials difficult to compression mold.

3.5. References

Chapter 4

Thermoreversible Cross-linking with Multiple Hydrogen Bonding Arrays

The objective of this chapter was to compare several multiple hydrogen bonding arrays, i.e., imide-diaminopyridine, triazole (ATA), imidazolidone (IM), (bis)urea and 2-ureido-4-pyrimidone (UPy) arrays as well as “non-organized” hydrogen bonds for the thermoreversible cross-linking of a maleated ethylene/propylene copolymer (MAN-g-EPM). The arrays are introduced via the reaction of their amine functionalities with the anhydride groups of MAN-g-EPM. Microphase-separated aggregates that act as physical cross-links exist in all hydrogen-bonded materials as well as in the MAN-g-EPM precursor. The network density is not changed upon the introduction of hydrogen bonds, which suggests that the hydrogen bonds are solely present within the aggregates and mainly improve the aggregate strength. The rubber properties are improved in the following order: MAN-g-EPM < “non-organized” << ATA < IM < urea < bisurea < UPy. Specific stacking of the urea and bisurea groups within the aggregates leads to an improved elasticity at elevated temperatures compared to the other materials. All materials with hydrogen bonds can be repeatedly compression molded at the respective processing temperature without chemical changes, indicating that the hydrogen bonds are indeed of thermoreversible nature. Finally, Mooney viscometry suggested that the “non-organized” hydrogen bonds and the ATA and IM arrays yield materials are reprocessable via thermoplastic processing techniques, such as extrusion or injection molding, whereas the (bis)urea and UPy materials are less suitable for these techniques.
4.1. Introduction

Hydrogen bonds can be used for thermoreversible cross-linking, since they weaken significantly at elevated temperatures. The strength of a single hydrogen bonding donor and acceptor pair is limited, but it is relatively easy to improve the strength by combining hydrogen bonds in arrays. Several hydrogen bonding arrays have been used to obtain reversible polymer networks. Stadler and co-workers reported on the modification of poly(butadiene) with grafted phenylurazole groups, which are capable of forming double hydrogen bonding dimers (see Figure 1.3a). The properties were improved in comparison to the non-modified poly(butadiene), but not to a large extent, due to the relatively weak association constant of phenylurazole groups (K = 10^2 L/mol in chloroform). Two double hydrogen bonding arrays per functional group were obtained via the addition of a carboxylic acid group to the phenylurazole, using 4-carboxyphenylurazole units, resulting in impressive mechanical properties, due to the formation of large assemblies of associated 4-carboxyphenylurazole groups (see Figure 1.3b). Lange et al. obtained soluble and, hence, reversible polymer networks using imide-diaminopyridine (DAD-ADA) triple hydrogen bonding arrays between melamine and three imide groups of styrene-maleimide copolymers (see Figure 1.4). The materials displayed a rheological behavior similar to covalent networks, although the weak association constant (K = 10^2 L/mol in chloroform) limited the properties.

Sijbesma, Meijer and co-workers developed a self-complementary quadruple hydrogen bonding array (DDAA), i.e., the 2-ureido-4-pyrimidone (UPy) unit, which forms extremely strong dimers with an association constant K of 6x10^7 L/mol in chloroform (see Figure 1.5). Reversible polymer networks were obtained from low-molecular-weight poly(ether) polyols functionalized with three UPy groups, with acceptable mechanical properties and a rheological behavior typical of covalent networks. Two research groups reported on the use of (bis)urea groups to obtain TPEs. Bouteiller and co-workers studied poly(dimethylsiloxanes) grafted with bisurea groups, while Versteegen et al. prepared segmented block copoly(ether ureas) with small bisurea blocks. The bisurea groups self-assemble into phase-separated stacks via strong, bifurcated hydrogen bonds (see Figure 1.6). Both groups obtained TPEs with excellent mechanical properties, while melting of the stacks at elevated temperatures resulted in processable materials. Chino et al. reported on the thermoreversible cross-linking of maleated rubbers with pendant triazole (ATA) groups (see Figure 1.7) and speculated that each functional group interacts via a six-point hydrogen bonding geometry. Reprocessing could be repeated at least ten times without affecting the mechanical properties. Recently, Leibler and co-workers obtained reversible polymer networks using low-molecular-weight polymers functionalized with three imidazolidone (IM) groups, which are capable of forming double hydrogen bonding dimers (see Figure 1.8).

In the previous chapters, the thermoreversible cross-linking of maleated ethylene/propylene copolymer (MAN-g-EPM) with ionic interactions (Chapter 2) and with hydrogen bonds (combined with ionic interactions) (Chapter 3) was discussed. Only minor improvements in tensile properties and elasticity were obtained upon cross-linking with hydrogen bonds, since they were not organized into arrays and suffered from low strength and poor directionality. The addition of ionic interactions with ammonium cations to the hydrogen bonds resulted in significantly improved properties, but
(re)processing of these materials was limited to temperatures below 120 °C, due to irreversible imide formation at higher temperatures.

This chapter presents our work on the thermoreversible cross-linking of the same MAn-g-EPM, now using several multiple hydrogen bonding arrays, i.e., the imide-diaminopyridine array between melamine and three imide groups and UPy, mono- and bisurea, ATA and IM arrays. A comparative study between different hydrogen bonding arrays for the same base polymer has never been made to the authors’ knowledge. Most of these arrays are self-complementary and are introduced into MAn-g-EPM using an aliphatic amine functionality. Such amine groups react instantaneously in diluted solution at room temperature with the anhydride groups of MAn-g-EPM to form amide-acids, which are subsequently converted to imides at elevated temperatures to obtain stable connections of the arrays to the polymer backbone. The imide-diaminopyridine array is obtained via the conversion of the anhydride groups to NH$_3$-imide (Chapter 3) followed by the addition of melamine. For completeness, the previously studied, “non-organized” hydrogen bonds are also included in the discussion. Scheme 4.1 shows an overview of all modified materials.

**Scheme 4.1.** Hydrogen bonding arrays used for the thermoreversible cross-linking of MAn-g-EPM.

First, the chemical structures of the reaction products are studied using Fourier transform infrared (FTIR) spectroscopy to determine the occurrence and the conversions of the modification reactions. The effect of the type of hydrogen bonding array and, concomitantly, the number and the strength of the hydrogen bonds and their organization, on the morphology, as studied with small-angle X-ray scattering (SAXS) and dynamic mechanical thermal analysis (DMTA), and the rubber properties, i.e., hardness, tensile properties and elasticity, is investigated. The effect of the degree of modification of MAn-g-EPM on the morphology and properties is studied for the IM array. Finally,
the (re)processability is studied via compression molding experiments and Mooney viscometry to determine for which array(s) the best property-processing balance is obtained.

4.2. Experimental section

4.2.1. Materials

Maleated ethylene/propylene copolymer (MAn-g-EPM, 49 wt% ethylene, 49 wt% propylene, 2.1 wt% maleic anhydride (Man), \(M_n = 40\) kg/mol, \(M_w = 90\) kg/mol) was provided by DSM Elastomers. It was dried for 1 h at 170 °C under reduced pressure with a low N\(_2\)-flow prior to use to convert all acid groups, formed upon hydrolysis, back to anhydride. N-octadecylamine (Aldrich), ammonia (NH\(_4\)OH in water, Aldrich), melamine (Aldrich), 3-amino-1,2,4-triazole (ATA, Aldrich), 1-(2-aminoethyl)imidazolidin-2-one (IM, Arkema France), 1-(6-aminohexyl)-3-hexylurea (urea, SyMO-Chem BV), N-(6-aminohexyl)-N'-([2-ethylhexylamino]carbonyl]amino|butyl)urea (bisurea, SyMO-Chem BV), N-(6-aminohexyl)-N'-([2-isopropyl-4-oxo-1,4-dihydropyrimidin-2-yl]urea (UPy, SupraPolix BV), tetrahydrofuran (THF, Biosolve) and dimethylsulfoxide (DMSO, Biosolve) were used as received.

4.2.2. Modification reactions of MAn-g-EPM

All modifications were aimed at 100% conversion based on the amount of anhydride groups, except the modifications with IM, for which different conversions (25, 50, 75 and 100%) were targeted. The octadecylamide-acid and the (bis)urea materials were obtained via the following procedure. Typically, 15 g of MAn-g-EPM was dissolved in 150 g of THF at 80 °C, after which the solution was cooled down to room temperature. The required amount of reactant (N-octadecylamine or amine-functional (bis)urea) was added to the solution, which was stirred for 1 h. The products were precipitated in acetone and dried for at least one day at 50 °C under vacuum. The UPy material was obtained via a similar procedure, except that the amine-functional UPy was dissolved in a 50/50 wt% mixture of THF and DMSO at 80 °C, which was subsequently added to the MAn-g-EPM solution at 80 °C. The urea, bisurea and UPy materials were compression molded between Teflon sheets for 20 min in a Collin press at 150 °C, while the octadecylamide-acid was compression molded at 80 °C. The di-acid was obtained after hydrolysis of the anhydride groups via exposure of compression-molded films of MAn-g-EPM for several days to normal atmosphere. NH\(_3\)-imide was prepared by exposing MAn-g-EPM to a NH\(_3\)-rich atmosphere for several days at room temperature, followed by compression molding at 180 °C to form the imide. NH\(_3\)-imide was subsequently dissolved in THF at 80 °C, after which melamine was added to the solution to obtain the imide-diaminopyridine array. The solvent was evaporated under a N\(_2\)-flow overnight and the resulting material was compression molded for 20 min at 180 °C. The modification reactions with ATA and IM were performed in the melt on a 50 g scale Haake Rheomix OS internal mixer in view of the poor solubility of the respective chemicals. The required amount of MAn-g-EPM was charged to the mixer at 150 °C and homogenized for 1 min. Next, the required amount of chemical was added, followed by mixing for 5 min at a rotation speed of 100 rpm. The products were compression molded for 20 min at 180 °C. The addition of melamine to the NH\(_3\)-imide was performed using this melt mixing procedure as well.

The names of the resulting hydrogen-bonded materials are shown in Scheme 4.1. The materials modified with IM are named IM-x, where \(x\) is the targeted conversion.
4.2.3. Characterization techniques

**Fourier transform infrared (FTIR) spectroscopy.** Samples were analyzed on a BioRad Excalibur 3000 spectrometer equipped with a Specac Golden Gate attenuated total reflection (ATR) setup over a spectral range from 650 up to 4000 cm\(^{-1}\) at a resolution of 4 cm\(^{-1}\), co-adding 35 scans.

**Small-angle X-ray scattering (SAXS).** SAXS experiments were performed on compression-molded samples at the DUBBLE beamline (BM26) at the European Synchrotron Radiation Facility (ESRF) in Grenoble (France). The data were collected using a 2D multiwire gas-filled detector with pixel array dimensions of 512 x 512. The detector was positioned at 2.5 m from the sample and the q scale was calibrated using the position of diffraction peaks from a standard silver behenate powder. The exposure time for each sample was 300 s and a wavelength of 1.2 Å was used. The experimental data were corrected for background scattering, i.e., subtraction of instrumental errors, and transformed into 1D-plots by azimuthal-angle integration using the FIT2D program developed by Dr. Hammersley of ESRF. The profiles were scaled for the sample thickness to allow a comparison of the intensities of different samples.

**Dynamic mechanical thermal analysis (DMTA).** Rectangular samples with dimensions of around 10 x 3 x 1 mm were measured over a temperature range from -100 to 250 °C at a heating rate of 3 °C/min and a frequency of 1 Hz on a DMA Q800 (TA Instruments) with film tension clamps.

**Hardness.** The hardness was measured on 6 mm thick samples using a Shore A durometer according to ASTM D2240-91.

**Tensile testing.** Dumbbell-shaped tensile bars with dimensions of 35 x 2 x 1 mm and a parallel specimen length of 17.5 mm were punched from compression-molded films. Tensile tests were performed with a constant speed of 0.5 mm/s at room temperature on a Zwick Z010 tensile tester equipped with a force cell of 20 N using TestXpert v7.11 software. All materials were tested in at least five-fold.

**Compression set (CS).** Cylindrical samples with a diameter of 13 mm and a thickness of around 6 mm were compressed for 22 h between two parallel plates with a linear deformation of 25 % at room temperature (CS\(_{23}\)) and at 70 °C (CS\(_{70}\)). CS was determined after a relaxation time of 30 min at room temperature using:

\[
CS = \frac{(t_0 - t_n)}{(t_0 - t_i)} \times 100\%
\]  

(4.1)

where \(t_n\) is the thickness of the spacer and \(t_0\) and \(t_i\) are the initial and final sample thickness, respectively.

**Mooney viscosity measurements.** Mooney viscosities were determined at various temperatures using a Mooney MV 2000vs (Alpha Technologies). A preheat time of 3 min was used and samples were measured for 4 min at a rotation speed of 2 rpm, resulting in ML(3+4) values.

4.3. Results and discussion

4.3.1. Chemical characterization of the hydrogen-bonded materials

The anhydride groups of the MAn-g-EPM precursor were converted to different functional groups capable of hydrogen bonding (Scheme 4.1) with 100 % targeted conversion. Details on the chemical structures of the octadecylamide-acid, the NH\(_3\)-imide and the di-acid were already discussed (Chapter 2 and 3). Modifications to obtain the imide-diaminopyridine array between melamine and imide groups from the NH\(_3\)-imide proved to be unsuccessful via either solution or melt procedures,
due to the poor solubility and high melting temperature of melamine, respectively, which are both related to the extremely strong self-complexation of melamine. In both approaches, melamine forms crystals within the rubber instead of interacting with the imide groups. The absence of the desired triple hydrogen bonding array results in mechanical properties similar to those of MAn-g-EPM. Therefore, this hydrogen bonding array is not included in the remainder of this discussion. The other hydrogen bonding arrays are connected as stable imides to the polymer backbone via the reaction of their amine functionality with the anhydride groups of MAn-g-EPM to form amide-acids, followed by imide formation during compression molding at high temperatures (Scheme 4.2).

**Scheme 4.2.** Modification of MAn-g-EPM with amine-functional hydrogen bonding arrays, where R represents the array.

\[
\begin{align*}
\text{O} & \\
\text{O} & \\
\text{O} & \\
\text{R-NH}_2 & \\
\text{O} & \\
\text{NH} & \\
\text{O} & \\
\text{OH} & \\
\text{R} & \\
\text{N} & \\
\text{O} & \\
\text{O} & \\
\end{align*}
\]

As shown in the previous chapters, FTIR spectroscopy is a very suitable technique to study the chemical structures of MAn-g-EPM after modification with hydrogen bonding arrays, since the positions and intensities of the carbonyl (C=O) stretching vibrations of the anhydride groups change upon reaction. Several of the hydrogen bonding arrays contain C=O groups as well, which may give an indication on the type of hydrogen bonding, since the position of their absorption bands depends strongly on the extent and nature of hydrogen bonding.

The FTIR spectra for the IM materials in Figure 4.1 show that the anhydride bands at 1865 and 1785 cm\(^{-1}\) of MAn-g-EPM, which originate from the anti-symmetric and symmetric C=O stretching vibrations, respectively,\(^{20,21}\) disappear gradually upon increasing the conversion to the IM functionality. The presence of new bands at 1705 and 1400 cm\(^{-1}\), originating from the anti-symmetric C=O stretching\(^{19,21,27}\) and, most probably, the C-N stretching\(^{22,23}\) vibrations of the imide, respectively, confirms that indeed the imide groups are formed. The (weak) band for the symmetric C=O stretching vibration of the imide,\(^{27}\) which is usually present at 1770 cm\(^{-1}\), is not observable, due to overlap with the anti-symmetric C=O stretching vibration of the residual anhydride groups at 1785 cm\(^{-1}\). Therefore, determination of the conversion using the anhydride band at 1785 cm\(^{-1}\) is prone to errors and is not performed. The appearance of a small shoulder on the low-wavenumber-side of the imide band at 1705 cm\(^{-1}\) suggests that at least some of the imidazolidone groups form hydrogen-bonded dimers, since they give a C=O stretching vibration band at 1680 cm\(^{-1}\).\(^{18}\) However, determination of the ratio of hydrogen-bonded (1680 cm\(^{-1}\)) and free species (band at 1699 cm\(^{-1}\)) is difficult, due to overlap with the imide band at 1705 cm\(^{-1}\).

For the other arrays at 100 % targeted conversion, the almost complete disappearance of the anhydride bands at 1865 and 1785 cm\(^{-1}\) in Figure 4.1 suggests high conversions of the anhydride groups. The absorption bands at 1705 and 1400 cm\(^{-1}\) for the urea and bisurea materials indicate that
the desired imides are also formed for these materials (see Figure 4.1b). The position of the C=O stretching vibration bands of the urea and bisurea groups depend highly on the nature of the hydrogen bonding, while the effect on the N-H stretching vibration around 1570 cm⁻¹ is only minor.14,24 Non-hydrogen-bonded urea groups have an absorption band at 1690 cm⁻¹, while weak and strong (stacking) hydrogen bonds can also be identified based on their bands at 1637 and 1615 cm⁻¹, respectively.14 The absorption band at 1635 cm⁻¹ for the urea and bisurea materials indicates that relatively weak hydrogen bonds are present and that no large stacks are formed. These results are different from previous observations in literature that strong stacks are formed for bisurea groups and that weak hydrogen bonds are present for mono-urea groups.14 A possible reason for this behavior is the presence of microphase-separated, anhydride-rich aggregates for the MAn-g-EPM precursor (Chapter 2) and for all hydrogen-bonded materials, as discussed in the next section. The formation of long stacks of hydrogen-bonded bisurea groups is rather difficult within these aggregates (radius of 20-25 Å),25 resulting in the formation of relatively small stacks.

For the UPy material, the significant overlap of the absorption bands from the C=O groups of the modified anhydride groups and the UPy arrays complicates determination of the exact nature of the connection, i.e., amide-acid or imide. However, the absence of an absorption band at 1400 cm⁻¹ suggests the presence of the amide-acid structure, most probably due to the maximum compression molding temperature of 150 °C to avoid thermal degradation reactions, as will be discussed in more detail later. UPy arrays can be present in two tautomeric forms, which differ largely in their association constants, namely the (desired) 2-ureido-4-pyrimidone and the 2-ureido-pyrimidin-4-ol, for which relatively strong DDAA and weak DADA arrays are formed, respectively.26 The observed absorption bands at 1699, 1654, 1583 and 1533 cm⁻¹ are typical for the 2-ureido-4-pyrimidone tautomer26 and, hence, the desired DDAA array.

For the ATA material, the aromatic imide band is observed at 1726 cm⁻¹ (Figure 4.1).27 Chino et al. observed a large absorption band at the same position after modification of maleated poly(isoprene) with ATA,16 but mistakenly attributed this band to the carboxylic acid of the amide-acid. The
reported reaction conditions (1 h at 150 °C), which highly favor imide formation,\textsuperscript{19,21} and the absence of the absorption band for the C=O stretching vibration of the amide\textsuperscript{19,20} around 1650 cm\textsuperscript{-1} clearly show that their interpretation is not correct. As a consequence, the suggested six-point hydrogen bonding geometry is not possible, as the ATA structure connected as an imide has only one hydrogen bonding donor per functional group (Scheme 4.1).

**4.3.2. Morphology of the hydrogen-bonded materials**

The morphology of the hydrogen-bonded materials was investigated using SAXS and DMTA. It was shown previously that microphase-separated, anhydride-rich aggregates are present for the MAn-g-EPM precursor, due to the large polarity difference between the polar anhydride groups and the apolar EPM chains (Chapter 2). In this chapter, no detailed evaluation of the SAXS results using a (refined) scattering model is performed, as was done for ionomers based on the same MAn-g-EPM, since this is far from straightforward. Rather, the qualitative changes in the scattering profiles are discussed, which is allowed after correction of the intensity for the sample thickness.

Figure 4.2 shows that broad scattering peaks are present for all hydrogen-bonded materials, which indicates that the microphase-separated aggregates persist after modification. The (large) increase in scattered intensity compared to MAn-g-EPM indicates that the (polar) arrays mainly reside within the aggregates. The intensity of the scattering peak increases with increasing conversion to IM (see Figure 4.2a), because of the enhanced electron density difference between the aggregates and the matrix upon the introduction of the highly polar IM groups. The peak maximum shifts to lower q-values for the IM materials with low conversions compared to the MAn-g-EPM, followed by a shift to higher q-values for higher conversions. These trends are similar to those observed for the K-ionomers (Chapter 2), for which the initial shift at low conversions was attributed to an increased aggregate size upon introduction of the ionic interactions, while the subsequent shift to higher q-values at higher conversions was attributed to tightening of the aggregates. It seems reasonable to assume that the same explanation holds for the current materials.

For the materials with different hydrogen bonding arrays targeted at 100 % conversion, the highest electron density differences and, concomitantly, intensities are observed for the highly polar arrays, i.e., bisurea and UPy, and, to a lesser extent, for IM and ATA. The urea material obviously contains groups with lower polarity than the bisurea material, which explains its lower intensity. Peak intensities were only somewhat higher for the di-acid, octadecylamide-acid and NH\textsubscript{3}-imide than for the MAn-g-EPM precursor (not shown here), since the respective functional groups are only slightly more polar than the anhydride groups, as discussed in Chapters 2 and 3. The position of the peak maximum shifts to lower q-values for the different arrays with the following order in peak position: bisurea < UPy < urea < IM < ATA < MAn-g-EPM, while the scattering peak becomes narrower as well. The introduction of the hydrogen bonding arrays results in stronger anchoring of the corresponding chain segments to the aggregates and, concomitantly, in a larger restricted mobility layer surrounding the aggregates, which explains the changes in the SAXS profiles.\textsuperscript{25} Consequently, the aforementioned order in peak position may be indicative of the relative strengths of the arrays, although care must be taken, since differences in the modification reactions also influence the aggregation process. The scattering peak positions did not change significantly for the
octadecylamide-acid, the NH₃-imide and the di-acid compared to MAn-g-EPM, because of their relatively weakness (Chapters 2 and 3).

Figure 4.2. SAXS profiles of MAn-g-EPM modified with (a) IM to various conversions and (b) different multiple hydrogen bonding arrays after compression molding at 175 °C.

DMTA experiments can also be used to study the morphology of these materials and demonstrated that the aggregates in the MAn-g-EPM precursor act as physical cross-links and increase the network density compared to the parent EPM (Chapter 2). Figure 4.3 shows the storage modulus as a function of the temperature for MAn-g-EPM and the hydrogen-bonded materials. The glass transition temperature, which is positioned at approx. -50 °C, and the rubber plateau modulus do not change significantly upon the introduction of hydrogen bonding (arrays) into MAn-g-EPM. The unaffected plateau modulus indicates that the apparent network density remains constant and suggests that the hydrogen bonding units are solely present within the aggregates and that no additional cross-links are formed.

The width of the rubber plateau increases upon the introduction of hydrogen bonds into the aggregates. The hydrogen bonds replace the relatively weak polar interactions between the anhydride groups, resulting in stronger aggregates that persist to higher temperatures. Only a minor broadening of the plateau occurs for the relatively weak, “non-organized” hydrogen-bonded materials, i.e., NH₃-imide, di-acid and octadecylamide-acid. Side reactions to form anhydrides and imides occur at elevated temperatures for the di-acid and octadecylamide-acid, respectively, resulting in a loss of hydrogen bonding capability and further narrowing of the rubber plateau. The plateau is much broader for the different multiple hydrogen bonding arrays. Thermal degradation occurs for the (bis)urea²⁴,²⁸ and UPy²⁹ arrays at temperatures exceeding 150 °C, as discussed in more detail in the final section. The plateau modulus does not decrease significantly up to 150 °C for the UPy and (bis)urea materials, indicating that the network persists within the stable temperature range, while the formation of irreversible cross-links causes the plateau to persist to even higher temperatures. The ATA and IM arrays are thermally stable within the experimental temperature range without irreversible reactions, as suggested by their unaffected FTIR spectra. The plateau is broader for the IM material than for ATA, suggesting that modification with IM results in
stronger hydrogen bonds and, hence, stronger aggregates. The plateau persists to 250 °C at any conversion with IM, although the modulus decreases less with temperature at higher conversions.

![Figure 4.3](image)

Figure 4.3. Storage modulus as a function of the temperature for MAn-g-EPM and the hydrogen-bonded materials.

4.3.3. Mechanical properties of the hydrogen-bonded materials

It was shown in the previous section that the hydrogen bonds are (mainly) present within the aggregates and improve the aggregate strength. Figure 4.4 shows representative tensile curves for the modification with IM to different conversions, while the average values of the hardness, the tensile strength (TS), elongation at break (EB) and modulus at 200 % strain (M200) and the compression sets (CS) at room temperature (CS23) and at 70 °C (CS70) are presented as a function of the conversion of the anhydride groups with IM in Figure 4.5 and Table 4.1.

![Figure 4.4](image)

Figure 4.4. Representative tensile curves for MAn-g-EPM cross-linked with IM to various conversions.

The hardness, TS and M200 increase continuously with increasing conversion, while CS23 and CS70 decrease and EB decreases slightly. The higher strength of the aggregates upon the introduction of the hydrogen bonding arrays results in an increased resistance against deformation, which explains
the increase in $M_{200}$ and hardness with increasing conversion. CS is a measure for the elasticity of a material and has values of 0 % for an ideally elastic material and 100 % for a fully plastic material. For materials containing (thermo)reversible interactions, CS is dependent on two different (relaxation) processes, namely plastic deformation during compression and elastic recovery after removal of the compression. The introduction of hydrogen bonds results in an increased resistance against plastic deformation during compression and, consequently, an improved CS.

![Figure 4.5.](a) Tensile properties (TS, EB and $M_{200}$) and (b) hardness and compression sets ($CS_{23}$ and $CS_{70}$) as a function of the conversion of MAn-g-EPM with IM.

### Table 4.1. Mechanical properties of MAn-g-EPM and the hydrogen-bonded materials.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Hardness (Shore A)</th>
<th>TS (MPa)</th>
<th>EB (%)</th>
<th>$M_{200}$ (MPa)</th>
<th>CS$_{23}$ (%)</th>
<th>CS$_{70}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MAn-g-EPM</td>
<td>38</td>
<td>0.4</td>
<td>560</td>
<td>0.4</td>
<td>88</td>
<td>100</td>
</tr>
<tr>
<td>NH$_3$-imide</td>
<td>49</td>
<td>0.7</td>
<td>440</td>
<td>0.7</td>
<td>76</td>
<td>100</td>
</tr>
<tr>
<td>octadecylamide-acid</td>
<td>54</td>
<td>1.7</td>
<td>760</td>
<td>1.1</td>
<td>60</td>
<td>98</td>
</tr>
<tr>
<td>di-acid</td>
<td>54</td>
<td>1.5</td>
<td>300</td>
<td>1.3</td>
<td>59</td>
<td>100</td>
</tr>
<tr>
<td>IM-25</td>
<td>46</td>
<td>1.2</td>
<td>500</td>
<td>0.7</td>
<td>65</td>
<td>90</td>
</tr>
<tr>
<td>IM-50</td>
<td>49</td>
<td>1.7</td>
<td>360</td>
<td>1.1</td>
<td>53</td>
<td>85</td>
</tr>
<tr>
<td>IM-75</td>
<td>53</td>
<td>1.9</td>
<td>430</td>
<td>1.2</td>
<td>45</td>
<td>78</td>
</tr>
<tr>
<td>IM-100</td>
<td>55</td>
<td>2.6</td>
<td>410</td>
<td>1.8</td>
<td>43</td>
<td>80</td>
</tr>
<tr>
<td>ATA</td>
<td>51</td>
<td>2.3</td>
<td>520</td>
<td>1.3</td>
<td>42</td>
<td>88</td>
</tr>
<tr>
<td>urea</td>
<td>54</td>
<td>2.2</td>
<td>390</td>
<td>1.2</td>
<td>26</td>
<td>65</td>
</tr>
<tr>
<td>bisurea</td>
<td>57</td>
<td>3.0</td>
<td>430</td>
<td>1.8</td>
<td>24</td>
<td>60</td>
</tr>
<tr>
<td>UPy</td>
<td>57</td>
<td>4.3</td>
<td>430</td>
<td>2.2</td>
<td>21</td>
<td>80</td>
</tr>
</tbody>
</table>

The trends in TS and EB with increasing conversion are similar to those observed for ionomers based on the same MAn-g-EPM precursor (Chapter 2). For ionomers, “ion hopping” allows ionic interactions to disconnect and the “free” ionic groups to hop between aggregates under stress.
The corresponding chain segments relax the applied stress, which prevents premature failure and increases EB. Upon entering other aggregates, the ionic groups can form ionic interactions and re-contribute to the network, which explains the increase in TS. Ion hopping occurred at any level of modification for the ionomers, resulting in a constant EB, due to the constant chain segment length between functional groups. Hydrogen bonds are physical interactions like ionic interactions, but weaker, as indicated by the lower stress levels required for failure compared to the ionomers (TS up to 10 MPa). Hopping is likely to occur for the hydrogen-bonded materials as well, which explains the similar trends in TS and EB as for ionomers. Hopping of hydrogen bonding arrays may be somewhat more difficult compared to ionic groups, due to the bulkiness and the directionality of the arrays, which requires a specific approach to other arrays to actually reform hydrogen bonds. This may explain the lower EB of the current materials compared to the ionomers (EB up to 800 %). Finally, it has to be noted that the extent and influence of the hopping processes depend highly on the deformation rate during the tensile tests.

Representative tensile curves for the different hydrogen-bonded materials are shown in Figure 4.6, while all mechanical properties are summarized in Table 4.1. The hardness increases for all materials compared to MAn-g-EPM. Only minor improvements in tensile properties and relatively high CS_{23} and (especially) CS_{70} are obtained for the “non-organized” materials, i.e., NH_{3}-imide, octadecylamide-acid and di-acid, due to their relatively weak hydrogen bonds. The high EB for the octadecylamide-acid material is most probably related to a plasticizing effect of the long, apolar octadecyl-tails on the aggregates. Significant improvements in the tensile properties and CS are achieved for all hydrogen bonding arrays compared to the “non-organized” hydrogen-bonds and the MAn-g-EPM precursor. The tensile properties improve in the following order: ATA \simeq urea \prec IM \prec bisurea \prec UPy, whereas the trends in CS are: ATA \simeq IM \prec urea \prec bisurea \prec UPy for CS_{23} and ATA \prec IM \simeq UPy \prec urea \prec bisurea for CS_{70}. Note that these orders are quite similar to those observed in the scattering peak positions in the SAXS pattern (Figure 4.2). A closer look at the organization of the different arrays is necessary to explain these differences.

![Figure 4.6](image-url)

**Figure 4.6.** Representative tensile curves for MAn-g-EPM and the hydrogen-bonded materials.

The triazole and imidazolidone arrays in the ATA and IM materials, respectively, are both capable of forming two hydrogen bonds, since the arrays contain one hydrogen bonding donor and (at least)
one acceptor. The better properties of the IM material are related to the specific positions of the donor and acceptor moieties, which enable the formation of a double hydrogen bonding dimer, whereas the structure of the triazole (ATA) ring is not optimal for dimerization (Scheme 4.1). Stacking of the five-membered rings of the IM arrays may occur under the right conditions\textsuperscript{31}, which is also likely to occur for the ATA material, due to the possibility of $\pi-\pi$ interactions between the aromatic rings. The close proximity of the arrays within the microphase-separated aggregates increases the probability of stacking. This stacking may improve the directionality and strength of hydrogen bonding, since larger structures between multiple hydrogen-bonded groups can be formed instead of dimers. This explains the significantly improved properties for the IM and ATA materials compared to the “non-organized” hydrogen-bonded materials, which are also capable of forming at least two hydrogen bonds (Scheme 4.1).

Urea groups are known to strongly associate via bifurcated (double) hydrogen bonds (see Figure 1.6).\textsuperscript{15} Versteegen et al. showed that extremely long stacks of bifurcated hydrogen bonds can be formed in segmented block copoly(ether ureas) as long as the urea blocks contain at least two urea groups (bisurea).\textsuperscript{13,14} FTIR experiments (Figure 4.1) suggested that only a limited number of groups are involved in the stacks for the current (bis)urea materials, due to the spatial confinement of the aggregates in which they reside. Higher stress levels are required to disrupt the bisurea groups from the corresponding stacks compared to the urea groups, which explains the better tensile properties for the bisurea material. Both CS\textsubscript{23} and CS\textsubscript{70} are only slightly better for the bisurea material compared to the urea material, which suggests that the elastic behavior for these materials is more or less independent of whether the stacks consist of one or two urea groups. The tensile properties of the urea and bisurea materials are only slightly better than for the IM and ATA materials, indicating that the respective stacks have a comparable resistance against tensile deformation and can bear similar stress levels before failure.

The highest TS and M\textsubscript{200} and lowest CS\textsubscript{23} are observed for the UPy material. Quadruple hydrogen bonds are formed between the UPy groups, for which the association is obviously much stronger than for the double hydrogen bonding dimers.\textsuperscript{1} Under proper conditions, stacking of UPy groups can also occur,\textsuperscript{32} which may be promoted by the close proximity of UPy groups within the aggregates. Therefore, high stress levels are required for deformation (M\textsubscript{200}) and failure (TS). Despite the presence of quadruple hydrogen bonding arrays, the difference in CS\textsubscript{23} is only small and CS\textsubscript{70} is higher for the UPy material compared to the urea and bisurea materials. Correlating CS to M\textsubscript{200} demonstrated that the (bis)urea materials have better CS\textsubscript{23} and CS\textsubscript{70} than expected from this correlation (not shown here), which may be attributed to the better stability of the specific stacks for these materials under compression. This also explains why the elastic behavior of these materials is significantly better than for the IM and ATA materials.

In conclusion, significantly improved mechanical properties are obtained for the multiple hydrogen bonding arrays compared to “non-organized” hydrogen bonds, due to the stronger association of the hydrogen bonds within the arrays and their stacking. Significant differences in the tensile and elastic properties are obtained depending on the type of hydrogen bonding array in the following order: MAn-g-EPM << “non-organized” < ATA < IM < urea < bisurea < UPy at room temperature. The specific stacking in the urea and bisurea materials improves the elasticity at 70 °C (CS\textsubscript{70})
compared to the other arrays, for which significant weakening of the hydrogen bonds results in pronounced plastic deformation during compression.

4.3.4. (Re)processability of the hydrogen-bonded materials

In this final section, the (re)processability of the different hydrogen-bonded materials is studied. Thermal degradation of the materials is important from a processing point of view, as it may limit the accessible temperature range. Our previous study (Chapter 3) showed that irreversible imide formation occurs for the octadecylamide-acid at temperatures of 120 °C and higher according to Scheme 4.2 (where R is the octadecyl tail), resulting in the loss of hydrogen bonding capability. Hydrogen bonding capability is also lost for the di-acid as a result of ring closure to anhydride, which proceeds at somewhat elevated temperatures of 120 °C and higher. This process is fully reversible, since the di-acid is re-formed upon hydrolysis. Urea and bisurea degrade at temperatures of 160 °C and higher to form isocyanate and amine groups, which may react further to other products. The stability of UPy groups is limited to temperatures of 150 °C and lower, due to the occurrence of extensive side reactions, resulting in the formation of di-alkylurea, isocytosine and possibly di-isocytosine-urea derived structures. The NH3-imide and the ATA and IM materials are stable up to at least 200 °C, as no irreversible side reactions are observed in their FTIR spectra.

A first indication of the (re)processability of the materials is obtained from compression molding experiments. All materials can be repeatedly compression molded into smooth and homogeneous films without changes in the FTIR spectra at the respective compression-molding temperatures (TCM) shown in Table 4.2. This demonstrates that the hydrogen bonds are of thermoreversible nature, even in the case of the relatively strong multiple hydrogen bonding arrays.

TPEs are typically processed using thermoplastic processing techniques with short timescales, such as injection molding or extrusion, instead of low-shear techniques with long timescales, e.g., compression molding. The common method to determine melt viscosities of TPEs is capillary rheometry. However, the long residence time within the storage cylinder during these experiments makes this method less suitable for the current materials in view of their susceptibility to degradation reactions. Instead, Mooney viscosities were determined at various temperatures below the respective degradation temperatures. Mooney viscosities below 80 MU are used as a guideline for applicability in thermoplastic processing techniques. The preheat time was extended from the common 1 min to 3 min to give the temperature-dependent interactions sufficient time to adjust. The corresponding Mooney viscosities (ML(3+4)) are given in Table 4.2 for MAn-g-EPM and the hydrogen-bonded materials, where an x indicates melt fracture during the measurement. The relatively short experimentation times prevent extensive degradation, as confirmed with FTIR spectroscopy on the measured materials.

Mooney viscosities increase for the hydrogen-bonded materials compared to the parent MAn-g-EPM at any temperature, while increasing the temperature results in a significant reduction. The “non-organized” hydrogen-bonded materials all have sufficiently low Mooney viscosities at temperatures below their respective degradation temperatures, as well as the ATA material at
150 and 200 °C and the IM material at 200 °C, albeit with a rather high value for the latter material. This suggests that these materials are suitable for the desired processing techniques.

### Table 4.2. (Re)processability of MAn-g-EPM modified with (multiple) hydrogen bonding (arrays).

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_{CM}$ (°C)</th>
<th>ML(3+4) (MU)$^*$</th>
<th>100 °C</th>
<th>150 °C</th>
<th>200 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>MAn-g-EPM</td>
<td>150</td>
<td></td>
<td>38</td>
<td>9</td>
<td>3</td>
</tr>
<tr>
<td>NH$_3$-imide</td>
<td>175</td>
<td></td>
<td>80</td>
<td>31</td>
<td>6</td>
</tr>
<tr>
<td>octadecylamide-acid</td>
<td>80</td>
<td></td>
<td>61</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>di-acid</td>
<td>125</td>
<td></td>
<td>103</td>
<td>29</td>
<td>-</td>
</tr>
<tr>
<td>ATA</td>
<td>175</td>
<td></td>
<td>124</td>
<td>63</td>
<td>25</td>
</tr>
<tr>
<td>IM</td>
<td>175</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>76</td>
</tr>
<tr>
<td>urea</td>
<td>150</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>-</td>
</tr>
<tr>
<td>bisurea</td>
<td>150</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>-</td>
</tr>
<tr>
<td>UPy</td>
<td>150</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>-</td>
</tr>
</tbody>
</table>

* An x indicates extensive melt fracture during the experiment.

Extensive melt fracture occurs for the IM, (bis)urea and UPy materials at temperatures of 150 °C and below. Leibler et al. described the rheological behavior of hydrogen-bonded materials and attributed a characteristic lifetime to the hydrogen bonds. The materials behave as permanent networks on timescales shorter than this lifetime and flow at longer timescales, due to the successive disconnection of hydrogen bonds. Apparently, the lifetimes of the stronger multiple hydrogen bonding arrays, i.e., IM, bis(urea) and UPy, are too long at 150 °C, which causes the materials to behave as a covalent network during the measurement, resulting in extensive melt fracture. This suggests that the (bis)urea and UPy materials are less suitable for thermoplastic processing techniques. Note that the rheological behavior of these materials is discussed in more detail in Chapter 7.

### 4.4. Conclusions

In this work, several multiple hydrogen bonding arrays, including imide-diaminopyridine, triazole (ATA), imidazolidone (IM), (bis)urea and 2-ureido-4-pyrimidone (UPy) arrays as well as “non-organized” hydrogen bonds were compared for the thermoreversible cross-linking of the same starting material (MAn-g-EPM). Attempts to obtain the imide-diaminopyridine array failed due to the poor miscibility of melamine with the imide-modified rubber. All other arrays were connected as stable imides to the EPM backbone via the reaction of their amine-functionality with the cyclic anhydride groups of MAn-g-EPM, as confirmed by FTIR spectroscopy, with the exception of the UPy material, for which the amide-acid is not further converted to imide. FTIR spectroscopy confirmed the presence of the desired DDAA tautomer for the UPy material and suggested that only small stacks of bifurcated hydrogen-bonded urea groups are formed for the (bis)urea materials.
SAXS measurements demonstrated the presence of microphase-separated aggregates that act as physical cross-links for the MAn-g-EPM precursor and all hydrogen-bonded materials. The hydrogen bonding groups are present within the polar aggregates, as indicated by the unaffected network density of the hydrogen-bonded materials compared to MAn-g-EPM. The aggregates become stronger upon the introduction of the hydrogen bonds and persist to higher temperatures, with the larger increases for the multiple hydrogen bonding arrays.

The tensile properties and elasticity are significantly improved for the multiple hydrogen bonding arrays compared to the “non-organized” hydrogen bonds, due to the stronger association of arrays and their possible stacking, in the following order: MAn-g-EPM < “non-organized” << ATA < IM < urea < bisurea < UPy at room temperature. The specific stacking in the urea and bisurea materials improves the elasticity at elevated temperatures (CS70) compared to the other arrays, due to an increased resistance against plastic deformation during compression. The properties improve with increasing conversion of MAn-g-EPM with IM, since polar interactions between anhydride groups are more and more replaced by stronger hydrogen bonding arrays within the aggregates.

Processing of the urea, bisurea and UPy materials is limited to temperatures of 150 °C and below to avoid thermal degradation, whereas the ATA and IM materials are stable to temperatures up to 200 °C. Below the respective degradation temperature, all materials can be repeatedly reprocessed via compression molding without significant chemical changes, indicating that the hydrogen bonds are indeed of thermoreversible nature. Mooney viscosity measurements suggested the applicability of MAn-g-EPM modified with the “non-organized” hydrogen bonds and the ATA and IM arrays for thermoplastic processing techniques, whereas the (bis)urea and UPy materials are less suitable.

4.5. References

Mooney viscosity experiments are generally used for non-cured rubber compounds, for which values below 80 MU are required for applicability in extrusion techniques. These measurements as well as the extrusion steps are typically performed at 100 °C to avoid premature cross-linking reactions. Obviously, higher temperatures can also be used for the current thermoreversibly cross-linked materials.
Chapter 5

Thermoreversible Covalent Cross-linking with Diols‡

The objective of this chapter was to thermoreversibly cross-link maleated ethylene/propylene copolymer (MAn-g-EPM) using the equilibrium reaction with linear aliphatic diols. Covalent hemi-ester cross-links are formed via the forward reaction of anhydride groups with the alcohol groups from the diols, while an equilibrium shift at elevated temperatures may result in their (partial) removal and in processable materials. Almost complete conversion to hemi-ester is obtained at low temperatures (50 to 75 °C) in the presence of a suitable catalyst (p-toluenesulfonic acid), whereas the conversions are low at elevated temperatures. The presence of microphase-separated aggregates that act as physical cross-links was demonstrated for the MAn-g-EPM precursor and all cross-linked materials. The network density does not change upon cross-linking, which suggests that the covalent cross-links are solely formed within the aggregates, resulting in stronger aggregates that persist to higher temperatures. The tensile strength and elasticity are significantly improved upon increasing the level of cross-linking, similarly to conventionally cross-linked elastomers, whereas the influence of the type of diol is less profound. The covalently cross-linked MAn-g-EPM is reprocessable via compression molding at temperatures of 175 °C and higher. Irreversible di-ester formation occurs for the longer diols, such as 1,10-decanediol, but does not prevent further reprocessing, while short diols, i.e., ethyleneglycol and 1,4-butanediol, evaporate out of the material. Both effects lower the level of cross-linking, resulting in a significant change in the mechanical properties. Finally, the reprocessability does not originate from the (desired) equilibrium shift, but from a continuous, dynamic exchange between cross-linked and non-cross-linked functional groups.

5.1. Introduction

An intriguing possibility to obtain TPE-like behavior is the use of thermoreversible covalent cross-links, using the inherent temperature dependence of equilibrium reactions. Covalent cross-links are formed via the forward reaction between suitable chemical functionalities at low temperature, while a shift in the equilibrium may result in their (partial) removal at elevated temperatures. Complete reversibility is not necessary, since only sufficient cross-links need to disconnect to permit adequate melt flow. The properties of the thermoreversible network are expected to be similar to those of a conventionally cross-linked network.1

A particularly suitable reaction for this purpose is the Diels-Alder [4+2] cycloaddition, because of the readiness of Diels-Alder adducts to undergo the reverse reaction (retro-Diels-Alder) upon heating (see Figure 1.9). Diels-Alder reactions between furan and maleimide groups2-4 and between two cyclopentadiene groups5,6 have been successfully applied for thermoreversible cross-linking. Urethane formation from isocyanates and hydroxyl groups is also thermoreversible7,8 and has been used for cross-linking of polymers.9,10 Previous work in our group showed that the reverse reaction at elevated temperatures results in the depolymerization of linear polyurethanes and in good processability, provided that the molecular weights are not too high.11-13 Nitroso dimerization14 and the reactions of azlactones with phenols15 and of carboxylic acids with vinyl ethers16 have also been used to obtain thermoreversible polymer networks. Finally, the reactions of cyclic anhydrides with alcohols17-20 and with (secondary) amines21,22 have been reported to be thermoreversible.

The thermoreversible cross-linking of maleated ethylene/propylene copolymers (MAn-g-EPM) with ionic interactions (Chapter 2), hydrogen bonds (combined with ionic interactions) (Chapter 3) and multiple hydrogen bonding arrays (Chapter 4) was discussed already. Here, the equilibrium reaction of the grafted anhydride groups of the same MAn-g-EPM with diols is used to form thermoreversible covalent cross-links, as shown schematically in Scheme 5.1. The first alcohol group of the diol reacts with a cyclic anhydride to form a hemi-ester,18-20 after which the actual (hemi-ester) cross-link is formed via the reaction of the second alcohol group with an anhydride from another MAn-g-EPM chain. The equilibrium of this reaction is dependent on the temperature and shifts back towards the starting materials at elevated temperatures.18-20 This reaction has mainly been studied for the modification of copolymers with a high maleic anhydride content, such as poly(styrene-co-maleic anhydride), with alcohols20,23-26 and their cross-linking with polyols.17,18,27,28 However, no unambiguous picture regarding the reversibility of this reaction emerges from these studies, since results ranging from full reversibility to complete irreversibility were reported. A possible complication is the formation of di-ester groups (Scheme 1), which is an irreversible reaction, due to the exclusion of water.26,29,30 This reaction, which is actually a simple acid/alcohol esterification, does not occur at low temperatures, but may become more prominent at elevated temperatures. Obviously, the participation of both alcohol groups of a diol in di-ester formation would result in the formation of an irreversible (di-ester) cross-link.

In this chapter, first a systematic study of the effects of the structure of the diol, the amount and the type of catalyst and the temperature on the experimental reaction rate and the equilibrium anhydride conversion is performed for solvent-cast films using time-resolved Fourier transform infrared
(FTIR) spectroscopy. This enables the determination of the optimal reaction conditions for the preparation of the cross-linked samples. The effects of the type and the amount of diol on the morphology, as studied with small-angle X-ray scattering (SAXS) and dynamic mechanical thermal analysis (DMTA), and on the rubber properties, i.e., hardness, tensile properties and compression set (CS), are studied for compression-molded films. These films are subsequently remolded at elevated temperatures to study the (re)processability and the effect on the chemical structures and the properties. Finally, solvent-cast films of diol-cross-linked MAn-g-EPM are subjected to heating-cooling cycles during time-resolved FTIR experiments to elucidate the mechanism of reversibility at elevated temperatures.

**Scheme 5.1.** Reaction scheme for the cross-linking of MAn-g-EPM with diols.

![Scheme 5.1. Reaction scheme for the cross-linking of MAn-g-EPM with diols.](image)

5.2. Experimental section

5.2.1. Materials

Maleated ethylene/propylene copolymer (MAn-g-EPM, 49 wt% ethylene, 49 wt% propylene, 2.1 wt% grafted maleic anhydride (MAn), M_n = 40 kg/mol, M_w = 90 kg/mol) was provided by DSM Elastomers. It was dried for 1 h at 170 °C under reduced pressure with a low N_2-flow prior to use to convert all carboxylic acid groups, formed upon hydrolysis, back to anhydride. Ethyleneglycol (EG, Aldrich), 1,4-butanediol (BD, Aldrich), 1,8-octanediol (OD, Aldrich), 1,10-decanediol (DD, Aldrich), 1,4-cyclohexanediethanol (CHDM, Aldrich), bisphenol A (BPA, Aldrich), 1,1,1-tris(hydroxymethyl)ethane (THME, Aldrich), p-toluene sulfonic acid monohydrate (PTSA, Aldrich), 1,4-diazabicyclo[2.2.2]octane (DABCO, Aldrich) and tetrahydrofuran (THF, Biosolve) were used as received.

5.2.2. Sample preparation

For time-resolved FTIR experiments, typically 1 g of MAn-g-EPM was dissolved in 10 g of THF at 60 °C, after which the solution was cooled down to room temperature. The required amounts of diol (equimolar: 0.5 mol of diol per mol of grafted MAn groups) and catalyst (PTSA or DABCO) were added to the solution, which was stirred for at least 30 min and subsequently used for FTIR experiments (see below). Samples for the study of the morphology and the mechanical properties were obtained via the following procedure.
Typically, 10 g of MA-n-g-EPM was dissolved in 100 g of THF at 60 °C, after which the solution was cooled down to room temperature. The required amounts of diol and catalyst (5 mol% PTSA) were added to the solution, which was stirred for at least 30 min. The solution was subsequently poured into a Teflon-covered Petri dish, after which the solvent was evaporated under a N₂-flow at room temperature. The resulting material was compression molded between Teflon sheets in a Collin press at 75 °C for 30 min. Cross-linked samples were subsequently cut into small pieces (mm-scale), followed by compression molding at various temperatures and times for reprocessability experiments.

### 5.2.3. Nomenclature

Samples for the study of the morphology and the mechanical properties are designated as X-y, where X is the abbreviation of the diol used and y is the targeted anhydride conversion (in %). Remolded samples are designated as X-Rz, where z is the number of reprocessing steps.

### 5.2.4. Characterization techniques

*Fourier transform infrared (FTIR) spectroscopy.* Time-resolved experiments at a constant temperature of 50 °C were performed on a BioRad Excalibur 3000 spectrometer equipped with a Specac Golden Gate attenuated total reflection (ATR) setup in a spectral range from 650 to 4000 cm⁻¹ at a resolution of 4 cm⁻¹, co-adding 20 scans at defined time intervals. Samples were obtained via solvent casting onto the diamond ATR crystal. Note that no reaction occurs prior to solvent casting, as experimentally validated with FTIR spectroscopy, since the reaction between cyclic anhydrides and alcohols is extremely slow in solution at room temperature. Compression-molded films were also analyzed with this setup.

Time-resolved experiments at constant elevated temperatures and reversibility experiments with defined temperature profiles were performed on a BioRad FTS6000 spectrometer equipped with a UMA500 FTIR microscope in a spectral range from 650 to 4000 cm⁻¹ at a resolution of 2 cm⁻¹, co-adding 20 scans. Samples were measured at defined time intervals in transmission with an exposed sample area of approximately 30 by 30 μm using a MCT detector. Thin films were obtained via solvent casting onto zinc selenide disks, which were subsequently kept in an oven for at least 12 h at 50 °C to obtain maximum conversion of the anhydride groups. The samples were exposed to the desired temperature (profile) using a Linkam TMS600 hotstage. For the reversibility experiments, samples were measured using the temperature profile depicted in Figure 5.1, where T_max is 150, 175 or 200 °C.

![Figure 5.1](image). Temperature profile for the reversibility experiments using time-resolved FTIR spectroscopy.
The conversion of the anhydride groups \( (X_{\text{Anh}}) \) is calculated (as a function of time) from the absorbance of the anti-symmetric carbonyl stretching (\( \text{C}=\text{O} \)) vibration band at 1785 cm\(^{-1} \) of the anhydride groups, using the absorbance of the band at 1460 cm\(^{-1} \), which originates from the overlapping anti-symmetric \( \text{CH}_3 \) bending and \( \text{CH}_2 \) scissoring vibrations of the EPM backbone, as internal reference:

\[
X_{\text{Anh}}(t) = \left(1 - \frac{\left(A_{1785} / A_{1460}\right)_{\text{rest}}}{\left(A_{1785} / A_{1460}\right)_{\text{ref}}}\right) \cdot 100\%
\]  

(5.1)

Small-angle X-ray scattering (SAXS). SAXS experiments were performed on compression-molded samples at the DUBBLE beamline (BM26) at the European Synchrotron Radiation Facility (ESRF) in Grenoble (France). The data were collected using a 2D multiwire gas-filled detector with pixel array dimensions of 512 x 512. The detector was positioned at 2 m from the sample and the q-scale was calibrated using the positions of diffracted peaks of silver behenate. The exposure time for each sample was 300 s and a wavelength of 1.2 Å was used. The experimental data were corrected for background scattering, i.e., subtraction of instrumental errors, and transformed into 1D-plots by azimuthal-angle integration using the FIT2D program developed by Dr. Hammersley of ESRF. The profiles were scaled for the sample thickness to allow a comparison of the intensities of different samples.

Dynamic mechanical thermal analysis (DMTA). Rectangular samples with dimensions of around 10 x 3 x 1 mm were measured over a temperature range from -100 to 250 °C at a heating rate of 3 °C/min and a frequency of 1 Hz on a DMA Q800 (TA Instruments) with film tension clamps.

Hardness. The hardness was measured on 6 mm thick samples using a Shore A durometer according to ASTM D2240-91.

Tensile testing. Dumbbell-shaped tensile bars with dimensions of 35 x 2 x 1 mm and a parallel specimen length of 17.5 mm were punched from compression-molded films. Tensile tests were performed at room temperature with a constant speed of 0.5 mm/s on a Zwick Z010 tensile tester equipped with a force cell of 20 N using TestXpert v7.11 software. All materials were tested at least in five-fold.

Compression set (CS). Cylindrical samples (diameter of 13 mm and thickness of approximately 6 mm) were compressed for 22 h between two parallel plates with a linear deformation of 25 % at room temperature (CS\(_{23}\)) or at 70 °C (CS\(_{70}\)). CS was determined after a relaxation time of 30 min at room temperature using:

\[
CS = \left(\frac{t_0 - t_f}{t_0 - t_n}\right) \times 100\%
\]  

(5.2)

where \( t_n \) is the thickness of the spacer and \( t_0 \) and \( t_f \) are the initial and final sample thickness, respectively.

5.3. Results and discussion

5.3.1. Determination of the optimal reaction conditions

The reaction of MAN-g-EPM with diols is not only dependent on the temperature, but also on other parameters, including the structure of the diol and the type and the amount of catalyst. Therefore, the effects of these variables on the reaction rate and the equilibrium anhydride conversion are investigated to determine the optimal reaction conditions. Table 5.1 gives an overview of the different diols used in this study. FTIR spectroscopy is a suitable technique to study the
anhydride/alcohol reaction, since the positions and the intensities of the carbonyl (C=O) stretching vibration bands of the cyclic anhydride groups change upon reaction.

Table 5.1. Overview of the diols (and triol) used for cross-linking of MAn-g-EPM.

<table>
<thead>
<tr>
<th>Chemical structure</th>
<th>Name (abbreviation)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HO-C&lt;sub&gt;n&lt;/sub&gt;H&lt;sub&gt;2n&lt;/sub&gt;-OH</td>
<td>n=2: ethyleneglycol (EG)</td>
</tr>
<tr>
<td></td>
<td>n=4: 1,4-butanediol (BD)</td>
</tr>
<tr>
<td></td>
<td>n=8: 1,8-octanediol (OD)</td>
</tr>
<tr>
<td></td>
<td>n=10: 1,10-decanediol (DD)</td>
</tr>
<tr>
<td>HO-C&lt;sub&gt;4&lt;/sub&gt;O</td>
<td>1,4-cyclohexanedimethanol (CHDM)</td>
</tr>
<tr>
<td>HO-</td>
<td>HO</td>
</tr>
<tr>
<td>HO-C&lt;sub&gt;3&lt;/sub&gt;O</td>
<td>1,1,1-tris(hydroxymethyl)ethane (THME)</td>
</tr>
</tbody>
</table>

Figure 5.2 shows FTIR spectra for the reaction of MAn-g-EPM with DD in the presence of 5 mol% of PTSA (based on the grafted anhydride groups) at 50 ºC as a function of the reaction time. The FTIR spectrum of the MAn-g-EPM precursor (t = 0 min) shows two absorption bands at 1785 cm<sup>-1</sup> (strong) and 1865 cm<sup>-1</sup> (weak), which are characteristic of saturated, cyclic anhydrides and originate from the anti-symmetric and symmetric C=O stretching vibrations, respectively. The intensities of the anhydride bands decrease upon increasing reaction time, while two new, partially overlapping bands appear at 1735 and 1710 cm<sup>-1</sup>, originating from the C=O stretching vibrations of the ester and carboxylic acid moieties of the hemi-ester. The reaction is almost completed after 6 h, indicating that high levels of cross-linking can be achieved.

The conversion of the grafted MAn groups (X<sub>Anh</sub>) was calculated from the FTIR spectra using Equation 5.1 and is shown in Figure 5.3 as a function of the reaction time for the reaction of MAn-g-EPM with DD at 50 ºC with and without a catalyst. The reaction is rather slow in the absence of a catalyst and does not reach the equilibrium conversion, even after 15 h. Both bases and acids can be used to catalyze this type of ring-opening esterification. The addition of 5 mol% of either the base DABCO or the acid PTSA results in a significant increase in the reaction rate, with PTSA being more effective than DABCO. The different shape of the conversion curve for the non-catalyzed reaction may be related to auto-catalysis by the relatively (weak) carboxylic acids of the hemi-esters formed upon reaction. The reaction rates increase for higher amounts of PTSA, although the difference between 5 and 10 mol% is only small. It should be noted that the addition of a true catalyst only influences the reaction rate, but not the position of the equilibrium, which is
positioned at $X_{Anh}$ of approximately 90%. Similar trends are observed for reactions at 100 °C (not shown here), but with higher reaction rates and a lower final $X_{Anh}$ of around 70%. Because of these results, a fixed amount of 5 mol% of PTSA is used for all further reactions.

![Figure 5.2](image1.png)

**Figure 5.2.** FTIR spectra for the reaction of MAn-g-EPM with DD in the presence of 5 mol% PTSA at 50 °C as a function of the reaction time. The spectra are shifted vertically for clarity.

![Figure 5.3](image2.png)

**Figure 5.3.** The conversion of the anhydride groups of MAn-g-EPM ($X_{Anh}$) as a function of reaction time for the reaction with DD using different amounts of DABCO or PTSA at 50 °C.

![Figure 5.4](image3.png)

**Figure 5.4.** The conversion of the anhydride groups of MAn-g-EPM ($X_{Anh}$) as a function of reaction time for the reactions with BD, DD, CHDM and BPA at 50 °C (5 mol% of PTSA).

Figure 5.4 shows $X_{Anh}$ as a function of the reaction time for the cross-linking reaction of MAn-g-EPM with different diols at 50 °C. The highest equilibrium conversions and reaction rates are observed for the linear aliphatic diols, i.e., BD and DD. The reactions with CHDM and BPA are significantly slower and do not reach equilibrium within 15-20 hrs and/or have lower equilibrium conversions. For CHDM, the lower reactivity in comparison to linear aliphatic diols is probably related to steric hindrance by the cyclohexane ring. The aromatic diol BPA has the lowest tendency to react with the anhydride groups, since aromatic alcohols are weaker nucleophiles, as indicated by their higher acidity (pKa ~10) compared to aliphatic alcohols (pKa ~16-18).
The final (equilibrium) conversions ($X_{Anh,eq}$) were determined for the reaction of MAn-g-EPM with DD as a function of the reaction temperature and are shown in Figure 5.5a. $X_{Anh,eq}$ has high values of about 90% at low temperature, but decreases with increasing temperature to values below 10% at 200 ºC, where the equilibrium is almost completely shifted towards anhydride and alcohol. These results show that the equilibrium of the anhydride/alcohol reaction and, consequently, the level of cross-linking are highly dependent on temperature. Therefore, cross-linking reactions are performed at temperatures as low as possible to obtain high conversions, while still enabling sufficient flow of the rubber, resulting in a compression molding temperature of 75 ºC.

![Graph showing equilibrium conversion vs. temperature](image)

**Figure 5.5.** (a) The equilibrium conversion of the anhydride groups of MAn-g-EPM ($X_{Anh,eq}$) as a function of the temperature for the reaction with DD (5 mol% of PTSA). The solid line was determined via the dependency of $X_{Anh,eq}$ on the temperature using the Van ‘t Hoff equation (Equation 5.5). (b) The equilibrium constant K versus the reciprocal temperature for the reaction of MAn-g-EPM with DD (5 mol% PTSA).

It is possible to determine the equilibrium constant K for this reaction. If the reactivity of the second alcohol group is assumed to be similar to the first one, Scheme 5.1 simplifies to:

\[
\text{anhydride + alcohol} \underset{k_d}{\overset{k_f}{\rightleftharpoons}} \text{hemi-ester}
\]

Then, the following equation of the equilibrium constant K is derived:

\[
K = \frac{k_f}{k_d} = \frac{[HE]}{[Anh] \cdot [Alc]}
\]

where [Anh], [Alc] and [HE] are the concentrations (in mol/g rubber) of the anhydride, alcohol and hemi-ester groups in the solvent cast films, respectively. K can be calculated from $X_{Anh,eq}$, since [Alc] is always equal to [Anh] for equimolar amounts of anhydride and alcohol groups and one hemi-ester is formed for each converted anhydride group. The Van ‘t Hoff equation describes the temperature dependency of K:

\[
\ln K = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R}
\]
According to this equation, a linear relationship should exist between ln(K) and the reciprocal temperature (in K), which is indeed the case, as shown in Figure 5.5b, with a correlation coefficient of 0.975. The calculated values of the standard enthalpy change ($\Delta H^0$) and entropy change ($\Delta S^0$) are -55 kJ/mol and -116 J/K·mol, respectively. Similarly to polymerization reactions, the so-called ceiling temperature ($T_{cl}$) can be calculated from these values, according to:\(^{34}\)

$$T_{cl} = \frac{\Delta H^0}{\Delta S^0} = 202 \ ^\circ C \ \text{(5.6)}$$

For polymerization reactions, $T_{cl}$ is the temperature above which the Gibb’s free energy becomes positive and where “no” polymerization occurs anymore.\(^{34}\) Alternatively, an already-formed polymer de-polymerizes at temperatures above $T_{cl}$, until the new equilibrium with free monomer is established. Translation of this concept to cross-linked systems defines $T_{cl}$ as the temperature above which “no” cross-linking takes place and an already-formed polymer network de-cross-links. Irreversible side reactions that may occur at elevated temperatures will limit de-polymerization or de-cross-linking. The kinetics of shifting the equilibrium may be slower for polymer networks compared to linear polymers, due to the lower mobility of the polymer chain segments.

### 5.3.2. Morphology of MAn-g-EPM cross-linked with diols

The covalent cross-linking of MAn-g-EPM with diols is expected to have a significant influence on the structure and properties. Samples were obtained via compression molding at 75 °C in the presence of 5 mol% of PTSA, which were determined to be the optimal reaction conditions. Cross-linking reactions were performed with different molar levels of DD and with equimolar levels of the other diols. The values of $X_{Anh}$ were calculated from the FTIR spectra (not shown here) and are given in Table 5.2. $X_{Anh}$ is always slightly lower than targeted at similar relative conversions of 90 % for the reaction with different molar levels of DD, since the equilibrium is not completely towards hemi-ester formation (see Figure 5.5). The level of cross-linking is high for most diols when targeting at 100 % conversion, as relatively high values of $X_{Anh}$ of about 90 % are obtained. Somewhat lower $X_{Anh}$ values (~ 80 %) are obtained for EG-100 and THME-100. For EG-100, the reaction may be hindered by the short, rigid spacer. Three anhydride groups have to react with one cross-linker molecule to obtain full conversion for the THME-100 sample, which is more difficult to achieve and may explain the lower $X_{Anh}$. Cross-linking reactions with the aromatic BPA were not successful due to its lower reactivity, resulting in low conversions at 75 °C.

The morphology of the cross-linked samples was investigated using SAXS and DMTA experiments. The SAXS profiles for MAn-g-EPM cross-linked with various molar levels of DD are shown in Figure 5.6. The scattering peak for the MAn-g-EPM precursor indicates that microphase-separated anhydride-rich aggregates are present, as was shown in Chapter 2. The driving force for the formation of these aggregates, which can be envisioned as spherical clusters enriched with anhydride groups, surrounded by a layer of polymer chain segments with restricted mobility, is the large difference in polarity between the polar anhydride groups and the apolar EPM chain segments. Fitting of the SAXS profiles of the current materials with the Yarusso-Cooper model\(^{35}\), which was shown to be the best model for ionomers based on other MAn-g-EPM grades\(^{36}\), is far from straightforward (Chapter 2). Therefore, no detailed evaluation of structural models for description
of the current morphology is performed, but the qualitative changes in the scattering curves are discussed, which is allowed by scaling the intensity to the sample thickness.

![SAXS profiles](image)

**Figure 5.6.** SAXS profiles of MAN-g-EPM cross-linked with (a) various molar levels of DD and (b) equimolar levels of different aliphatic diols (all with 5 mol% PTSA and compression molded at 75 °C). The intensity of DD-25 is divided by a factor of 2 for clarity.

A scattering peak is also present after cross-linking of MAN-g-EPM with any molar level of DD, indicating that the aggregates remain upon cross-linking. The intensity of the peak increases significantly for DD-25 compared to MAN-g-EPM, while it decreases again for DD-50, DD-75 and DD-100. The partial conversion of the anhydride groups to the more polar hemi-esters results in an increased electron density difference between the aggregates and the matrix and consequently, a stronger microphase separation, which most probably causes the initial increase in intensity. Disruptive effects on the aggregate formation, due to the inclusion of more and more apolar decyl-spacers, may explain the subsequent decrease in intensity for higher X_{Anh}. The scattering peak maximum shifts to lower q-values upon increasing X_{Anh}, while the peak becomes narrower. It was shown that the main parameter affecting the position of the peak maximum is the size of the restricted mobility layer surrounding the aggregates. Dipolar interactions between the anhydride groups are replaced by strong covalent cross-links and additional hydrogen bonds between the carboxylic acid moieties of the hemi-esters upon the reaction with diols. As a result, the polymer chain segments are anchored more strongly to the aggregates, resulting in a larger restricted mobility layer, which explains the shift in the peak maximum to lower q-values. Note that the size of the aggregates themselves is also expected to increase, due to the inclusion of the relatively large decyl-spacers. However, this qualitative analysis does not allow final conclusions regarding the size of the aggregates. The SAXS profiles for DD-50, DD-75 and DD-100 are more or less similar, which indicates that the aggregate structure is hardly affected for higher conversions.

The peak intensity increases for MAN-g-EPM after cross-linking with equimolar amounts of different aliphatic diols, with the largest increase for the BD-100. The lower intensity of the EG-100 and THME-100 materials may be related to the rigidity of the short cross-links, which may disturb the aggregates to a certain extent, resulting in a poorer electron density difference. The apolar alkyl-spacers for the longer linear diols, i.e., OD-100 and DD-100, and the bulky cyclohexane group for
CHDM-100, disturb aggregate formation as well, resulting in lower peak intensities. The peak maximum shifts to lower q-values for all diols, again due to the introduction of strong cross-links and the resulting larger restricted mobility layer. The smaller shifts for THME-100 and EG-100 are most probably related to their lower X_{Anh}.

The microphase-separated aggregates for MAn-g-EPM act as physical cross-links and increase the network density compared to the parent EPM, as was demonstrated with DMTA experiments (Chapter 2). Figure 5.7 shows the storage moduli as a function of the temperature for MAn-g-EPM and the materials cross-linked with various molar levels of DD. The glass transition temperature positioned around -50 °C and the rubber plateau modulus do not change significantly upon cross-linking of MAn-g-EPM with DD. The latter indicates that the network density remains approximately constant and that the covalent cross-links are only formed within the aggregates. The aggregates become stronger upon cross-linking and persist to higher temperatures, as indicated by the extended rubber plateau for higher levels of cross-linking. An additional transition occurs around 200 °C, which may be related to irreversible di-ester formation, as will be discussed later. The storage modulus curves for MAn-g-EPM cross-linked with equimolar levels of other diols are very similar to that of DD-100 and are not shown here.

![Figure 5.7](image)

**Figure 5.7.** Storage modulus as a function of the temperature for EPM and MAn-g-EPM before and after cross-linking with various molar levels of DD (5 mol% PTSA, compression molded at 75 °C).

### 5.3.3. Mechanical properties of MAn-g-EPM cross-linked with diols

Figure 5.8a shows representative tensile curves for MAn-g-EPM cross-linked with various molar levels of DD, while average values of the hardness, the tensile strength (TS), the elongation at break (EB) and the modulus at 200 % strain (M_{200}) and the compression sets (CS) at room temperature (CS{23}) and at 70 °C (CS_{70}) are presented as a function of X_{Anh} in Table 5.2 and Figure 5.8b. The mechanical properties change significantly upon cross-linking with DD, as covalent cross-links replace the relatively weak polar interactions between the anhydride groups. TS increases and subsequently levels off for higher X_{Anh}, while the hardness and M_{200} increase continuously and CS_{23}, CS_{70} and EB decrease continuously. These changes as a function of X_{Anh} are similar to the behavior of conventionally cross-linked rubbers with varying degrees of cross-linking.37
Figure 5.8. (a) Representative tensile curves for MAn-g-EPM cross-linked with various molar levels of DD and (b) tensile properties and CS as a function of $X_{Anh}$ for cross-linking with DD (5 mol% PTSA, compression molded at 75 °C). Note that EB is divided by a factor 10 for clarity.

Table 5.2. Anhydride conversions and mechanical properties for MAn-g-EPM cross-linked with various diols at different molar levels (5 mol% PTSA, compression molded at 75 °C).

<table>
<thead>
<tr>
<th>Sample</th>
<th>$X_{Anh}$ (%)</th>
<th>Hardness (Shore A)</th>
<th>TS (MPa)</th>
<th>EB (%)</th>
<th>$M_{200}$ (MPa)</th>
<th>CS$_{23}$ (%)</th>
<th>CS$_{70}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MAn-g-EPM</td>
<td>0</td>
<td>38</td>
<td>0.4</td>
<td>560</td>
<td>0.4</td>
<td>88</td>
<td>100</td>
</tr>
<tr>
<td>DD-25</td>
<td>22</td>
<td>47</td>
<td>1.4</td>
<td>490</td>
<td>0.8</td>
<td>51</td>
<td>80</td>
</tr>
<tr>
<td>DD-50</td>
<td>46</td>
<td>49</td>
<td>1.5</td>
<td>410</td>
<td>0.9</td>
<td>31</td>
<td>61</td>
</tr>
<tr>
<td>DD-75</td>
<td>68</td>
<td>52</td>
<td>1.8</td>
<td>330</td>
<td>1.2</td>
<td>23</td>
<td>-</td>
</tr>
<tr>
<td>DD-100</td>
<td>90</td>
<td>54</td>
<td>1.6</td>
<td>250</td>
<td>1.4</td>
<td>16</td>
<td>46</td>
</tr>
<tr>
<td>EG-100</td>
<td>77</td>
<td>55</td>
<td>2.0</td>
<td>420</td>
<td>1.2</td>
<td>36</td>
<td>-</td>
</tr>
<tr>
<td>BD-100</td>
<td>90</td>
<td>55</td>
<td>2.1</td>
<td>270</td>
<td>1.6</td>
<td>26</td>
<td>-</td>
</tr>
<tr>
<td>OD-100</td>
<td>92</td>
<td>54</td>
<td>1.4</td>
<td>230</td>
<td>1.3</td>
<td>14</td>
<td>-</td>
</tr>
<tr>
<td>CHDM-100</td>
<td>92</td>
<td>55</td>
<td>1.7</td>
<td>240</td>
<td>1.5</td>
<td>16</td>
<td>-</td>
</tr>
<tr>
<td>THME-100</td>
<td>82</td>
<td>54</td>
<td>2.0</td>
<td>250</td>
<td>1.6</td>
<td>21</td>
<td>-</td>
</tr>
</tbody>
</table>

In these systems, the introduction of covalent cross-links does not result in an increase in the cross-link density, as demonstrated by DMTA experiments (Figure 5.7), but rather increases the strength of the aggregates. This results in an increased resistance against deformation upon increasing $X_{Anh}$ and, thus, in a higher $M_{200}$ and hardness. CS is a measure for the elasticity of a material and has values of 0 % for an ideally elastic material and 100 % for a fully plastic material. For materials containing (thermo)reversible interactions, CS depends on two (relaxation) processes, namely plastic deformation during compression and elastic recovery after removal of the compression. The introduction of covalent cross-links results in an improved resistance against plastic deformation and, consequently, an improved (lower) CS with increasing $X_{Anh}$. More significant plastic deformation occurs at higher temperatures, which explains the much poorer CS$_{70}$ than CS$_{23}$. 
Similar trends for M_{200} and CS were observed during previous work on the cross-linking of the same MAn-g-EPM with ionic interactions (Chapter 2), hydrogen bonds combined with ionic interactions (Chapter 3) and multiple hydrogen bonding arrays (Chapter 4). However, for those materials, TS increased constantly and EB remained almost constant with increasing aggregate strength, while much higher values of TS (up to 10 MPa) and EB (up to 800 %) were observed. An “ion hopping” mechanism is responsible this: ionic groups, as well as hydrogen bonds, can disconnect their interactions and hop between aggregates during deformation, which allows stress relaxation for the corresponding chain segments and prevents premature failure to increase EB. These “free” groups can re-form their interactions upon encountering other free groups after entering a new aggregate and contribute to the network again, which explains the increase in TS.

For the current materials, hopping is possible for the weak polar interactions between anhydride groups, but definitely not for the covalent cross-links during the tensile experiment, since the equilibrium of the reaction is extremely slow at low temperatures. For the latter, chemical bonds have to break once the stress level becomes too high, eventually resulting in premature failure and lower TS and EB values. More and more covalent cross-links are introduced at the expense of the polar interactions upon increasing X_{Anh}, which results in less hopping and a decreasing EB. TS increases initially, since the material can bear relatively high stress levels before chemical bonds are broken. At a certain X_{Anh}, the stress level becomes sufficiently high to break chemical bonds, which explains the subsequent leveling off of TS.

![Graph](image)

**Figure 5.9.** Representative tensile curves for MAn-g-EPM cross-linked with equimolar levels of different aliphatic diols (5 mol\% PTSA and compression molded at 75 °C).

Representative tensile curves for MAn-g-EPM cross-linked with equimolar levels of various diols are shown in Figure 5.9, while the hardness, tensile properties and CS_{23} are given in Table 5.2. All properties are significantly changed upon cross-linking with any diol. The differences between the different diols are relatively small compared to the effects upon changing X_{Anh}. The hardness is increased compared to MAn-g-EPM, but is more or less similar for all cross-linked materials. The tensile properties of BD-100 are significantly better compared to OD-100, DD-100 and CHDM-100, due to the disturbing effect of the longer alkyl-spacers on the aggregate formation for the latter materials. The lower (better) CS_{23} for the longer diols may be related to the higher flexibility of the
spacer, which may allow better elastic recovery after removal of the compression. The different
tensile behavior of EG-100 and its higher $CS_{23}$ are most probably related to the significantly lower
$X_{Anh}$, which has a major influence on the mechanical properties (Figure 5.8). Cross-linking with a
triol (THME-100) does not result in significant improvements in the tensile properties or CS.

5.3.4. (Re)processability of MAn-g-EPM cross-linked with diols

It was shown in the previous section that the introduction of covalent cross-links results in
significantly improved tensile strength and elasticity compared to MAn-g-EPM. The question now
arises whether the covalent cross-links are thermoreversible and whether these materials are truly
reprocessable. In an initial approach, compression-molded films of DD-100 were cut into small
pieces and compression molded for varying times at temperatures between 100 and 200 °C.
Insufficient flow occurs at temperatures of 150 °C and below, even after several hours, resulting in
heterogeneous and only partially-fused films. Homogeneous, fully-fused films are only obtained
after compression molding for 20 min at 175 and 200 °C, indicating that the DD-100 sample is
indeed reprocessable, but only at more elevated temperatures.

It is possible to calculate the gel point ($X_{gel}$) for this system, i.e., the $X_{Anh}$ for which a network is
just formed, and to determine the minimal temperature required for the disappearance of the
network ($T_{gel}$) via interpolation of the data in Figure 5.5a. The average anhydride functionality of
the MAn-g-EPM chains ($f$) is calculated according to:

$$f = \frac{M_{EPM} \cdot DG \cdot 1000}{M_{Anh} \cdot 100} = 8.5$$  \hspace{1cm} (5.7)

where $M_{EPM}$ is the number-average molecular weight of the EPM precursor (40 kg/mol), DG is the
degree of grafting (2.1 wt%) and $M_{Anh}$ is the molecular weight of the grafted anhydride
(99.07 g/mol). According to Stockmayer,\(^{39}\) $X_{gel}$ for equimolar ratios of starting functional groups,
i.e., anhydride and alcohol, is given by:

$$X_{gel} = \frac{1}{f - 1} \cdot \frac{1}{g - 1} = 0.365$$  \hspace{1cm} (5.8)

where $g$ is the functionality of the diol (equal to 2). Interpolation in Figure 5.5a results in $T_{gel}$ of
155 °C. This approach is only used as a rough estimate, since the current cross-links are present
within multi-functional microphase-separated aggregates instead of being only di-functional. An
additional complication is the occurrence of irreversible side reactions, which limit the reversibility
to a certain extent, as will be shown later in this section. Nevertheless, this exercise demonstrates
that highly elevated temperatures are required for suitable flow of diol-cross-linked MAn-g-EPM.

The materials cross-linked with equimolar levels of different diols could all be remolded into
homogeneous films at a temperature of 175 °C. The DD-100 material was subjected to an additional
second remolding step. Two completely different types of behavior are observed based on the
changes in the FTIR spectra and the mechanical properties upon remolding, distinguishing between
the short (EG-100 and BD-100) and longer diols (OD-100, DD-100 and CHDM-100).
To illustrate this, the FTIR spectra of BD-100 and DD-100 before and after reprocessing are shown in Figure 5.10, while $X_{\text{Anh}}$ is given in Table 5.3. The FTIR spectra of EG-R1 (similar to BD-R1), OD-R1 and CHDM-R1 (both similar to DD-R1) are not shown here. The intensity of the anhydride band at 1785 cm$^{-1}$ increases significantly upon remolding for all diols, resulting in a lowered $X_{\text{Anh}}$. The main differences are observed for the relative intensities of the ester and carboxylic acid bands at 1735 and 1710 cm$^{-1}$, respectively. Upon reprocessing of DD-100, the intensity of the carboxylic acid band decreases, while the ester band does not change significantly. The most evident explanation for these changes is that a significant fraction of hemi-ester is converted to di-ester and anhydride groups according to Scheme 5.2, which is an irreversible reaction due to water evaporation.$^{26,29,30}$ Di-ester formation limits the reversibility, although its extent is too low to prevent further reprocessing, as fully-fused films are still obtained after remolding of DD-R1 at 175 °C. The increased intensity of the anhydride band and the decreased intensity of the carboxylic acid band for DD-R2 compared to DD-R1 show that further di-ester and anhydride formation occurs during the second remolding step.

**Figure 5.10.** FTIR spectra of MAn-g-EPM cross-linked with BD and DD (5 mol% PTSA) before and after reprocessing. The spectra are shifted vertically for clarity.

**Figure 5.11.** Representative tensile curves of MAn-g-EPM cross-linked with equimolar levels of BD and DD before and after remolding at 175 °C (5 mol% PTSA).

**Scheme 5.2.** Di-ester and anhydride formation from two hemi-esters at elevated temperatures.

For BD-100, the intensities of both the ester and the carboxylic acid bands decrease, while their ratio remains more or less constant. This indicates that di-ester formation as for DD-R1 (Scheme 5.2) is unlikely, since this would result in a decrease of the intensity of the carboxylic acid band compared to the ester band. A shift of the anhydride/hemi-ester equilibrium according to...
Scheme 5.1 cannot be responsible for these changes, since in that case, the FTIR spectra would be similar before and after remolding, as the forward reaction would occur again upon cooling. The significant reformation of anhydride groups may be explained by the evaporation of (a fraction of) the diol during compression molding. The mold was opened at regular time intervals during compression molding to remove trapped air. The boiling point of EG is 196-198 °C, which allows evaporation of EG at 175 °C. Evaporation of BD with a boiling point of 228 °C is unlikely, but a reaction of BD to form the volatile tetrahydrofuran (THF, boiling point of 66 °C) is known to occur in the presence of acid catalysts at moderately elevated temperatures.\textsuperscript{40,41} Here, two types of acids are present, i.e., the catalyst PTSA and the carboxylic acid groups in the hemi-ester. The evaporation of EG and BD (via THF formation) apparently competes with irreversible di-ester formation and prevents it to a large extent.

Figure 5.11 shows representative tensile curves of BD-100 and DD-100 before and after remolding. The tensile properties change significantly upon remolding, as is the case for all diols (Table 5.3). Remolding results in a decrease in $X_{\text{Anh}}$, which explains the decreased $M_{200}$, the increased EB and CS\textsubscript{23} and the minor changes in TS, similarly to the trends observed in Figure 5.8b. The changes in properties are smaller for the longer, less volatile diols, which is related to their higher $X_{\text{Anh}}$ after remolding. The film for DD-R1 was not completely homogeneous, so the presence of small defects may explain the relatively low TS and EB for this material.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$X_{\text{Anh}}$ (%)</th>
<th>TS (MPa)</th>
<th>EB (%)</th>
<th>$M_{200}$ (MPa)</th>
<th>CS\textsubscript{23} (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EG-R1</td>
<td>44</td>
<td>1.9</td>
<td>590</td>
<td>0.8</td>
<td>42</td>
</tr>
<tr>
<td>BD-R1</td>
<td>49</td>
<td>1.9</td>
<td>580</td>
<td>0.8</td>
<td>43</td>
</tr>
<tr>
<td>OD-R1</td>
<td>65</td>
<td>1.8</td>
<td>350</td>
<td>1.0</td>
<td>23</td>
</tr>
<tr>
<td>DD-R1</td>
<td>65</td>
<td>1.2</td>
<td>240</td>
<td>1.1</td>
<td>18</td>
</tr>
<tr>
<td>DD-R2</td>
<td>56</td>
<td>1.6</td>
<td>320</td>
<td>1.0</td>
<td>-</td>
</tr>
<tr>
<td>CHDM-R1</td>
<td>54</td>
<td>1.9</td>
<td>380</td>
<td>1.0</td>
<td>29</td>
</tr>
</tbody>
</table>

### 5.3.5. Mechanism of (re)processability studied with FTIR spectroscopy

As discussed above, MAn-g-EPM cross-linked with diols can indeed be reprocessed via compression molding. Unfortunately, FTIR spectroscopy of samples before and after compression molding does not unambiguously show which mechanism of reversibility is involved, as the (chemical) changes during the actual compression molding step at elevated temperatures remain unclear. Therefore, FTIR spectroscopy was performed on solvent-cast films during heating-cooling cycles according to Figure 5.1. Figure 5.12 shows the changes in the FTIR spectra of MAn-g-EPM cross-linked with DD and BD during the experiment with $T_{\text{max}}$ of 175 °C. The cross-linking reaction is almost completed after 1 day at 50 °C for both DD and BD, as indicated by the low intensity of the anhydride band at 1785 cm\textsuperscript{-1}. 
Thermoreversible Covalent Cross-linking with Diols

Figure 5.12. FTIR spectra of MAn-g-EPM cross-linked with (a) DD and (b) BD during two cycles of heating for 20 min at 175 °C followed by cooling for 30 min at 50 °C (5 mol% PTSA). The spectra are scaled on the EPM backbone band at 1460 cm⁻¹ and shifted vertically for clarity.

The intensity of the anhydride band increases during the first heating step for MAn-g-EPM cross-linked with DD, while the intensity of the carboxylic acid band at 1710 cm⁻¹ decreases. The unaffected intensity of the ester band at 1735 cm⁻¹ indicates that the amount of ester, present in either hemi- or di-ester groups, does not change upon heating. The anhydride and ester bands do not change in intensity during cooling at 50 °C, which shows that the changes during heating are irreversible and that the (desired) shift in equilibrium from hemi-ester towards anhydride and alcohol does not occur at elevated temperature. Rather, the observed changes are related to irreversible di-ester and anhydride formation (Scheme 5.2), which occurs rather fast, since significant changes are only observed initially. The small increase in intensity of the carboxylic acid band at 1710 cm⁻¹ upon cooling is related to the re-formation of some hydrogen-bonded dimers, which disappear to some extent at elevated temperature to yield an absorption band around 1760-1735 cm⁻¹. This band is not visible during heating, due to overlap with the ester band. No significant reactions occur during the second heating-cooling cycle, as indicated by the similar FTIR spectra as for the first cycle.

A more pronounced increase in the intensity of the anhydride band occurs for MAn-g-EPM cross-linked with BD during the first heating step compared to DD, while both the ester and carboxylic acid bands decrease in intensity. These changes are irreversible, as the intensities of the anhydride or ester bands do not change during the subsequent cooling step. These results show that no shift in the anhydride/hemi-ester equilibrium occurs for BD as well. Again, the observed increase in the carboxylic acid band upon cooling is related to the reformation of hydrogen bonds. As discussed in the previous section, the evaporation of BD (via THF formation) most probably causes the observed changes in the FTIR spectra. The intensity of the carboxylic acid band is still somewhat lower compared to the ester band, which suggests that some di-ester (and anhydride) formation occurs for the BD-cross-linked MAn-g-EPM during this experiment. The changes in the FTIR spectra become somewhat more pronounced during the second heating-cooling cycle, indicating that some further evaporation of the cross-linker occurs.
Similar trends are observed for both DD and BD during experiments with $T_{\text{max}}$ of 150 and 200 °C (not shown here), although the di-ester formation for DD and the evaporation of BD become more pronounced at 200 °C. The changes in the FTIR spectra after the heating-cooling cycles are comparable to the changes after compression molding (Figure 5.10) for MAn-g-EPM cross-linked with both DD and BD, indicating that similar processes occur during these experiments.

These results show that the anhydride/hemi-ester equilibrium does not shift upon heating or cooling, although it was previously shown that the anhydride/alcohol reaction is highly temperature-dependent (Figure 5.5). First of all, the kinetics of shifting the equilibrium may become rather slow for polymer networks. Furthermore, the cross-links are present within microphase-separated aggregates, which persist to the reprocessing temperatures (Figure 5.7). Diffusion of the polymer chain segments within the aggregates and the surrounding restricted mobility layer is much slower compared to the chains within the matrix, resulting in even slower kinetics. Finally, the anhydride/hemi-ester equilibrium is significantly affected by di-ester formation and/or evaporation of short diols at elevated temperatures. The combination of these effects most probably explains why no shift in the equilibrium is observed at elevated temperatures.

Therefore, the original concept of de-cross-linking of hemi-esters to anhydride and alcohol groups at elevated temperatures is falsified. However, flow does occur for all cross-linked samples during compression molding. This seemingly contradiction is explained by the dynamics of the system, i.e., a continuous exchange between cross-linked and non-cross-linked groups, which of course becomes faster at elevated temperatures. The hemi-ester cross-links continuously disconnect, which gives freedom of movement to two previously-connected chain segments. The free functional groups can leave the aggregate and hop between aggregates, where they can react with other groups to re-form cross-links. Some of the chain segments become restricted in their movement, due to the formation of irreversible di-ester connections or even cross-links, although to such a low extent that flowability is retained. This mechanism, which is quite similar to the ion-hopping mechanism for ionomers, explains the flowability of these materials without a net shift in the anhydride/hemi-ester equilibrium. The diol-cross-linked MAn-g-EPM behaves as covalently cross-linked network during mechanical testing, due to the extremely slow equilibrium dynamics at low temperatures.

### 5.4. Conclusions

In this chapter, the thermoreversible covalent cross-linking of MAn-g-EPM with diols was studied. Cross-links are formed via the reversible reaction of the cyclic anhydride groups of MAn-g-EPM with the alcohols of the diol to yield hemi-esters. FTIR spectroscopy showed that the addition of a catalyst is necessary to obtain sufficiently fast reactions and that the acid PTSA is more suitable for this than the base DABCO. The use of aliphatic diols results in high conversions at 50 °C for solvent-cast films and at 75 °C for compression-molded samples, whereas aromatic diols are much less reactive. The anhydride/hemi-ester equilibrium is highly dependent on the temperature, as the anhydride conversions are high at low temperature and low at elevated temperatures.

SAXS measurements demonstrated the presence of microphase-separated aggregates that act as physical cross-links for both MAn-g-EPM and all cross-linked materials. DMTA showed that the
cross-linking with diols does not increase the network density, which suggests that the hemi-ester cross-links are solely formed within the aggregates. The covalent cross-links anchor the polymer chain segments more strongly to the aggregates, resulting in stronger aggregates that persist to higher temperatures. The mechanical properties change significantly upon cross-linking. $M_{200}$ increases for increasing $X_{Anh}$, while EB and CS decrease and TS increases to a plateau value. These trends are comparable to the behavior of conventionally cross-linked elastomers as a function of the cross-link density, but differ from the observations for MAn-g-EPM-based ionomers. The influence of the structure of the diol on the properties is relatively small compared to the effect of $X_{Anh}$.

The cross-linked materials can be compression molded at temperatures of 175 °C and higher, indicating that the cross-links are indeed thermoreversible. Significant irreversible di-ester formation occurs for longer diols, such as DD, but does not prevent further reprocessing. Short, volatile diols evaporate out of the material at elevated temperatures, which may occur via THF formation for BD. The mechanical properties change significantly after reprocessing, due to the decreased $X_{Anh}$. FTIR experiments showed that the reprocessability of these materials does not originate from a shift of the anhydride/hemi-ester equilibrium at elevated temperatures, despite the demonstrated temperature dependence of this reaction. Rather, a continuous, dynamic exchange between cross-linked and non-cross-linked species, which allows cross-links to continuously disconnect, is thought to be responsible for the processability.

5.5. References

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35 Yarusso, D. J.; Cooper, S. L. Macromolecules 1983, 16, 1871-1880.
Chapter 6

Thermoreversible Covalent Cross-linking with Diamines and Amino-alcohols

Maleated ethylene/propylene copolymer (MAn-g-EPM) was thermoreversibly cross-linked using di-functional cross-linkers containing different combinations of alcohol and primary, secondary and tertiary amine groups. Covalent cross-links are formed via the equilibrium reaction of the grafted anhydride groups with di-functional cross-linkers containing primary and secondary amines and alcohols, while a shift of the equilibrium at elevated temperatures may result in their (partial) removal. Ionic interactions with ammonium cations are introduced upon neutralization of the hydrolyzed anhydride groups with tertiary amines. Microphase-separated aggregates that act as physical cross-links are already present in the MAn-g-EPM precursor. The aggregates persist upon cross-linking with an unaffected network density, which suggests that the covalent or ionic cross-links are only formed within the aggregates. The strong covalent cross-links yield an improved elasticity compared to the relatively weak ionic interactions, but poorer tensile properties, which is attributed to the role of the ion hopping process for the ionic interactions. The materials are truly reprocessable via compression molding at elevated temperatures if ionic interactions or covalent cross-links containing only secondary amine and alcohol groups are used. Irreversible imide formation prevents flow for covalent cross-linkers containing primary amine groups. The reprocessability of the materials with covalent cross-links does not originate from the expected equilibrium shift, but from a continuous, dynamic exchange between cross-linked and non-cross-linked functional groups.

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6.1. Introduction

In Chapter 5, the thermoreversible covalent cross-linking of maleated ethylene/propylene copolymer (MAn-g-EPM) with diols was studied. The cross-linked materials were reprocessable via compression molding, indicating that the equilibrium reaction of anhydrides with alcohols to form hemi-esters (Scheme 6.1A) indeed results in thermoreversible covalent cross-links. The reversibility was somewhat limited due to irreversible di-ester formation\(^1\,^2\) at elevated temperatures, although its extent was not high enough to prevent reprocessability. The original concept of formation of hemi-ester cross-links via the forward reaction at low temperatures and their (partial) removal after a shift in the equilibrium at elevated temperatures was falsified. Instead, a continuous, dynamic exchange between cross-linked and non-cross-linked (“free”) functional groups was responsible for the reprocessability of these materials.

Scheme 6.1. Reaction scheme for the modification of MAn-g-EPM with alcohols and amines.

This chapter discusses the thermoreversible cross-linking of the same MAn-g-EPM, now using difunctional cross-linkers containing different combinations of alcohol and/or amine groups, mainly aimed to improve the reversibility. The reaction with primary (1°) amines may be less suitable for thermoreversible cross-linking, as the initially-formed 1° amide-acids are prone to irreversible imide formation already at moderately elevated temperatures (Scheme 6.1B).\(^3\,^6\) The use of
secondary (2°) amines results in a thermoreversible reaction, since imide formation is not possible (Scheme 6.1C). Tertiary (3°) amines cannot react with cyclic anhydride groups, but may be used to neutralize carboxylic acid groups. Therefore, the addition of 3° amines to hydrolyzed anhydride groups will result in the formation of ionic interactions with ammonium cations (Scheme 6.1D). As a consequence, covalent cross-links are formed for any combination of alcohol and 1° and 2° amine groups, while ionic interactions are obtained for two 3° amine groups and a combination of ionic interactions and covalent bonds for cross-linkers with one 3° amine group.

First, the chemical structures and the anhydride conversions of the cross-linked materials are determined using Fourier transform infrared (FTIR) spectroscopy. Next, the cross-linked materials are compression molded at various temperatures to determine their reprocessability, while FTIR spectroscopy is used to study whether (undesired) reactions occur. The effects of the type of cross-linker on the morphology, as studied by small-angle X-ray scattering (SAXS) and dynamic mechanical thermal analysis (DMTA), and the mechanical properties, i.e., hardness, tensile properties and compression set (CS), are studied for the reprocessable materials. Selected materials are subjected to heating-cooling cycles during time-resolved FTIR experiments to elucidate the mechanism of reversibility at elevated temperatures.

**6.2. Experimental section**

**6.2.1. Materials**

Maleated ethylene/propylene copolymer (MAn-g-EPM, 49 wt% ethylene, 49 wt% propylene, 2.1 wt% maleic anhydride (MA), M_n = 40 kg/mol, M_w = 90 kg/mol, DSM Elastomers) was dried for 1 h at 170 °C under reduced pressure with a low N_2-flow prior to use to convert all carboxylic acid groups, formed upon hydrolysis, back to anhydride. Ethylenediamine (1°-1°), N,N'-dimethylethlenediamine (2°-2°), N,N,N',N'-tetramethylethlenediamine (3°-3°), N-methylethlenediamine (1°-2°), N,N-dimethylethlenediamine (1°-3°), N,N,N'-trimethylethlenediamine (2°-3°), ethanolamine (1°-OH), 2-(methylamino)ethanol (2°-OH), ethyleneglycol (OH-OH), N,N-dimethylethanolamine (OH-3°) and p-toluenesulfonic acid monohydrate (all from Aldrich) and tetrahydrofuran (THF, Biosolve) were used as received.

**6.2.2. Sample preparation**

Typically, 15 g of MAn-g-EPM was dissolved in 150 g of THF at 60 °C, after which the solution was cooled down to room temperature. MAn-g-EPM was partially (around 50 %) or fully hydrolyzed via exposure to water from air for prolonged time at room temperature prior to the modification reactions with cross-linkers containing one and two 3° amine groups, respectively. For the modification with the OH-OH cross-linker, 5 mol% of p-toluenesulfonic acid was added to the solution as a catalyst. Next, the required amount of cross-linker (0.5 mol of di-functional cross-linker per mol of anhydride group) was added to the solution, which was stirred for at least 30 min. The resulting solution or gel was poured into a Teflon-covered Petri dish and dried for several days under a N_2-flow at room temperature, followed by drying under vacuum for one day at 50 °C. The cross-linked materials were compression molded between Teflon sheets for 20 min at 125 and 150 °C and for 30 min at 175 °C in a Collin press to determine the optimal reprocessing conditions. Samples were compression molded for 20 min at 175 °C for characterization purposes and reversibility experiments.
6.2.3. Characterization techniques

*Fourier transform infrared (FTIR) spectroscopy.* Compression-molded films were analyzed on a BioRad Excalibur 3000 spectrometer equipped with a Specac Golden Gate attenuated total reflection (ATR) setup over a spectral range from 650 to 4000 cm\(^{-1}\) at a resolution of 4 cm\(^{-1}\), co-adding 20 scans. The conversion of the anhydride groups (X\(_{Anh}\)) is calculated from the absorbance of the anti-symmetric carbonyl stretching (C=O) vibration band at 1785 cm\(^{-1}\) of the anhydride groups, using the absorbance of the band at 1460 cm\(^{-1}\), which originates from the overlapping anti-symmetric CH\(_3\) bending and CH\(_2\) scissoring vibrations of the EPM backbone, as internal reference:

\[
X_{Anh} = \left(1 - \frac{A_{1785}/A_{1460}}{A_{1785}/A_{1460}}_{\text{cross-linked}}\right) \times 100\%
\]

(6.1)

Reversibility experiments were performed on thin (~100 μm) compression-molded films on a BioRad FTS6000 spectrometer equipped with a UMA500 FTIR microscope over a spectral range from 650 to 4000 cm\(^{-1}\) at a resolution of 2 cm\(^{-1}\), co-adding 20 scans. Samples were measured on a zinc selenide disk in transmission mode with an exposed sample area of approximately 30 by 30 μm using a MCT detector. Samples were exposed to the temperature profile in Figure 5.1 with a Linkam TMS600 hotstage.

*Small-angle X-ray scattering (SAXS).* SAXS experiments were performed on compression-molded samples at the DUBBLE beamline (BM26) at the European Synchrotron Radiation Facility (ESRF) in Grenoble (France). The data were collected using a 2D multiwire gas-filled detector with pixel array dimensions of 512 x 512. The detector was positioned at 2.5 m from the sample and the q-scale was calibrated using the positions of diffracted peaks of silver behenate. The exposure time for each sample was 300 s and a wavelength of 1.2 Å was used. The experimental data were corrected for background scattering, i.e., subtraction of instrumental errors, and transformed into 1D-plots by azimuthal-angle integration using the FIT2D program developed by Dr. Hammersley of ESRF. The profiles were scaled for the sample thickness to allow a comparison of the intensities of different samples.

*Dynamic mechanical thermal analysis (DMTA).* Rectangular samples with dimensions of around 10 x 3 x 1 mm were measured over a temperature range from -100 to 250 °C at a heating rate of 3 °C/min and a frequency of 1 Hz on a DMA Q800 (TA Instruments) with film tension clamps.

*Hardness.* The hardness was measured on 6 mm thick samples using a Shore A durometer according to ASTM D2240-91.

*Tensile testing.* Dumbbell-shaped tensile bars with dimensions of 35 x 2 x 1 mm and a parallel specimen length of 17.5 mm were punched from compression-molded films. Tensile tests were performed with a constant speed of 0.5 mm/s at room temperature on a Zwick Z010 tensile tester equipped with a force cell of 20 N using TestXpert v7.11 software. All materials were tested in at least five-fold.

*Compression set (CS).* Cylindrical samples with a diameter of 13 mm and a thickness of approx. 6 mm were compressed for 22 h between two parallel plates with a linear deformation of 25 % at room temperature (CS\(_{23}\)) or at 70 °C (CS\(_{70}\)). CS was determined after a relaxation time of 30 min at room temperature using:

\[
CS = \left(\frac{t_0 - t_f}{t_0 - t_n}\right) \times 100\%
\]

(6.2)

where \(t_0\) is the thickness of the spacer and \(t_n\) and \(t_f\) are the initial and final sample thickness, respectively.
6.3. Results and discussion

6.3.1. Cross-linking reactions of MAn-g-EPM

The MAn-g-EPM precursor is cross-linked in solution using equimolar amounts of various difunctional cross-linkers with the same ethylene spacer, which are shown in Table 6.1 including their abbreviations. The chemical reactions of the cyclic anhydride groups of MAn-g-EPM with 1° or 2° amines are extremely fast in solution without a catalyst even at room temperature,\(^3,8\) resulting in immediate gelation for the 1°-1°, 1°-2° and 2°-2° cross-linkers. For the 1°-OH, 2°-OH, OH-OH and 3°-OH cross-linkers, the reaction of the cyclic anhydride groups with alcohols does not occur in solution even in the presence of a catalyst (Chapter 5), so no gelation occurs and cross-links are only formed after solvent evaporation. Then the reactions are catalyzed by a suitable catalyst (p-toluenesulfonic acid) for the OH-OH cross-linker (Chapter 5) or by the (1°, 2° or 3°) amine groups\(^9\) for the reactions with cross-linkers containing one OH-functionality. The solutions become somewhat more viscous for the reactions with the 1°-3°, 2°-3° and 3°-3° cross-linkers, due to the formation of ionic interactions between the 3° amine groups and the neutralized carboxylic acids.

Table 6.1. Overview of the different cross-linkers used in this study.

<table>
<thead>
<tr>
<th>Cross-linker</th>
<th>Name (abbreviation)</th>
<th>Cross-linker</th>
<th>Name (abbreviation)</th>
</tr>
</thead>
</table>
| \[
\begin{array}{c}
\text{H} \\
\text{H} \\
\text{N} \\
\text{H} \\
\text{H} \\
\text{H}
\end{array}
\] | ethylenediamine \((1°-1°)\) | \[
\begin{array}{c}
\text{N} \\
\text{N}
\end{array}
\] | \[
\begin{array}{c}
\text{H} \\
\text{H} \\
\text{N} \\
\text{N}
\end{array}
\] | \[
\begin{array}{c}
\text{N} \\
\text{N}
\end{array}
\] | \[
\begin{array}{c}
\text{H} \\
\text{H} \\
\text{N} \\
\text{N}
\end{array}
\] | \[
\begin{array}{c}
\text{N},\text{N},\text{N'},\text{N'}-tetra- \\
\text{methylethylene diamine} \\
(3°-3°)
\end{array}
\] | \[
\begin{array}{c}
\text{N},\text{N'},\text{N'}- \\
tetramethylethylene diamine \\
(3°-3°)
\end{array}
\] |
| \[
\begin{array}{c}
\text{H} \\
\text{H} \\
\text{N} \\
\text{H}
\end{array}
\] | N-methyl ethylenediamine \((1°-2°)\) | \[
\begin{array}{c}
\text{N} \\
\text{H}
\end{array}
\] | ethyleneglycol \((\text{OH-OH})\) |
| \[
\begin{array}{c}
\text{H} \\
\text{H} \\
\text{N} \\
\text{N}
\end{array}
\] | N,N-dimethyl ethylenediamine \((1°-3°)\) | \[
\begin{array}{c}
\text{N} \\
\text{N}
\end{array}
\] | aminoethanol \((1°-\text{OH}°)\) |
| \[
\begin{array}{c}
\text{H} \\
\text{H} \\
\text{N} \\
\text{N}
\end{array}
\] | N,N'-dimethyl ethylenediamine \((2°-3°)\) | \[
\begin{array}{c}
\text{N} \\
\text{H}
\end{array}
\] | 2-(methylamino) ethanol \((2°-\text{OH}°)\) |
| \[
\begin{array}{c}
\text{H} \\
\text{H} \\
\text{N} \\
\text{N}
\end{array}
\] | N,N,N'-trimethyl ethylenediamine \((2°-3°)\) | \[
\begin{array}{c}
\text{N} \\
\text{H}
\end{array}
\] | N,N-dimethyl ethanolamine \((\text{OH}-3°)\) |

The conversions of the cyclic anhydride groups \((X_{\text{Anh}})\) were calculated from the respective FTIR spectra (not shown here) using the (decreased) intensity of the band at 1785 cm\(^{-1}\) (Equation 6.1) and are given in Table 6.2. They are not determined for the cross-linkers with 3° amine groups, since the use of partially or fully hydrolyzed starting materials results in unreliable calculations. Conversions of approx. 80 % and higher are obtained for the covalently cross-linked materials,
indicating relatively high levels of cross-linking, with the exception of the 1°-2° cross-linker, which may be related to inhomogeneous reaction within the highly viscous reaction medium.

Table 6.2. Overview of the absorption bands for the cross-linked materials and their (suggested) chemical structures.

<table>
<thead>
<tr>
<th>Cross-linker</th>
<th>$X_{anhyd}$ (%)</th>
<th>Ester</th>
<th>Acid</th>
<th>Amide-I</th>
<th>Carboxylate</th>
<th>Amide-II</th>
<th>Suggested structure(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1°-1°</td>
<td>82</td>
<td></td>
<td>1710</td>
<td>1641</td>
<td>1548</td>
<td>amide-acid</td>
<td></td>
</tr>
<tr>
<td>1°-2°</td>
<td>67</td>
<td></td>
<td>1711</td>
<td>1640$^*$</td>
<td>1545</td>
<td>amide-acid</td>
<td></td>
</tr>
<tr>
<td>2°-2°</td>
<td>89</td>
<td></td>
<td>1713</td>
<td>1643$^*$</td>
<td></td>
<td>(2°) amide-acid</td>
<td></td>
</tr>
<tr>
<td>1°-OH</td>
<td>77</td>
<td>1737</td>
<td>1709</td>
<td>1642</td>
<td>1549</td>
<td>amide-acid + hemi-ester</td>
<td></td>
</tr>
<tr>
<td>2°-OH</td>
<td>84</td>
<td>1736</td>
<td>1707</td>
<td>1634$^*$</td>
<td></td>
<td>(2°) amide-acid + hemi-ester</td>
<td></td>
</tr>
<tr>
<td>OH-OH</td>
<td>81</td>
<td>1739</td>
<td>1709</td>
<td></td>
<td></td>
<td>hemi-ester</td>
<td></td>
</tr>
<tr>
<td>1°-3°</td>
<td>-</td>
<td>1709</td>
<td>1654</td>
<td>$\approx$1560$^*$</td>
<td>$\approx$1560$^*$</td>
<td>amide-acid + carboxylate-acid</td>
<td></td>
</tr>
<tr>
<td>2°-3°</td>
<td>-</td>
<td></td>
<td>1713</td>
<td>1644</td>
<td>1569</td>
<td>amide-acid + carboxylate-acid</td>
<td></td>
</tr>
<tr>
<td>OH-3°</td>
<td>-</td>
<td>$\approx$1725$^*$</td>
<td>$\approx$1725$^*$</td>
<td>1568</td>
<td>hemi-ester + carboxylate-acid</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3°-3°</td>
<td>-</td>
<td></td>
<td>1712</td>
<td>1568</td>
<td></td>
<td>carboxylate-acid</td>
<td></td>
</tr>
</tbody>
</table>

$^*$ Broad overlapping absorption band centered at given value.

Table 6.2 gives an overview of which absorption bands are present for the cross-linked materials and suggests which chemical structures are formed. Some absorption bands are broad, due to the presence of two overlapping bands. Two new, partially overlapping absorption bands at 1735 and 1710 cm$^{-1}$ appear for the hemi-esters formed upon the reaction of cyclic anhydrides with alcohols, which originate from the C=O stretching vibrations of the ester and carboxylic acid groups, respectively.$^{10}$ The 1° amide-acid formed upon the reaction of cyclic anhydrides with 1° amines gives absorption bands at 1710 cm$^{-1}$, originating from the carboxylic acid group, and at 1640 and 1550 cm$^{-1}$, which are assigned to the C=O (amide-I) and N-H (amide-II) stretching vibrations of the amide, respectively, while the 2° amide-acid only gives the carboxylic acid and amide-I bands.$^{3,8}$ After the neutralization of the hydrolyzed anhydride groups with 3° amines, absorption bands are observed at 1710 and 1560 cm$^{-1}$, originating from the C=O stretching vibrations of the carboxylic acid and carboxylate, respectively.$^{11}$ The broad amide-I bands for the 2° amide-acids (1°-2°, 2°-2° and 2°-OH cross-linkers) suggest the presence of two different hydrogen-bonded species, possibly both intra- and intermolecular hydrogen-bonded. Table 6.2 shows that the respective expected reaction products are indeed obtained.
6.3.2. (Re)processability of the cross-linked materials via compression molding

It was shown in the previous section that the cross-linking reactions of the MAn-g-EPM precursor with all cross-linkers were successful. The question arises which of these materials are indeed reprocessable. For this purpose, cross-linked materials were compression molded at temperatures of 125, 150 and 175 °C. The materials compression molded at 175 °C were subsequently cut into small pieces (mm scale) and subjected to a second compression molding step at 175 °C. The resulting films were judged for their appearance, where good flow indicates a fully-fused, homogeneous film, sufficient flow a fused film with (some) defects and insufficient/poor flow a poorly-fused, heterogeneous film. The FTIR spectra of MAn-g-EPM cross-linked with the 1°-1°, 2°-2°, 3°-3° and OH-OH cross-linkers before and after compression molding are shown in Figure 6.1.

The materials with covalent cross-links, involving only 1° and 2° amine and OH groups, flow insufficiently during compression molding at 125 °C to obtain a defect-free material. The respective equilibrium reactions with the anhydride groups are highly temperature-dependent and apparently higher temperatures are required to have sufficient or good flow. Indeed, good flow occurs for MAn-g-EPM cross-linked with 2°-2°, 2°-OH and OH-OH during compression molding at 150 and 175 °C and during the second compression molding step (at 175 °C). The FTIR spectra for MAn-g-EPM cross-linked with 2°-2° do not change significantly upon compression molding, except for the intensity ratios within the broad amide band centered around 1640-1630 cm⁻¹, which indicates that the ratio of the differently hydrogen-bonded amide groups changes (reversibly). These results suggest that no undesired (irreversible) side reactions occur and explain the good flowability. The intensity of the anhydride band at 1785 cm⁻¹ increases for MAn-g-EPM cross-linked with OH-OH, while both the ester and the carboxylic acid bands at 1735 and 1710 cm⁻¹ decrease in intensity. Chapter 5 showed that these changes originate from evaporation of the volatile diol and not from the formation of irreversible chemical bonds, which explains the good flowability. Some irreversible di-ester formation occurs at 175 °C, as indicated by the decrease of the intensity of the carboxylic acid band compared to the ester band, but not to an extent to prevent sufficient flow.

Figure 6.1. FTIR spectra of MAn-g-EPM cross-linked with (a) the 1°-1° and 2°-2° and (b) OH-OH and 3°-3° cross-linkers before and after compression molding at various temperatures. The spectra are scaled on the EPM backbone band at 1460 cm⁻¹ and shifted vertically for clarity.
Therefore, the second compression molding step for this material was performed at 150 °C. The changes in the FTIR spectra for MAn-g-EPM cross-linked with 2°-OH (not shown here) are similar to those of the corresponding functional groups (OH and 2° amine) in Figure 6.1, resulting in the absence of irreversible side reactions and, consequently, good flow.

MAn-g-EPM cross-linked with 1°-1° does not flow sufficiently at any of the compression molding temperatures. A large absorption band appears at 1705 cm⁻¹ after both the first and second compression molding step, which originates from the C=O stretching vibration of the imide and indicates irreversible imide formation (Figure 6.1a). The anhydride/1° amide-acid equilibrium allows some flow during the first compression molding step, although further flow is prevented by the (relatively fast) formation of irreversible (imide) cross-links. As expected, this irreversible network does not flow anymore during the second compression molding step. Imide formation occurs also for MAn-g-EPM cross-linked with 1°-2° and 1°-OH (FTIR spectra not shown here), resulting in the formation of an irreversible imide-connection of the cross-linker to MAn-g-EPM during the first compression molding step. Both materials flow only somewhat during compression molding at 150 or 175 °C and do not flow sufficiently anymore during the second molding step at 175 °C. These results suggest that reversibility of both parts of the cross-link is necessary under the current reprocessing conditions. A possible explanation for this behavior is that disconnected cross-linker molecules can diffuse more easily than cross-linkers connected to a polymer chain.

The materials reacted with cross-linkers with one or two 3° amines contain ionic interactions and flow very well at all compression molding temperatures, which is related to the relative weakness of ionic interactions with ammonium cations. The FTIR spectra of MAn-g-EPM cross-linked with 3°-3° (Figure 6.1b) show that no significant chemical changes occur during the first compression molding step at any temperature, while the increase in the anhydride band during the second compression molding step at 175 °C may be related to the (partial) evaporation of the cross-linker (boiling point of 120 °C). The changes in the FTIR spectra for MAn-g-EPM cross-linked with 1°-3°, 2°-3° and OH-3° are similar to those shown in Figure 6.1 for the corresponding OH and 1° and 2° amine groups. However, reversibility of the chemical bonds is not necessary for good flow, since the ionic interactions from the 3° amines already allow good reprocessability.

In conclusion, reprocessable materials (for at least two times) are obtained for (1) covalently cross-linked materials if no irreversible chemical reactions occur for both functional groups of the cross-linker (2° amine or OH), effectively excluding 1° amine groups, or for (2) materials with ionic interactions, i.e., cross-linkers with at least one 3° amine group.

6.3.3. Morphology of the cross-linked materials

The next step after the identification of the reprocessable MAn-g-EPM/cross-linker combinations is to study the effect of cross-linking on the morphology. The SAXS profiles of the cross-linked materials after the first compression molding step at 175 °C (OH-OH at 150 °C) are shown in Figure 6.2. Again, only the qualitative changes in the scattering curves are discussed, which is allowed by scaling the intensity to the sample thickness.

The scattering peak in the SAXS profiles remains for all cross-linked materials, indicating that the aggregates persist upon cross-linking. The intensity of the scattering peak increases in all cases
compared to MAn-g-EPM, which may be related to a stronger microphase separation and, hence, larger electron density difference between the aggregates and the matrix, due to the higher polarity of the functional groups compared to anhydride groups. The peak intensities are lower for MAn-g-EPM reacted with cross-linkers containing 1° amine groups, due to the lower polarity of imides.

For the covalently cross-linked materials (Figure 6.2a), the peak maximum shifts to lower q-values for the cross-linkers with OH groups (OH-OH, 1°-OH and 2°-OH), whereas no significant shift occurs for those containing only 1° and 2° amine groups (1°-1°, 1°-2° and 2°-2°). This difference is most probably related to the use of the polar solvent THF for the cross-linking reactions, which results in the disappearance of the aggregates of the MAn-g-EPM precursor. For the cross-linkers containing OH groups, the cross-links are not formed in solution, but only after solvent evaporation, i.e., after the aggregates have re-formed. The shift in the peak maximum may be explained by a larger restricted mobility layer surrounding the aggregates, as the strong covalent cross-links anchor the corresponding chain segments strongly to the aggregates. The formation of covalent cross-links occurs already in solution in the absence of aggregates for the cross-linkers containing only 1° and 2° amine groups. After solvent evaporation, a tendency for aggregate formation exists, but the covalent network limits this process to a certain extent, although reorganization may occur during compression molding in view of the increased chain mobility and the (partial) disconnection of the cross-links. This may explain the unaffected peak position for the amine cross-linkers.

The position of the peak maximum does not change significantly for the cross-linkers with 3° amine groups (Figure 6.2b). The ionic interactions with ammonium cations result in relatively weak cross-links and, hence, no large changes in the size of the restricted mobility layer are expected. This fully agrees with the unaffected position of the scattering peak maximum for amide-salts based on MAn-g-EPM, which contain also ionic interactions with ammonium cations (Chapter 3).

DMTA experiments were also used to study the morphology of these materials and demonstrated that the aggregates in MAn-g-EPM act as physical cross-links that increase the network density compared to the parent EPM (Chapter 2). Figure 6.3 shows the storage modulus as a function of the
temperature for MAn-g-EPM and some of the cross-linked materials. The 1°-OH material behaves similarly to the 2°-2° and 2°-OH materials, while the 1°-3° and OH-3° materials behave similarly to the 2°-3° and 3°-3° materials (not shown here). The glass transition temperature positioned at approx. -50 °C and the rubber plateau modulus do not change significantly upon cross-linking. The unaffected rubber plateau modulus indicates that the network density is not changed upon cross-linking and suggests that the covalent and ionic cross-links are only formed within the aggregates. The same was concluded for cross-linking of MAn-g-EPM with ionic interactions (Chapter 2), multiple hydrogen bonding arrays (Chapter 4) and covalent cross-links with diols (Chapter 5). Upon cross-linking, the relatively weak polar interactions between anhydride groups are replaced with stronger ionic interactions and/or covalent cross-links. The aggregates are strengthened and persist to higher temperatures, as indicated by the increased width of the rubber plateau upon cross-linking. For the materials with the relatively weak ionic interactions (2°-3° and 3°-3° as well as 1°-3° and OH-3°), a drop in the rubber modulus occurs around 160-170 °C, indicating flow. For the covalently cross-linked MAn-g-EPM (2°-2°, 2°-OH and OH-OH as well as 1°-OH), only a gradual decrease in the rubber modulus occurs within the experimental temperature range (up to 250 °C).

![Graph] Figure 6.3. Storage modulus as a function of the temperature for MAn-g-EPM cross-linked with the 2°-2°, 2°-OH, OH-OH, 2°-3°, and 3°-3° cross-linkers.

### 6.3.4. Mechanical properties of the cross-linked materials

The mechanical properties were determined for the cross-linked materials after compression molding at 175 °C. The properties of the materials cross-linked with 1°-1° and 1°-2° could not be determined, because the poor flowability resulted in inhomogeneous films after compression molding. A comparison of Table 6.2 and 6.3 shows that $X_{\text{Anh}}$ decreases slightly for the 2°-2°, 1°-OH and 2°-OH cross-linkers after compression molding compared to the dried cross-linked materials, whereas it decreases significantly for the OH-OH cross-linker, due to the aforementioned evaporation of ethyleneglycol during compression molding. Again, no $X_{\text{Anh}}$ was determined for the cross-linkers with 3° amine groups, since the use of partially or fully hydrolyzed starting materials results in unreliable calculations.

Representative tensile curves of the cross-linked materials are shown in Figure 6.4, while Table 6.3 shows average values of the hardness, the tensile strength (TS), the elongation at break (EB) and the
modulus at 200% strain ($M_{200}$), and the compression sets (CS) at room temperature (CS$_{23}$) and at 70 °C (CS$_{70}$). The mechanical properties are significantly changed for all cross-linked materials compared to MAn-g-EPM. The main differences in properties are observed between the materials with covalent cross-links and those with ionic interactions (and covalent bonds), especially in EB and CS, whereas the differences within series are relatively small.

![Figure 6.4](image)

**Figure 6.4.** Representative tensile curves for MAn-g-EPM cross-linked with (a) covalent cross-links and (b) ionic interactions. Note that the scales of the x-axes are different for clarity.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$X_{Anh}$ (%)</th>
<th>TS (MPa)</th>
<th>EB (%)</th>
<th>$M_{200}$ (MPa)</th>
<th>Hardness (Shore A)</th>
<th>CS$_{23}$ (%)</th>
<th>CS$_{70}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MAn-g-EPM</td>
<td>0</td>
<td>0.4</td>
<td>560</td>
<td>0.4</td>
<td>38</td>
<td>88</td>
<td>100</td>
</tr>
<tr>
<td>$2^\circ-2^\circ$</td>
<td>88</td>
<td>2.4</td>
<td>310</td>
<td>1.7</td>
<td>56</td>
<td>27</td>
<td>68</td>
</tr>
<tr>
<td>$1^\circ$-OH</td>
<td>71</td>
<td>1.5</td>
<td>230</td>
<td>1.3</td>
<td>50</td>
<td>20</td>
<td>52</td>
</tr>
<tr>
<td>$2^\circ$-OH</td>
<td>79</td>
<td>1.6</td>
<td>220</td>
<td>1.5</td>
<td>52</td>
<td>24</td>
<td>46</td>
</tr>
<tr>
<td>OH-OH*</td>
<td>56</td>
<td>1.9</td>
<td>400</td>
<td>1.1</td>
<td>48</td>
<td>31</td>
<td>64</td>
</tr>
<tr>
<td>$1^\circ$-3$^\circ$</td>
<td>-</td>
<td>1.8</td>
<td>590</td>
<td>1.2</td>
<td>50</td>
<td>56</td>
<td>100</td>
</tr>
<tr>
<td>$2^\circ$-3$^\circ$</td>
<td>-</td>
<td>2.5</td>
<td>680</td>
<td>1.4</td>
<td>54</td>
<td>56</td>
<td>100</td>
</tr>
<tr>
<td>OH-3$^\circ$</td>
<td>-</td>
<td>2.3</td>
<td>700</td>
<td>1.3</td>
<td>55</td>
<td>50</td>
<td>92</td>
</tr>
<tr>
<td>3$^\circ$-3$^\circ$</td>
<td>-</td>
<td>2.8</td>
<td>830</td>
<td>1.3</td>
<td>52</td>
<td>44</td>
<td>88</td>
</tr>
</tbody>
</table>

*Material was compression molded at 150 °C.

The higher EB and (in most cases) TS and poorer CS for the materials with ionic interactions are all related to the occurrence of ion hopping$^{13}$. This mechanism allows ionic groups to disconnect and to “hop” between aggregates under deformation, which results in stress relaxation of the corresponding chains segments and prevention of premature failure, leading to higher values of EB.
The “free” groups can form new interactions upon entering a new aggregate and contribute to the network again, thereby increasing TS. Hopping is obviously not possible for covalent cross-links, due to the extremely slow equilibrium at room temperature. For these materials, chemical bonds have to break at too high stress levels, resulting in premature failure and lower EB (and TS). Hopping causes significant plastic deformation during compression for the materials with ionic interactions, resulting in a higher CS than for the covalently cross-linked materials.

Significant differences are observed for the hardness and M200 for the materials with covalent cross-links, due to the differences in XAnh and, hence, the strength of the aggregates. The significantly lower XAnh for the OH-OH cross-linker compared to the other cross-linkers (1°-OH, 2°-OH and 2°-2°) explains its larger EB and the somewhat higher CS23 and CS70. The poor CS70 for the 2°-2° cross-linker compared to the 1°-OH and 2°-OH cross-linkers may be related to the relatively fast anhydride/2° amide-acid equilibrium. For the materials with ionic interactions, the differences in tensile properties are only small, except for the 1°-3° cross-linker, which is most probably caused by the weaker aggregation with the less polar imide groups. The poorer CS23 and CS70 for the 1°-3° and 2°-3° cross-linkers compared to the OH-3° and (especially) 3°-3° cross-linkers may be related to differences in the anhydride conversion, which could not be determined, as discussed previously.

6.3.5. Mechanism of (re)processability studied with FTIR spectroscopy

The materials containing ionic interactions could all be compression molded at temperatures as low as 125 °C, while the covalently cross-linked materials containing solely 2° amine or OH groups could be compression molded into homogeneous films at somewhat elevated temperatures of 150 and 175 °C. The flowability for the materials with ionic interactions results from “ion hopping”, which is the generally accepted mechanism for the flow of ionomers.13,14 Ionic groups can continuously disconnect and hop between aggregates, thereby allowing polymer chains to flow without breaking all ionic associations simultaneously. The relative weakness of the ionic interactions with ammonium cations, as demonstrated by all experiments in this study, allows flow via this mechanism already at relatively low temperatures.

The situation is different for the covalently cross-linked materials, for which the equilibrium reaction is responsible for the flowability. This is supported by the lack of flowability for the 1°-1° cross-linker after the formation of an irreversible network. Unfortunately, FTIR spectroscopy of samples before and after compression molding does not unambiguously show which mechanism of reversibility is involved for the other materials, as the (chemical) changes during the actual compression molding step at elevated temperatures remain unclear. For this purpose, thin films of the cross-linked materials were subjected to the heating-cooling cycles schematically depicted in Figure 5.1 and studied with time-resolved FTIR spectroscopy. Figure 6.5 shows the changes in the FTIR spectra for the 2°-2° cross-linker during this experiment.

The FTIR spectrum for the compression-molded film (t = 0 min) shows an absorption band at 1710 cm⁻¹ for the carboxylic acid and a relatively broad band for the amide, again consisting of two overlapping bands at 1648 and 1622 cm⁻¹, although their presence is much clearer for these experiments in transmission. During the first heating step at 175 °C, the intensity of the anhydride band at 1785 cm⁻¹ increases, while the intensity of the carboxylic acid band decreases. The more or
less unaffected total intensity of the overlapping amide bands suggests that the total amount of amide groups does not change, although the ratio of the differently hydrogen-bonded amide groups changes. The FTIR spectra do not change significantly upon cooling to 50 °C, which shows that the changes during the first heating step are irreversible and that the (desired) shift in equilibrium from amide-acid to anhydride and amine does not occur. Rather, an irreversible reaction to form di-amide and anhydride groups according to Scheme 6.2 seems to be responsible for the observed changes. This reaction may become more prominent at elevated temperatures and is irreversible due to the exclusion of water. No further chemical changes occur during the second heating-cooling cycle. These observations are different from those during compression molding, where no significant chemical changes occurred (Figure 6.1). This may be caused by the open system during the FTIR experiments, whereas it is relatively closed during compression molding.

Figure 6.5 FTIR spectra of MAn-g-EPM cross-linked with 2°-2° during two cycles of heating for 20 min at 175 °C followed by cooling for 30 min at 50 °C. The spectra are scaled on the EPM backbone band at 1460 cm⁻¹ and shifted vertically for clarity.

Scheme 6.2. Di-amide and anhydride formation from two amide-acids at elevated temperatures.

\[ \text{2°-OH cross-linker} \xrightarrow{\Delta T} \text{di-amide} + \text{di-ester} \]

The changes in the FTIR spectra during this experiment for the OH-OH cross-linker, are similar to those observed for the cross-linking of MAn-g-EPM with 1,4-butanediol in Chapter 5. The equilibrium does not shift during the heating step, while evaporation of the (short) ethyleneglycol cross-linker is responsible for the observed changes. The intensities of the ester and amide bands remain similar for the 2°-OH cross-linker (not shown here), while the anhydride band increases in intensity and the intensity of the carboxylic acid band decreases. Again, irreversible chemical reactions are responsible for these changes and not a shift in the anhydride/cross-linker equilibrium, since the FTIR spectra do not change upon cooling. Both di-amide (Scheme 6.2) and di-ester formation (Scheme 5.2) may occur for the 2° amine and OH groups, respectively.
Although the changes in these experiments are different from those observed before and after compression molding, the main conclusion is that an equilibrium shift is not responsible for the flow of these materials at elevated temperatures and that the cross-links do not disappear upon heating. These results are similar to those observed for the cross-linking of MAn-g-EPM with diols (Chapter 5). This is most probably related to the rather slow kinetics of shifting the equilibrium and the occurrence of irreversible side reactions for some materials. However, flow does occur for the covalently cross-linked materials during compression molding. This seemingly contradiction is explained by a continuous, dynamic exchange between cross-linked and non-cross-linked species for these equilibrium reactions (Chapter 5). Cross-links can continuously disconnect and re-connect, which gives free functional groups and the corresponding chain segments freedom of movement. This mechanism, which is quite similar to ion hopping,\textsuperscript{13,14} explains the flowability of these materials without a net equilibrium shift.

6.4. Conclusions

In this chapter, the thermoreversible cross-linking of MAn-g-EPM with di-functional cross-linkers containing different combinations of 1º, 2º or 3º amine and alcohol groups was studied. The cyclic anhydride groups of MAn-g-EPM undergo reversible chemical reactions with 1º and 2º amines to form amide-acids and with alcohols to form hemi-esters. Covalent cross-links are formed via the forward reaction at low temperature, if any combination of these functional groups is used, while a shift in the equilibrium may result in their (partial) removal at elevated temperatures. Ionic interactions with ammonium cations are formed upon the neutralization of hydrolyzed anhydride groups with 3º amines.

FTIR spectroscopy confirmed the occurrence of the desired cross-linking reactions and showed that conversions of 80 % or higher are obtained for the covalently cross-linked materials. Microphase-separated aggregates that act as physical cross-links are present for both the MAn-g-EPM precursor and all cross-linked materials, as demonstrated by SAXS. DMTA experiments showed that cross-linking of MAn-g-EPM does not change the network density, suggesting that the covalent cross-links and ionic interactions are only present within the aggregates. Both types of interactions increase the strength of the aggregates, which consequently persist to higher temperatures, with the larger improvements for the covalent cross-links. Covalent cross-linking results in better elasticity (lower CS) compared to the relatively weak ionic interactions, but in poorer tensile properties. These differences are all related to ion hopping for the ionic interactions. The differences in properties within each series, i.e., covalent cross-links or ionic interactions, are relatively small.

Cross-linking of MAn-g-EPM with ionic interactions results in materials that flow very well during compression molding at temperatures between 125 and 175 ºC, due to their relative weakness and the occurrence of ion hopping. Irreversible imide formation prevents sufficient flow at any compression molding temperature for covalently cross-linked materials containing at least one 1º amide-acid, especially during the second molding step. Good flow occurs for the covalent cross-linkers containing only 2º amine and/or alcohol groups during compression molding at 150 and (especially) 175 ºC, since no irreversible chemical bonds are formed. FTIR experiments showed that the reprocessability of the latter materials does not originate from the (desired) shift in
equilibrium, but from a continuous, dynamic exchange between cross-linked and non-cross-linked groups at elevated temperatures. In conclusion, truly reprocessable materials (via compression molding) are obtained for (1) covalent cross-links with only alcohol and 2º amine groups, effectively excluding 1º amines, and for (2) ionic interactions with 3º amines.

6.5. References

Chapter 7

(Re)processability and Rheological Behavior

The main objective of this chapter was to evaluate the thermoplastic processing characteristics of the thermoreversible cross-linked MAn-g-EPM materials, in particular for application in extrusion and injection molding. The presence of microphase-separated aggregates that act as physical cross-links plays a decisive role in the rheological behavior of these materials. All the studied thermoreversible interactions, i.e., ionic interactions, hydrogen bonding and covalent cross-links, are confined within these aggregates and have a characteristic average lifetime (relaxation time), after which they can disconnect. Diffusion of the polymer chain segments containing the “free” functional groups results in flow via hopping-like processes, despite the persistence of the aggregates at the processing temperatures. Ionic interactions with ammonium cations, “non-organized” hydrogen bonds, hydrogen bonds combined with ionic interactions and some multiple hydrogen bonding arrays (triazole and imidazolidone arrays) seem to be suitable for thermoplastic processing techniques with short timescales, due to a sufficient reduction of the lifetimes at the respective processing temperatures, while compression molding is also possible. Short-timescale processing will not be possible for ionic interactions with zinc and potassium cations, covalent cross-links and the other multiple hydrogen bonding arrays (urea, bisurea and 2-ureido-4-pyrimidone), since the lifetimes are too long at elevated temperatures, resulting in a predominantly elastic response. However, the latter materials can be repeatedly compression molded, because relaxation of some of the cross-links allows shaping of the materials in such experiments with typically long timescales.
7.1. Introduction

In the previous chapters of this thesis, several different thermoreversible cross-linking methods were used for the same starting material, i.e., maleated ethylene/propylene (MAn-g-EPM) copolymer, to obtain thermoplastic elastomers (TPEs). The studied cross-linking methods include ionic interactions with metal (Chapter 2) and ammonium cations (Chapter 6), hydrogen bonds combined with ionic interactions (Chapter 3), “non-organized” hydrogen bonds and multiple hydrogen bonding arrays (Chapter 4) and covalent cross-links (Chapters 5 and 6). Several multiple hydrogen bonding arrays known from literature, including 2-ureido-4-pyrimidone (UPy),¹ (bis)urea,²,³ triazole (ATA)⁴ and imidazolidone (IM)⁵ groups, were used for this purpose. Reversible covalent cross-links were introduced via the reversible reactions⁶,⁷ of the cyclic anhydride groups of MAn-g-EPM with diols, diamines and amino-alcohols. So far, the chemical structures, the morphology, the mechanical properties and the (re)processability via compression molding were discussed for the different series of thermoreversibly cross-linked MAn-g-EPM (Scheme 7.1) separately in Chapters 2-6.

Scheme 7.1. Chemical structures of various series of thermoreversibly cross-linked MAn-g-EPM.

It was shown that all cross-linked materials are repeatedly processable via compression molding, except potassium (K)-ionomers at high levels of neutralization. These results demonstrate that the different cross-links are indeed thermoreversible and that these materials are in principle recyclable. Commercial TPEs are generally processed via thermoplastic processing techniques, in particular extrusion or injection molding, in view of the short residence times and, hence, relatively low
production costs. Therefore, the current materials should also be processable via these techniques to be able to compete with commercial TPEs.

This chapter studies the rheological behavior of the different series of thermoreversibly cross-linked MAn-g-EPM (Scheme 7.1) in more detail. Two main issues will be addressed. First, melt viscosities are determined via capillary rheometry and Mooney viscometry to study whether the current materials are suitable for the desired thermoplastic processing techniques. Secondly, oscillatory shear experiments are performed to study the rheological behavior and the network structure in more detail, as well as tensile and compression tests at elevated temperatures.

7.2. Experimental section

7.2.1. Materials

Maleated ethylene/propylene copolymer (MAn-g-EPM, 49 wt% ethylene, 49 wt% propylene, 2.1 wt% maleic anhydride (MAn), M_n = 40 kg/mol, M_w = 90 kg/mol) and the parent EPM copolymer (50 wt% ethylene, 50 wt% propylene, M_n = 40 kg/mol, M_w = 90 kg/mol) were provided by DSM Elastomers. MAn-g-EPM was dried for 1 h at 170 ºC under reduced pressure with a low N_2-flow prior to use to convert all carboxylic acid groups, formed upon hydrolysis, back to cyclic anhydrides. Experimental details for the preparation of the Zn- and K-ionomers (Chapter 2), the amide-acid and -salts (Chapter 3), the NH_3-imide (Chapter 3) and the ATA, IM, bisurea and UPy materials (Chapter 4) can be found in the respective chapters. The ammonium-ionomer and the urea, HDA, DD and MAE materials were obtained via the following (melt) procedure instead of the previously performed solution reactions (Chapters 4-6) to obtain sufficient quantities of the materials. Typically, 45 g of MAn-g-EPM was loaded to a 50 g scale Haake Rheomix internal mixer at a rotation speed of 60 rpm at 80 ºC for the modifications with N,N'-dimethyl-1,6-hexanediol (HDA, Aldrich), 2-methyl-aminoethanol (MAE, Aldrich) and 1,10-decanediol (DD, Aldrich), at 150 ºC for 1-(6-aminohexyl)-3-hexylurea (urea, SyMO-Chem BV) and at 175 ºC for the ammonium-ionomer (with N,N,N',N'-tetramethylethylenediamine from Aldrich). For the modification with DD, 5 mol% of p-toluenesulfonic acid (Aldrich) was added. After homogenization for 1 min, the rotation speed was increased to 100 rpm. Then, the required amount of cross-linker (one mol of functional group per mol of anhydride) was added, followed by further mixing for 5 min. The anhydride conversions and the chemical structures, as determined with Fourier transform infrared (FTIR) spectroscopy, and the tensile and elastic properties of the melt-cross-linked materials were comparable to those of the solution-cross-linked materials that were discussed in the previous chapters.

The materials were compression molded for 20 min between Teflon sheets in a Collin press at 175 ºC, except the amide-acid and -salts, which were compression molded at 80 ºC to avoid imide formation, and EPM, MAn-g-EPM and the urea, bisurea and UPy materials, which were compression molded at 150 ºC.

7.2.2. Capillary rheometry

The rheological behavior was studied using a Göttfert Rheograph 6000 capillary rheometer with a capillary with a diameter of 1 mm and a length-to-diameter ratio of 30. The materials were preheated for 5 min, after which the samples were extruded at different shear rates at 200 ºC.
7.2.3. Mooney viscosity measurements

Mooney viscosities were determined at a rotation speed of 2 rpm at temperatures of 100, 150 and 200 °C using a Mooney MV 2000vs of Alpha Technologies. The materials were preheated for 3 min, after which the ML(3+4) was determined by rotating at 2 rpm for 4 min.

7.2.4. Oscillatory shear experiments

Experiments were performed on a strain-controlled Rheometrics RMS 800 rheometer with a 25 mm parallel plate geometry. Dynamic frequency sweeps were performed on disk-shaped samples (diameter of 25 mm, thickness of approx. 1 mm) at 150 or 200 °C over an angular frequency range from 500 to 10⁻² rad/s at a constant strain of 5 %. Strain sweeps confirmed that the response of the materials at this strain level is within the linear viscoelastic regime.

Alternatively, experiments were performed on selected samples on an Advanced Rheometrics Expansion System (ARES) from TA Instruments with a 25 mm parallel plate geometry, equipped with a 2KFRT dual range transducer and a HR actuator. Dynamic frequency sweeps were performed on disk-shaped samples (diameter of 25 mm, thickness of approx. 3 mm) at 150 or 200 °C in a N₂-rich atmosphere over an angular frequency range from 100 to 10⁻⁴ rad/s at a constant strain of 5 %.

7.2.5. Tensile and compression testing

Dumbbell-shaped tensile bars with dimensions of around 80 x 5 x 2.5 mm and a parallel specimen length of 54 mm were punched from compression-molded films of the MAE material. Tensile tests were performed at 150 °C with various constant linear strain rates between 10⁻³ and 10 mm/s on a Zwick Z100 tensile tester equipped with a 100 N force cell using the TestXpert v8.1 software. A temperature chamber was used to achieve the experimental temperature. The samples were mounted in the setup at least 10 min prior to testing to obtain equilibrium temperature conditions. The measurements were performed to failure of the samples.

Cylindrical samples with a diameter of 13 mm and a thickness of approx. 10 mm were punched from compression-molded films of the MAE material. Uniaxial compression tests were performed at 150 °C on a servo-hydraulic MTS Elastomer Testing System 810. The samples were compressed between two parallel, flat steel plates under true strain control at constant true strain rates between 2x10⁻⁵ and 0.2 s⁻¹. A temperature chamber was used to obtain the correct experimental temperature. The samples were mounted in the setup at least 10 min prior to testing to obtain equilibrium temperature conditions and were lubricated using Teflon spray. The measurements were performed up to a true strain of 1. Note that some barreling of the samples occurred at higher deformations.

7.3. Results and discussion

7.3.1. Determination of melt viscosities

The common method to determine melt viscosities of TPEs is capillary rheometry. Initial experiments were performed at 200 °C on, amongst others, the MAng-EPM precursor, Zn- and K-ionomers and materials with a multiple hydrogen bonding array (ATA) and with covalent cross-links (1,10-decanediol, DD). Proper flow was achieved for the MAng-EPM precursor and the ATA material. However, extensive melt fracture occurred for the ionomers and the DD material, which
indicates that these materials behave as irreversible networks during the experiment. The relatively long residence time within the storage cylinder (exceeding 30 min) may introduce systematic errors, such as extensive irreversible di-ester formation for the DD-material (Chapter 5). This may also be a problem for several other materials, including the (bis)urea and UPy hydrogen bonding arrays (Chapter 4) and the HDA and MAE materials (Chapter 6). Furthermore, the residence times of the capillary rheometry measurements do not resemble those of thermoplastic processing techniques, such as extrusion and injection molding.

As an alternative, Mooney viscosity measurements are used to determine whether these materials are suitable for these processing techniques. Industrial experience tells that Mooney viscosities below 80 Mooney units (MU) are typically required for processability. The experiments were performed at various temperatures (100, 150 and 200 °C) for all series of thermoreversibly cross-linked MAN-g-EPM (Scheme 7.1) and the EPM and MAN-g-EPM precursor. The measured Mooney viscosities (ML(3+4)) are given in Table 7.1, where x indicates the occurrence of melt fracture during the measurement. The preheat time was extended from the common 1 min to 3 min to give the temperature-dependent interactions sufficient time to adjust, which was confirmed by the constant torque levels during the last minutes of the experiment. The closed system and the short experimental times prevented irreversible side reactions, as was confirmed with FTIR spectroscopy.

**Table 7.1.** Mooney viscosities of EPM, MAN-g-EPM and the different series of thermoreversibly cross-linked MAN-g-EPM.

<table>
<thead>
<tr>
<th>Sample</th>
<th>ML(3+4)*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>100 °C</td>
</tr>
<tr>
<td>EPM</td>
<td>6</td>
</tr>
<tr>
<td>MAN-g-EPM</td>
<td>38</td>
</tr>
<tr>
<td>Zn- and K-ionomers</td>
<td>-</td>
</tr>
<tr>
<td>NH3-imide</td>
<td>80</td>
</tr>
<tr>
<td>amide-acid</td>
<td>61</td>
</tr>
<tr>
<td>amide-salt (2 equiv.)</td>
<td>103</td>
</tr>
<tr>
<td>amide-salt (5 equiv.)</td>
<td>50</td>
</tr>
<tr>
<td>ATA</td>
<td>124</td>
</tr>
<tr>
<td>IM</td>
<td>-</td>
</tr>
<tr>
<td>(bis)urea</td>
<td>-</td>
</tr>
<tr>
<td>UPy</td>
<td>-</td>
</tr>
<tr>
<td>covalent cross-links</td>
<td>-</td>
</tr>
<tr>
<td>ammonium-ionomer</td>
<td>-</td>
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</tbody>
</table>

*An x indicates melt fracture during the experiment.*

The MAN-g-EPM precursor has a higher Mooney viscosity than the parent EPM at any temperature, which demonstrates that the anhydride-rich aggregates are still present in the melt and have a
significant influence even at highly elevated temperatures. SAXS experiments confirmed that these aggregates indeed persist above the processing temperatures. The ammonium-ionomers, the “non-organized” hydrogen bonds, the hydrogen bonds combined with ionic interactions and the ATA and IM (only at 200 °C) multiple hydrogen bonding arrays all have higher Mooney viscosities than the MAN-g-EPM precursor, because of the introduction of stronger (physical) cross-links into the aggregates. The Mooney viscosities are sufficiently low to allow thermoplastic processing techniques for all these materials, except for the 2 equiv. amide-salt. The amide-salts were only measured at 100 °C, because irreversible imide formation occurs at higher temperatures (Chapter 3). The ionic interactions in the amide-salts are still relatively strong at 100 °C, which explains the high Mooney viscosity for the 2 equiv. amide-salt. The lower viscosity of the 5 equiv. amide-salt compared to the 2 equiv. amide-salt is most probably related to the excess of N-octadecylamine (melting temperature is approx. 55 °C) acting as a plasticizer. The IM material may be on the borderline of (re)processable in view of its relatively high ML(3 + 4) of 76 MU at 200 °C.

Extensive melt fracture was observed for the Zn- and K-ionomers and the covalently cross-linked materials (DD, HDA and MAE) at temperatures of 150 and 200 °C and for the other multiple hydrogen bonding arrays, i.e., IM, (bis)urea and UPy, at 150 °C. The melt fracture was evident from the appearance of the samples after the experiments, which were torn apart, especially in the sample centre. The (bis)urea and UPy materials cannot be measured at higher temperatures in view of their limited thermal stability (Chapter 4). These results suggest that these materials behave as irreversible networks during the experiment, thereby resulting in extensive melt fracture. Performing the experiments at lower rotation speeds did not result in an improvement. The next sections will first present a discussion on the lifetimes of the different thermoreversible interactions, after which the materials will be studied using oscillatory shear experiments.

7.3.2. Characteristic lifetimes of the thermoreversible interactions

The morphology studies of the different series of thermoreversibly cross-linked MAN-g-EPM with small-angle X-ray scattering (SAXS) and dynamic mechanical thermal analysis (DMTA) in Chapters 2-6 demonstrated that microphase-separated, anhydride-rich aggregates are present for the MAN-g-EPM precursor. The driving force for microphase separation is the polarity difference between the polar anhydride groups and the apolar EPM chains. These aggregates acts as physical cross-links and increase the network density compared to the parent EPM. The aggregates persist upon cross-linking with any of the aforementioned methods without a change in the network density, which indicates that the interactions are mainly located within the aggregates. These cross-links effectively replace the weak interactions between the anhydride groups and significantly increase the aggregate strength. DMTA experiments showed that the network persists above the respective compression molding temperatures. Despite this behavior, these materials can be repeatedly compression molded into homogeneous films, which indicates that the interactions are thermoreversible. The explanation for this seemingly contradictory behavior can be found in the ratio of the characteristic lifetimes of the interactions to the timescales of the processing technique.

For ionomers, flow usually is achieved at the processing temperatures in the presence of the ionic aggregates via low-shear applications, such as compression molding. This behavior is
commonly attributed to the “ion hopping” mechanism, as originally proposed by Cooper. The ionic interactions have a characteristic average lifetime or, alternatively, relaxation time, after which they can disconnect. The “free” ionic groups can leave their aggregate and “hop” between aggregates, where they can form new ionic interactions (see Figure 1.2). This mechanism allows stress relaxation in the corresponding chain segments and flow of the ionomer without breaking all ionic interactions simultaneously.

The effect of the incorporation of hydrogen bonding units into polymers on the rheological behavior was extensively studied by Stadler and co-workers. They demonstrated that the terminal relaxation times of poly(butadiene) are significantly extended upon the introduction of phenylurazole groups. Leibler et al. developed the “sticky reptation” model to describe the rheological behavior of these materials. The associating phenylurazole dimers, the so-called stickers, have a characteristic average lifetime, after which (dis)connection processes can occur. The materials behave as permanent networks on timescales shorter than this lifetime, whereas successive disconnection of stickers at longer timescales allows diffusion of the connected chain segments via reptation. This behavior is quite similar to ion hopping process, except that only dimers are present for these materials and no aggregates. This facilitates hopping-like processes and results in significantly shorter relaxation times. Indeed, Stadler and co-workers demonstrated that the terminal relaxation times increase significantly if the hydrogen bonding groups form large clusters instead of dimers. A similar behavior is expected for the current hydrogen-bonded materials, since the hydrogen bonds are present inside the aggregates (Chapter 4).

It was demonstrated in Chapters 5 and 6 for the thermoreversible covalent cross-linking of MAn-g-EPM with diols, diamines and amino-alcohols that the ideal concept of removal of cross-links at elevated temperatures via a shift in the equilibrium does not apply. Rather, the reprocessability (via compression molding) is caused by a continuous, dynamic exchange between cross-linked and non-cross-linked (“free”) functional groups, which also has a characteristic lifetime. Chain segments with free functional groups can subsequently diffuse between aggregates. This mechanism, which is again quite similar to ion hopping, explains the flow without a true shift in equilibrium.

In summary, all types of interactions have a characteristic lifetime, after which the aforementioned hopping-like processes can occur. The processability is determined by the lifetime of the interactions in relation to the experimental timescale, for which the (dimensionless) Deborah number (De) can be defined:

\[
\text{De} = \frac{\text{relaxation time material}}{\text{timescale of experiment}}
\]  

For large De values, the interactions do not have enough time to disconnect, resulting in elastic network-like behavior. For small De values, the materials behave in a viscous manner and flow, since the interactions are given sufficient time for their respective relaxation processes.

### 7.3.3. Oscillatory shear experiments

In this section, the rheological behavior and the characteristic relaxation times for the different series of thermoreversibly cross-linked MAn-g-EPM are studied in more detail, for which
oscillatory shear experiments were used. Figure 7.1 compares the storage (G’) and loss (G’’) moduli as a function of the angular frequency (ω) for EPM and MAn-g-EPM.

![Graph](image1.png)

**Figure 7.1.** Storage (G’, ▲) and loss (G’’, ♦) moduli as a function of angular frequency (ω) for (a) EPM and MAn-g-EPM at 150 °C and (b) MAn-g-EPM at 150 and 200 °C (measured on RMS 800).

The different rheological behavior of MAn-g-EPM and the parent EPM, which both have the same molecular weight (distribution), demonstrates that the anhydride-rich aggregates in MAn-g-EPM play an important role even at the elevated temperatures. The aggregates still act as (weak) physical cross-links and alter the rheological behavior compared to the parent EPM, for which only entanglements are present. The presence of aggregates increases the resistance against deformation, which explains the higher G’ and G’’ for MAn-g-EPM than for EPM. For EPM, G’ is proportional to ω² (slope of 2) and G’’ to ω¹ (slope of 1) at low frequencies, which indicates that the terminal flow region is reached (Figure 7.1a). This region is approached but not reached for MAn-g-EPM at 150 and 200 °C within this frequency range, due to the presence of the aggregates. (Figure 7.1b).

A crossover of G’ and G’’ is an indication that a material enters the terminal flow region at lower frequencies, since the viscous behavior (G’’) starts to dominate over the elastic behavior (G’). Therefore, the inverse of the crossover frequency is used as a measure for the characteristic relaxation time of the material. The crossover frequency is observed around 10 rad/s at 150 °C for MAn-g-EPM, indicating a relaxation time of about 0.1 s, and shifts to a higher frequency of around 200 rad/s at 200 °C (relaxation time of about 0.005 s), due to the increased mobility at higher temperatures. This crossover occurs at even higher frequencies for EPM, since G’’ dominates over G’ over the whole frequency range, and is therefore not visible. These results indicate that the relaxation times of EPM and MAn-g-EPM are short and explains their very low Mooney viscosities and easy processability via both short- and long-timescale processing techniques.

The Mooney experiments showed that the introduction of the thermoreversible cross-links into MAn-g-EPM significantly increases the melt viscosities and that melt fracture occurs in the case of strong interactions. It is therefore expected that the relaxation times become rather long, so the crossover of G’ and G’’ may shift to low frequencies that are not accessible with conventional dynamic mechanical measurements. Time-temperature superposition (TTS) can be used to overcome this problem for materials with a rheologically simple behavior by horizontally shifting
the different viscoelastic parameters, such as $G'$ and $G''$, with the shift factor $a_T$. However, TTS of both $G'$ and $G''$ with the same $a_T$ failed for all current materials in the temperature range from 150 to 200 °C, with the exception of EPM and MAN-g-EPM and the weakly hydrogen-bonded NH$_3$-imide. All other thermoreversibly cross-linked materials are rheologically complex materials, so the use of TTS is not allowed. Failure of TTS is generally observed for ionomers. This suggests that there are multiple relaxation mechanisms with a different temperature dependence, including the reptation of the backbone chains and the hopping-like processes for the cross-links. A further complication for the use of TTS for some of the current materials is the occurrence of irreversible side reactions at elevated temperatures. Therefore, the $G'$ and $G''$ curves for these materials are given at specific temperatures and are not displayed as mastercurves.

Figure 7.2 shows $G'$ and $G''$ as a function of the frequency at 150 °C for the NH$_3$-imide, the ammonium-ionomer and the ATA, IM and urea arrays. $G'$ and $G''$ drop significantly in the relatively short experimental frequency range for the NH$_3$-imide and approach the terminal flow region. A crossover of $G'$ and $G''$ is observed around 2.5 rad/s (relaxation time of about 0.4 s), indicating that the characteristic relaxation time of the NH$_3$-imide is somewhat longer than for MAN-g-EPM, due to the relatively weak hydrogen bonds. The relaxation times are still relatively short for the ammonium-ionomer, which is evident from the significant drop in $G'$ and $G''$ approaching a crossover at lower frequency. The multiple hydrogen bonding arrays were measured over a broader frequency range. A crossover is observed around 2x10$^{-3}$ rad/s (relaxation time of about 500 s) for the ATA material, which demonstrates that the relaxation times become rather long. These results suggest that the relaxation times of the NH$_3$-imide, the ammonium-ionomer and the ATA material are sufficiently short to obtain acceptable Mooney viscosities (Table 7.1).

The plateau in $G'$ extends over the whole frequency range for the IM and urea materials, indicating that the relaxation times are extremely long (Figure 7.2b). These materials behave as an elastic network over this frequency range, which explains the melt fracture during the Mooney viscosity measurements. $G'$ decreases gradually with decreasing frequency for the IM material, which indicates the occurrence of some relaxation processes. The increase in $G'$ for the urea material at low frequency conflicts with physical principles and indicates that the material changes during the measurement. Side reactions occur for the urea material at 150 °C, resulting in the formation of irreversible cross-links (Chapter 4). This was confirmed by re-measuring the sample at 150 °C, which results in higher absolute values of $G'$ and a persisting plateau in $G''$ Figure 7.2c). Finally, the plateau in $G'$ persists also over the whole frequency range down to 10$^{-2}$ rad/s for the bisurea and UPy materials (not shown here).

Some of the hydrogen-bonded materials were also measured at 200 °C, for which the $G'$ and $G''$ curves are shown in Figure 7.3. The crossover of $G'$ and $G''$ is now observed around 60 rad/s for the NH$_3$-imide (relaxation time of about 0.02 s) and around 0.2 rad/s for the ATA material (relaxation time of about 5 s), indicating that the relaxation times become shorter at higher temperatures. No crossover is observed at 200 °C for the IM material within this (short) frequency range, although a significant gradual decrease of $G'$ occurs. This demonstrates that some relaxation processes are occurring for the IM material, which explains the acceptable but relatively high Mooney viscosity.
Figure 7.2. Storage ($G'$, ▲) and loss ($G''$, ♦) moduli as a function of the angular frequency ($\omega$) at 150 °C for (a) the NH$_3$-imide and the ammonium-ionomer (measured on RMS 800), (b) the IM and ATA materials (measured on the ARES) and (c) the urea material (measured on the ARES). The urea sample was measured again after the first measurement.

Figure 7.3. Storage ($G'$, ▲) and loss ($G''$, ♦) moduli as a function of angular frequency ($\omega$) at 200 °C for (a) the NH$_3$-imide and the ATA material and (b) the IM material (measured on RMS 800).
Figure 7.4 shows $G'$ and $G''$ as a function of the frequency at 200 °C for the Zn-ionomer and the covalently cross-linked materials (DD, MAE and HDA). The plateau in $G'$ persists over the whole frequency range down to $10^{-4}$ rad/s for the DD and Zn-100 materials, indicating that their characteristic relaxation times are extremely long, even at 200 °C. The K-ionomers behave similarly to the Zn-ionomer (not shown here). The increase in $G''$ at lower frequency for the MAE material suggests that the terminal flow region may be approached at somewhat lower frequency. A drop in $G'$ and a significant increase in $G''$ are observed below a frequency of around 1 rad/s for the HDA material, indicating that the material starts to relax. However, at even lower frequencies, $G'$ subsequently increases again accompanied by a decrease in $G''$, which is again caused by chemical changes in the material, i.e., irreversible di-amide formation (according to Scheme 6.2), which results in the formation of an irreversible network that prevents further flow.

![Graph](image.png)

**Figure 7.4.** Storage ($G'$, ▲) and loss ($G''$, ♦) moduli as a function of angular frequency ($\omega$) at 200 °C for (a) the DD and MAE materials and (b) the HDA and Zn-100 materials (measured on ARES).

Again, these chemical changes cause a higher $G'$ and a persisting plateau in $G''$ upon re-measuring the HDA sample. The absolute values of $G'$ are also somewhat higher upon re-measuring for the MAE material and the Zn-ionomer, albeit much less compared to the HDA sample. Irreversible side reactions occur for the MAE sample, which can be di-amide (Scheme 6.2) and/or di-ester formation (Scheme 5.2). Further neutralization may occur for the Zn-ionomer during prolonged exposure to temperatures of 200 °C, since full neutralization was not achieved during solution neutralization (Chapter 2). The rheological behavior of the DD sample is unaffected upon re-measuring the sample, indicating that no irreversible side reactions occur. The anhydride/amide-acid exchange is much faster than the anhydride/hemi-ester exchange, which explains why the onset of flow is observed for the HDA sample and not for the MAE and especially the DD materials. (Chapter 6).

In conclusion, the oscillatory shear experiments demonstrate that the characteristic relaxation times become extremely long for several series of thermoreversibly cross-linked MAN-g-EPM, including ionic interactions with metal cations, covalent cross-links and some of the multiple hydrogen bonding arrays. This causes melt fracture during Mooney viscometry and prevents the use of thermoplastic processing techniques with short timescales. The relaxation times are sufficiently short to allow common melt processing for the “non-organized” hydrogen bonds, ionic interactions...
with ammonium cations and the ATA and IM multiple hydrogen bonding arrays, as indicated by a
crossover of $G'$ and $G''$ or a significant decrease in $G'$ during the oscillatory shear experiments.

In order to access even lower frequencies, stress relaxation experiments were performed. However,
unreliable and non-reproducible results were obtained, which is most probably related to recovery
of internal stresses that were introduced during compression molding of the samples.

### 7.3.4. Tensile and compression testing at elevated temperatures

Another important rheological issue for the current materials is whether they have a yield stress at
elevated temperatures at high stress levels, especially for the materials that are not suitable for
common melt processing. The presence of a yield stress would provide the possibility to force the
materials into flow via plastic deformation. Note that a yield stress can also be observed for
thermoplastic vulcanizates. In a first approach, creep experiments were performed at elevated
temperatures on a parallel plate geometry for the covalently cross-linked materials. These
experiments failed because of slip during the experiment. Therefore, uniaxial tensile and
compression experiments were performed at 150 °C to determine whether a yield stress can be
observed as a function of the deformation rate. The MAE material was chosen for these experiments
in view of its unsuitability for thermoplastic processing techniques. The MAE material can be
properly compression molded at 150 °C, indicating that the interactions are sufficiently reversible at
this temperature to allow flow under proper conditions, i.e., long experimental timescales. Uniaxial
compression tests were performed in addition to tensile tests, since they are less sensitive to failure
mechanisms and localization phenomena and capture the intrinsic deformation behavior.

Figure 7.5 shows the results of both tensile and compression tests on the MAE material at 150 °C.
The engineering stress ($\sigma_{\text{eng}}$) is shown as a function of the engineering strain at various constant
linear strain rates for the tensile tests. The true stress ($\sigma_{\text{true}}$) is shown as a function of the true strain
for the compression tests at various constant true strain rates. Note that the strain rates in both types
of experiments were chosen such in such a way that the deformation rates scaled for the sample size
are comparable. It is evident from these experiments that the MAE material does not yield at any
deformation rate. Therefore, it is concluded that this material does not have a yield stress.

For a better interpretation of the results, the respective data are shown in Mooney plots in Figure
7.6, for which the Mooney stress is plotted as a function of the inverse of the deformation ratio $\lambda$.
The Mooney stress ($\sigma_M$) is given by (with $\sigma_{\text{true}} = \sigma_{\text{eng}} \lambda$):

$$
\sigma_M = \frac{\sigma_{\text{eng}}}{(\lambda - (1/\lambda^2))} = \frac{\sigma_{\text{true}}}{(\lambda^2 - 1/\lambda)}
$$  \hspace{1cm} (7.2)

where $\lambda = L/L_0$, with $L$ and $L_0$ being the length of the deformed and non-deformed sample,
respectively. Consequently, $\lambda$ is larger than 1 for tensile experiments and smaller than 1 in
compression. The analysis of a material via Mooney plots compares its deformation behavior to that
of an ideal rubber, for which $\sigma_{\text{eng}}$ in uniaxial tensile or compression is given by:

$$
\sigma_{\text{eng}} = G(\lambda - (1/\lambda^2))
$$  \hspace{1cm} (7.3)

For an ideal rubber, $\sigma_M$ is constant and independent of $1/\lambda$ and is equal to the shear modulus $G$. 
Figure 7.5. (a) Engineering stress ($\sigma_{\text{eng}}$) as a function of the engineering strain in tension and (b) true stress ($\sigma_{\text{true}}$) as a function of the true strain in compression for the MAE material at various strain rates measured at 150 °C.

Figure 7.6 demonstrates that, at a given strain rate, $\sigma_M$ is more or less constant in both tension and compression for the MAE material at 150 °C. This indicates that this material behaves almost like an ideal rubber at a given strain rate. There is no indication for strain softening or hardening effects, which would result in a significant (linear) decrease and increase in $\sigma_M$ with $1/\lambda$, respectively. Some strain hardening may occur for the highest strain rate in compression, although it is only a minor effect. The behavior in compression and tensile tests is similar for this material, suggesting that this material is not really sensitive to the presence of defects in tension.

The shear modulus, i.e., the constant value of $\sigma_M$, is highly dependent on the deformation rate and decreases significantly with decreasing strain rate. This agrees with the observations from the oscillatory shear experiments (Figure 7.4) that the (storage) plateau modulus decreases gradually at lower frequencies. This demonstrates that some relaxation of the thermoreversible cross-links occurs via hopping-like processes, which become more prominent at lower frequencies and, hence, longer timescales. However, the rubber-elastic response is retained to a large extent even at the long timescales, as is evident from the persisting, albeit decreasing, rubber plateau in oscillatory shear and the ideal rubber-like behavior in uniaxial deformation.

These findings for the MAE material probably explain the behavior of all covalently cross-linked materials, the Zn- and K-ionomers and some of the multiple hydrogen bonding arrays. The predominant elastic response of these materials is retained at the processing temperatures even at long timescales. However, some relaxation occurs, i.e., the number of elastically active cross-linking points decreases in time, especially at longer timescales, which explains why the materials can be shaped by compression molding. Hopping-like processes allow “free” chain segments to adjust to the deformed shape and to attain a more preferable conformation. This process more or less forces the materials into their new shape if given sufficient time, although they do not really flow in a viscous manner. In short-timescale experiments, the response of these materials is highly rubber elastic, which explains their inapplicability for thermoplastic processing techniques, as well
as the persisting rubber plateau in the DMTA experiments and the relatively good elastic behavior at room temperature for these materials.

![Graphical representation of Mooney stress vs. inverse deformation ratio](image)

**Figure 7.6.** Mooney stress ($\sigma_M$) of the MAE material at 150 °C as a function of the inverse of the deformation ratio ($1/\lambda$) for (a) tensile ($1/\lambda<1$) and (b) compression tests ($1/\lambda>1$).

### 7.4. Conclusions

The objective of this chapter was to study the applicability of the different series of thermoreversibly cross-linked MAnt-g-EPM for thermoplastic processing techniques, in particular extrusion and injection molding. All types of cross-links are present in microphase-separated aggregates at the processing temperatures and have characteristic lifetimes, after which they can disconnect. The corresponding chain segments can flow without breaking all their associations simultaneously via hopping-like processes. The ratio of the relaxation times of the elastically active cross-linking points and the experimental timescales determines the eventual processability.

Mooney viscosity measurements suggested that ionic interactions with ammonium cations, “non-organized” hydrogen bonds, hydrogen bonds combined with ionic interactions and some of the multiple hydrogen bonding arrays (ATA and IM) yield materials that are suitable for thermoplastic processing techniques. Oscillatory shear experiments demonstrated that the characteristic relaxation times of these materials are relatively short at the processing temperatures.

Extensive melt fracture occurs during Mooney viscosity measurements for ionic interactions with K and Zn cations, covalent cross-links and the other multiple hydrogen bonding arrays (UPy, urea and bisurea), which demonstrates their inapplicability for thermoplastic processing techniques. Oscillatory shear experiments showed that the relaxation times are extremely long, resulting in predominantly elastic behavior, which prevents extrusion and injection molding. Compression molding of these materials is possible, because some relaxation via hopping-like processes allows shaping of the materials.
7.5. References


Mooney viscosity experiments are generally used for non-cured rubber compounds, for which values below 80 MU are required for applicability in extrusion techniques. These measurements as well as extrusion are typically performed at 100 °C to avoid premature cross-linking reactions. For the current thermoreversibly cross-linked materials, obviously higher temperatures are also possible.

SAXS experiments showed that the scattering peak in the SAXS profile of MAn-g-EPM did not change at all upon heating to temperatures as high as 200 °C.

Chapter 8

Comparison of the Rubber Properties and the (Re)processability

The objectives of this chapter were first to establish structure-property and structure-processing relationships and next to make a comparison of the different series of thermoreversibly cross-linked maleated ethylene/propylene copolymers (MAn-g-EPM), as prepared in Chapters 2-6. Peroxide-cured, gumstock EPDM and thermoplastic vulcanizates are also included in the comparison. The network structure does not change significantly upon cross-linking, but mainly the aggregate strength is affected. The aggregate strength and the extent of hopping-like processes determine the tensile properties and the compression set (CS). A correlation exists between the behavior in CS and the (re)processability: materials with good CS are not processable via thermoplastic processing techniques, while materials that are suitable for these processing techniques have a relatively poor CS. A wide range of tensile and elastic properties can be obtained depending on the chosen cross-linking method. Most types of interactions result in a good CS at room temperature, but more pronounced plastic deformation during compression yields a significantly higher CS at 70 °C for all materials. All materials are suitable for recycling purposes, since they can be repeatedly compression molded. The best property-processing balance is obtained for some of the multiple hydrogen bonding arrays (triazole and imidazolidone arrays) and hydrogen bonds combined with ionic interactions, although their elastic behavior at higher temperatures is rather poor.
8.1. Introduction

This thesis evaluated several different thermoreversible cross-linking methods for the same starting material, viz. maleated ethylene/propylene copolymer (MAn-g-EPM), with the aim to obtain thermoplastic elastomers (TPEs). The structures, mechanical properties and (re)processability via compression molding were discussed separately for each cross-linking method, namely ionic interactions with metal (Chapter 2) and ammonium (Chapter 6) cations, “non-organized” hydrogen bonds (Chapters 3 and 4), hydrogen bonds combined with ionic interactions (Chapter 3), multiple hydrogen bonding arrays (Chapter 4), and covalent cross-links with diols, diamines and amino-alcohols (Chapters 5 and 6). In addition, some materials that are able to form π-π interactions were prepared (Appendix A). The (re)processability of the different series of thermoreversibly cross-linked MAn-g-EPM was discussed in Chapter 7 with the emphasis on two issues, i.e., the possibility for recycling via compression molding and the applicability of thermoplastic processing techniques, in particular extrusion or injection molding.

Here, first a general description of the structure of these materials is given, since it has a major influence on both the properties and the melt (re)processability. Structure-property and structure-processing correlations are established to gain a better understanding of the behavior of the materials. Next, the tensile and elastic properties and the (re)processability are compared for the different thermoreversible cross-linking methods to determine for which type(s) of thermoreversible cross-links the best property-processing balance is obtained. Thermoset cross-linked, gumstock (i.e., no fillers) EPDM rubber and thermoplastic vulcanizates (TPVs) with a comparable hardness are included in the discussion to position the materials relatively to commercial materials.

8.2. Structure-property and structure-processing relationships

8.2.1. General description of the structure

The structures of the different series of thermoreversibly cross-linked MAn-g-EPM were studied in Chapters 2-6 using small-angle X-ray scattering (SAXS) and dynamic mechanical thermal analysis (DMTA). It was demonstrated that microphase-separated, anhydride-rich aggregates are already present for the MAn-g-EPM precursor. The driving force for the formation of these aggregates is the polarity difference between the polar anhydride groups and the apolar EPM backbone. These aggregates act as multi-functional physical cross-links and significantly increase the network density of MAn-g-EPM compared to the parent EPM.

The aggregates persist upon the introduction of the thermoreversible cross-links, independent of the chosen cross-linking method. The network density is not affected, which indicates that the cross-links are solely formed within the aggregates. In most cases, the functional groups actually have an increased polarity after cross-linking compared to the anhydride groups. The unaffected overall network structure allows a direct comparison of the strength and characteristic relaxation times of the different interactions. The cross-links replace the relatively weak polar interactions between anhydride groups, resulting in stronger aggregates that persist to higher temperatures. Consequently, the main parameter determining the properties and (re)processability of the current materials is not the network density, as is the case for thermoset cross-linked elastomers, but...
rather the strength of the aggregates, which is mainly determined by the nature and the strength of the cross-links.

8.2.2. Correlations of the tensile and elastic properties to the structure

The aggregate strength is the main determining factor for the properties and (re)processability, which is the resistance of the aggregates against deformation. Note that this strength is affected by the experimental timescale (or strain rate during tensile testing) as well as the temperature, since hopping processes occur for the thermoreversible cross-links, as will be discussed later. Both the hardness and the modulus at 200% strain (M200) depend mainly on the resistance of a material against deformation and are therefore both reasonable parameters to represent the aggregate strength. No real linear relationship between M200 and the hardness is observed (not shown here), which is most probably related to the relatively “large” error in hardness (± 1 Shore A) in comparison to the narrow variation in hardness (45-60 Shore A). Therefore, the various rubber properties are evaluated as a function of M200 as a measure of the aggregate strength.

Figure 8.1 shows the tensile strength (TS) as a function of M200 for the various series of thermoreversibly cross-linked MAn-g-EPM. TS increases with M200 and, hence, the aggregate strength. Actually, two series with a linear but different dependency of TS on M200 are distinguished, as the increase in TS with M200 is steeper for the potassium (K) and zinc (Zn) ionomers than for the other materials. For all materials, higher stress levels are required for failure of the materials with stronger aggregates, which explains the increase in TS with M200. Under deformation, hopping processes can occur, as was originally proposed by Cooper3 for ionomers. Reversible interactions can disconnect, which allows the corresponding chain segments to relax the applied stress, thereby preventing premature failure. The “free” functional groups can enter other aggregates, where they can reconnect and contribute to the network again. This explains why a higher TS than expected can be obtained. As discussed in the previous chapters, hopping of functional groups occurs during deformation for the physical interactions, such as ionic interactions and (multiple) hydrogen bonding (arrays), but not for the covalent cross-links, due to the extremely slow exchange between cross-linked and free groups at the experimental temperatures. Hopping has a significant positive influence on TS for the K- and Zn-ionomers, most probably due to the higher bond energy of these interactions compared to the hydrogen bonds and the relatively weak ionic interactions with ammonium cations. This results in a steeper increase in TS with increasing M200 for these ionomers, while its effect is much less pronounced for the other interactions, resulting in a lower dependency of TS on M200.

No clear correlation exists between the elongation at break (EB) and M200 for the different series together, as shown in Figure 8.2. This demonstrates that the aggregate strength is not the (only) determining factor for EB. Rather, EB is mainly determined by the nature of the reversible interactions, which govern the extent and the characteristic timescales of hopping3. Extensive hopping seems to occur for the ionic interactions with either metal or ammonium cations, resulting in relatively high values of EB. Hopping is apparently more difficult for the (highly) directional multiple hydrogen bonding arrays, π-π interactions and hydrogen bonds combined with ionic
interactions. Finally, hopping does not occur for the covalent cross-links, due to the extremely slow exchange between cross-linked and free groups at room temperature, resulting in a low EB.

Figure 8.1. Tensile strength (TS) as a function of the modulus at 200 % strain ($M_{200}$) for thermoreversibly cross-linked MAn-g-EPM, with hydrogen bonding abbreviated as HB.

Figure 8.2. Elongation at break (EB) as a function of the modulus at 200 % strain ($M_{200}$) for thermoreversibly cross-linked MAn-g-EPM, with hydrogen bonding abbreviated as HB.
Figure 8.3. Compression set at 23 °C (CS23) as a function of the modulus at 200 % strain (M200) for thermoreversibly cross-linked MAn-g-EPM, with hydrogen bonding abbreviated as HB.

Figure 8.4. Compression set at 70 °C (CS70) as a function of the modulus at 200 % strain (M200) for thermoreversibly cross-linked MAn-g-EPM, with hydrogen bonding abbreviated as HB.

Figure 8.3 shows the compression set (CS) at room temperature (CS23) as a function of M200 for the different series of thermoreversibly cross-linked MAn-g-EPM. The (bis)urea arrays are shown separately from the other multiple hydrogen bonding arrays in view of their better elastic behavior (Chapter 4). CS23 improves (decreases) with increasing M200 and again two series with both a linear but different dependency on M200 can be distinguished. The first correlation with lower (better)
CS$_{23}$ at a given M$_{200}$ is observed for the ionic interactions with metal cations, the covalent cross-links and the (bis)urea arrays, while the CS improvement is less for the hydrogen bonding (arrays), the $\pi$-$\pi$ interactions and the ionic interactions with ammonium cations. For materials with thermoreversible interactions, CS is determined by two different (relaxation) processes, namely plastic deformation during compression and elastic recovery after removal of the compression. The lifetimes of the interactions at room temperature determine the extent of plastic deformation during prolonged compression. These characteristic times are not only determined by the aggregate strength, but also by the nature of the interaction. The latter determines the extent and the relaxation times of the hopping-like process for physical interactions (Chapters 2-4) as well as covalent cross-links (Chapters 5 and 6). Ionic interactions with metal cations, covalent cross-links and (bis)urea arrays yield longer relaxation times at similar aggregate strength, resulting in a better resistance against plastic deformation than for the other interactions and a better dependency of CS$_{23}$ on M$_{200}$.

These two series are still distinguishable for CS at 70 °C (CS$_{70}$) in relation to M$_{200}$, although the dependencies are somewhat different than those for CS$_{23}$, as becomes evident from Figure 8.4. First, CS$_{70}$ is significantly higher than CS$_{23}$ in all cases, which indicates that plastic deformation during compression becomes more prominent, due to shortening of the characteristic relaxation times with increasing temperature for all type of interactions. A more or less linear correlation of CS$_{70}$ with M$_{200}$ remains for the series of materials with the better CS$_{23}$ correlation, i.e., ionic interactions with metal cations, covalent cross-links and (bis)urea arrays. For these materials, the relaxation times remain rather long and a certain resistance against plastic deformation is retained, albeit less than at room temperature. No clear correlation is found anymore for the (other) hydrogen bonds, $\pi$-$\pi$ interactions and ionic interactions with ammonium cations, for which the shortened relaxation times result in a poor resistance against plastic deformation and, consequently, high CS$_{70}$.

8.2.3. Correlation of the (re)processability to the structure

The applicability of the current materials for thermoplastic processing techniques was studied in Chapter 7 with the help of Mooney viscosity measurements. These experiments suggested that several types of interactions are applicable for standard thermoplastic processing techniques, whereas other types are not, due to their (too) long relaxation times. No correlation of the Mooney viscosity with M$_{200}$ is observed, which demonstrates that the aggregate strength is not the (only) determining factor for the processability. A qualitative correlation does exist with the behavior during CS measurements. Melt fracture occurs for the systems that displayed the better dependency of CS$_{23}$ and CS$_{70}$ on the aggregate strength, i.e., ionic interactions with metal cations, covalent cross-links and (bis)urea arrays. Alternatively, the apparent (re)processable materials displayed a weaker dependency of CS$_{23}$ on the aggregate strength and extremely high CS$_{70}$ values, viz. hydrogen bonding (arrays), $\pi$-$\pi$ interactions and ionic interactions with ammonium cations. The reason for this behavior can be found in the characteristic timescales.

It was demonstrated in Chapter 7 that all types of thermoreversible cross-links are present within the aggregates and that they have a characteristic lifetime or alternatively relaxation time. After this lifetime, the cross-links can disconnect, which allows the chain segments containing the “free” functional groups to diffuse between aggregates. This mechanism was originally proposed by
Comparison of the Rubber Properties and the (Re)processability

Cooper for ionomers,3 but is applicable for the other types of cross-links as well. The lifetime of the cross-links has to be shorter than the experimental timescale to allow flow of the material. The extent of hopping-like processes and, consequently, the characteristic relaxation times depend mainly on the type of interaction and not the aggregate strength. All materials can be repeatedly compression molded into homogeneous films, because the interactions are allowed sufficient time to disconnect and to participate in hopping-like processes during these low-shear and long-timescale conditions. The desired thermoplastic processing techniques, such as extrusion and injection molding, have typically short timescales. Therefore, the processability depends mainly on whether the relaxation times become sufficiently short at the processing temperatures.

Therefore, the correlation between the CS behavior and the (re)processability is not completely surprising, since both types of experiments depend mainly on the relaxation times of the interactions, although they are performed at completely different temperatures and timescales. This demonstrates that there is not a sharp step in the relaxation times with temperature from long to short. Rather, a gradual decrease of the relaxation times occurs for the current materials over the whole temperature range, which starts already at relatively low temperatures, as indicated by the significantly higher CS70 than CS23. The long relaxation times at low temperatures do not decrease sufficiently at the processing temperatures to allow short-timescale processing for the materials with relatively good elastic behavior. Sufficiently short relaxation times at the processing temperatures are only obtained for the interactions that already have rather short relaxation times at low temperatures and therefore display relatively poor elastic behavior.

8.3. Comparison of the thermoreversible cross-linking methods

8.3.1. General remarks

The previous sections established correlations of the properties and the melt processability with the structure for the thermoreversibly cross-linked MAn-g-EPM. For practical rubber applications, usually a certain balance between the properties and (re)processability is required, which is an important issue, since better properties are usually achieved at the expense of the (re)processability and vice versa. In this section, the different series of thermoreversibly cross-linked MAn-g-EPM are compared for the tensile and elastic properties and (re)processability, which is allowed because all cross-linked materials have a similar hardness of 45-60 Shore A. Table 8.1 gives an overview of the range of properties (hardness, TS, EB, M200, CS23 and CS70) for the different materials.

The current materials do not contain any additives, such as processing oil or reinforcing fillers, to keep the analysis as straightforward as possible. This of course complicates a comparison with commercial products, like irreversibly cross-linked elastomers and TPEs, since these materials generally containing large amounts of additives and, of course, are optimized for the particular application. Therefore, peroxide-cured gumstock (no oil and fillers) EPDM4 with similar hardness is included in the comparison. Of course, these materials cannot be considered as commercial products. The only types of commercial TPEs with a comparable hardness range are blends of poly(styrene)-poly(butadiene)-poly(styrene) tri-block copolymers with oil and poly(propylene) (PP) and thermoplastic vulcanizates (TPVs). Since the current materials are based on MAn-g-EPM,
TPVs containing dispersions of cross-linked EPDM in PP\textsuperscript{5} are chosen for the comparison. Note that this comparison is not completely fair, since TPVs contain significant amounts of processing oil and a rigid thermoplastic matrix.

**Table 8.1.** Mechanical properties for the different series of thermoreversibly cross-linked MAN-g-EPM, PP/EPDM TPVs and peroxide-cured gumstock EPDM.

<table>
<thead>
<tr>
<th>Series</th>
<th>Hardness (Shore A)</th>
<th>TS (MPa)</th>
<th>EB (%)</th>
<th>M\textsubscript{200} (MPa)</th>
<th>CS\textsubscript{23} (%)</th>
<th>CS\textsubscript{70} (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>MAN-g-EPM</td>
<td>38</td>
<td>0.4</td>
<td>560</td>
<td>0.4</td>
<td>88</td>
<td>100</td>
<td>Chapter 2-6</td>
</tr>
<tr>
<td>K-ionomers</td>
<td>53-56</td>
<td>2.7-9.9</td>
<td>680-820</td>
<td>1.0-2.1</td>
<td>15-36</td>
<td>39-78</td>
<td>Chapter 2</td>
</tr>
<tr>
<td>Zn-ionomers</td>
<td>45-57</td>
<td>1.0-4.5</td>
<td>660-680</td>
<td>0.5-1.3</td>
<td>22-51</td>
<td>54-83</td>
<td>Chapter 2</td>
</tr>
<tr>
<td>Hydrogen bonds and ionic interactions</td>
<td>54-61</td>
<td>2.9-4.8</td>
<td>480-620</td>
<td>1.8-2.1</td>
<td>24-33</td>
<td>60-100</td>
<td>Chapter 3</td>
</tr>
<tr>
<td>“Non-organized” hydrogen bonds</td>
<td>49-56</td>
<td>0.7-1.7</td>
<td>300-890</td>
<td>0.7-1.3</td>
<td>56-76</td>
<td>98-100</td>
<td>Chapter 3,4</td>
</tr>
<tr>
<td>Multiple hydrogen bonding arrays</td>
<td>51-53</td>
<td>1.9-4.3</td>
<td>390-520</td>
<td>1.2-2.2</td>
<td>21-45</td>
<td>60-88</td>
<td>Chapter 4</td>
</tr>
<tr>
<td>Covalent cross-links</td>
<td>48-56</td>
<td>1.4-2.4</td>
<td>220-420</td>
<td>1.1-1.6</td>
<td>14-36</td>
<td>46-68</td>
<td>Chapter 5,6</td>
</tr>
<tr>
<td>Ammonium-ionomers</td>
<td>50-55</td>
<td>1.8-2.5</td>
<td>590-830</td>
<td>1.2-1.4</td>
<td>44-56</td>
<td>88-100</td>
<td>Chapter 6</td>
</tr>
<tr>
<td>(\pi-\pi) interactions</td>
<td>51-52</td>
<td>0.7-1.0</td>
<td>520-680</td>
<td>0.8</td>
<td>70-82</td>
<td>100</td>
<td>Appendix A</td>
</tr>
<tr>
<td>PP/EPDM TPVs</td>
<td>46-57</td>
<td>3.2-4.4</td>
<td>330-450</td>
<td>1.2-2.3</td>
<td>14-32</td>
<td>23-37</td>
<td>5</td>
</tr>
<tr>
<td>Peroxide-cured EPDM</td>
<td>46-57</td>
<td>1.4-2.9</td>
<td>100-250</td>
<td>1.0-2.0</td>
<td>1-7</td>
<td>2-11</td>
<td>4</td>
</tr>
</tbody>
</table>

*Only \(M_{100}\) values were reported.

For applications, generally high TS and EB and low CS are desired for both cross-linked elastomers and TPEs. For conventional elastomers, usually a compromise is required, since increasing the cross-link density typically results in a decrease in both EB and CS.\textsuperscript{1,2} Therefore, a combination of high EB and good CS is usually difficult to achieve for conventional elastomers. For TPE-like behavior, the materials should be (re)processable via thermoplastic processing techniques, such as extrusion or injection molding. The requirements in properties vary per application, which makes it difficult to give a desired range of properties. Note that the thermoreversibly cross-linked MAN-g-EPM may be further optimized via compounding, similarly to conventionally cross-linked elastomers.\textsuperscript{1,2} Processing oil is added to lower the viscosity and to improve the processability, while reinforcing fillers, such as carbon black or silica, are added to improve the (tensile) properties.

**8.3.2. Comparison of the rubber properties**

Figure 8.5 compares the tensile properties of the different series of thermoreversibly cross-linked MAN-g-EPM by showing TS as a function of EB. A wide variety in tensile properties is obtained depending on the chosen cross-linking method in the following order from poor to good:
Comparison of the Rubber Properties and the (Re)processability

MAn-g-EPM < \(\pi-\pi\) interactions < “non-organized” hydrogen bonds < covalent cross-links < ammonium-ionomers < multiple hydrogen bonding arrays < Zn-ionomers < hydrogen bonds combined with ionic interactions < K-ionomers.

As discussed in the previous section, TS increases for any cross-linking method compared to the MAn-g-EPM precursor, whereas the occurrence of hopping-like processes cause a wide variation of EB between the different series (Figure 8.2). The relatively low EB (and TS) for covalent cross-links are related to the absence of hopping processes at low temperatures, due to the extremely slow equilibrium dynamics. The “non-organized” hydrogen bonds, \(\pi-\pi\) interactions and amine-ionomers have a relatively low TS because of their low aggregate strength. The best tensile properties are obtained for the K-ionomers, due to extensive ion hopping, while good tensile properties are obtained for the Zn-ionomers, the multiple hydrogen bonding arrays and the hydrogen bonds combined with ionic interactions.

All cross-linked materials have better to superior tensile properties in comparison with peroxide-cured gumstock EPDM, due to the absence of hopping processes for the latter materials. The only exceptions are the series of “non-organized” hydrogen bonds and \(\pi-\pi\) interactions, due to their low TS. Especially the values of EB are significantly higher than for conventional elastomers with sufficiently high cross-link densities.

It is important to realize that commercial elastomers are always optimized compounds containing, amongst others, large amounts of processing oil and reinforcing fillers, which affect the tensile properties significantly.\(^1\)\(^2\) Therefore, the effect of compounding on the properties (and the (re)processability) is an important remaining issue. The effect of processing oil is investigated in Chapter 9, albeit with the main purpose to improve the melt processability. Based on the tensile properties, several materials, including multiple hydrogen bonding arrays, hydrogen bonds combined with ionic interactions and Zn- and K-ionomers, can compete with commercial PP/EPDM TPVs of similar hardness, even without optimization via compounding.

Figure 8.6 compares the elastic behavior at room temperature and at 70 °C for the different series of materials by showing CS\(_{70}\) as a function of CS\(_{23}\). For the different series of thermoreversibly cross-linked MAn-g-EPM, the following order in elastic behavior from poor to good is established:

MAn-g-EPM < \(\pi-\pi\) interactions < “non-organized” hydrogen bonds < ammonium-ionomers < hydrogen bonds combined with ionic interactions < multiple hydrogen bonding arrays < Zn-ionomers < K-ionomers \(\approx\) covalent cross-links.

Quite acceptable values of CS\(_{23}\) are obtained for several series of thermoreversibly cross-linked MAn-g-EPM, which are even below 20 % in some cases. However, as discussed in the previous section, the values of CS\(_{70}\) are significantly higher than CS\(_{23}\) for all series of thermoreversibly cross-linked MAn-g-EPM. This behavior was attributed to the gradual shortening in relaxation times, even at moderately elevated temperatures. Consequently, better elastic behavior at elevated temperatures is obtained for the materials with long relaxation times, especially K-ionomers and covalently cross-linked MAn-g-EPM.
Figure 8.5. Tensile strength (TS) as a function of elongation at break (EB) for thermoreversibly cross-linked MAn-g-EPM, (PP/EPDM) TPVs and peroxide-cured (Px) gumstock EPDM rubber. The dashed arrow indicates the desired combination of properties.

Figure 8.6. Compression set (CS) at 70 °C (CS\textsubscript{70}) as a function of CS at 23 °C (CS\textsubscript{23}) for thermoreversibly cross-linked MAn-g-EPM, (PP/EPDM) TPVs and peroxide-cured (Px) gumstock EPDM rubber. The dashed arrow indicates the desired combination of properties.

The current materials are inferior with respect to the elastic behavior compared to the peroxide-cured gumstock EPDM. Irreversibly cross-linked EPDM has superior CS\textsubscript{23} and CS\textsubscript{70} values, since the covalent network is stable even at elevated temperatures. It should be noted that CS\textsubscript{70} would
increase somewhat compared to CS$_{23}$ in the case of sulfur-vulcanized EPDM, because of the instability of the sulfur bridges at elevated temperatures.\textsuperscript{1,2} The PP/EPDM TPVs also have much better CS$_{70}$ values compared to the current materials, while CS$_{23}$ is comparable with several series of thermoreversibly cross-linked MAn-g-EPM (see Figure 8.6). The elastic behavior of TPVs is mainly determined by the irreversibly cross-linked EPDM phase and will not deteriorate significantly upon increasing temperature up to the melting temperature of the PP phase.

### 8.3.3. Comparison of the property-processing balance

Figure 8.7 shows the (qualitative) (re)processability of the different series of materials and distinguishes between not processable, poorly and easily processable via compression molding and processable via extrusion or injection molding. It is evident that indeed a qualitative correlation exists between CS and the (re)processability, as was suggested in the previous section. The materials with relatively good CS$_{23}$ are consequently difficult to process and vice versa. All series of thermoreversibly cross-linked MAn-g-EPM have a processing advantage over the peroxide-cured (gumstock) EPDM, since they are processable via compression molding or even via short-timescale processing techniques, whereas conventional elastomers are intrinsically not reprocessable. Unfortunately, the current materials have inferior elastic properties compared to irreversibly cross-linked elastomers. By far the best balance between (elastic) properties and (re)processability is obtained for commercial PP/EPDM TPVs, although this comparison is not completely fair.

![Figure 8.7](image_url)

**Figure 8.7.** Compression set at 23 °C (CS$_{23}$) as a function of (qualitative) (re)processability for thermoreversibly cross-linked MAn-g-EPM, (PP/EPDM) TPVs and peroxide-cured (Px) gumstock EPDM. Four regions in (re)processability are distinguished, namely not reprocessable (region 1), poorly reprocessable via compression molding (region 2), easily reprocessable via compression molding (region 3) and suitable for extrusion and/or injection molding (region 4). Variations are present within region 4, which is based on the inverse of the Mooney viscosities (Chapter 7). The dashed arrow indicates the desired combination of CS$_{23}$ and processability.
Figure 8.7 further demonstrates that best property-processing balance is obtained for some of the multiple hydrogen bonding arrays (ATA and IM) and the hydrogen bonds combined with ionic interactions. The other materials with good elastic behavior, using ionic interactions with metal cations, covalent cross-links and (bis)urea arrays, are not processable via the desired processing techniques. The other materials that have a good reprocessability display poor elastic behavior, as is the case for “non-organized” hydrogen bonds, π-π interactions and ionic interactions with ammonium cations. This balance becomes poorer if the elastic behavior at higher temperatures is taken into account. Note that Chapter 9 discusses two different approaches to improve this balance, namely the addition of processing oil and a reduction of the anhydride content.

8.4. Conclusions

In the first part of this chapter, structure-property and structure-processing relationships were established for the different series of thermoreversibly cross-linked MAN-g-EPM. All interactions are present within microphase-separated aggregates at a similar network density, which allows a comparison of the strength of the aggregates and the characteristic relaxation times of the different interactions. The main effect of the introduction of thermoreversible cross-links into the aggregates is an increase in the aggregate strength compared to MAN-g-EPM.

The tensile and elastic properties were evaluated as a function of the aggregate strength, which is represented by $M_{200}$. TS increases with increasing $M_{200}$ with two series with a linear but different correlation, with the better correlation for K- and Zn-ionomers than for the other series of materials. No clear correlation is observed for EB as a function of $M_{200}$, which is most probably due to the dependence of EB on the extent of hopping-like processes. CS$_{23}$ decreases with $M_{200}$, for which two series with a linear but different correlation are distinguished. The better correlation (also for CS$_{70}$) is obtained for interactions that yield relatively long relaxation times, including K- and Zn-ionomers, covalent cross-links and (bis)urea arrays. The shorter relaxation times for hydrogen bonding (arrays), π-π interactions and ionic interactions with ammonium cations result in a poorer correlation of CS$_{23}$ as well as high CS$_{70}$ values. The main determining factor for the processability is the characteristic relaxation time of the interactions, which decreases gradually over the whole temperature range. A qualitative (linear) correlation is observed between CS and the reprocessability. The materials with the better CS dependency are not (re)processable via thermoplastic processing techniques, since the long relaxation times at low temperatures are not sufficiently reduced at elevated temperatures. Sufficiently short relaxation times at the processing temperatures to allow (re)processability are only obtained for the interactions that already have rather short relaxation times at low temperatures and therefore display poor elastic behavior.

The different series of thermoreversibly cross-linked MAN-g-EPM were mutually compared for the tensile and elastic properties and the (re)processability, which is allowed because of their similar hardness. A wide range in tensile properties (TS and EB) is possible depending on the type of interaction. In most cases, significantly better tensile properties are obtained compared to peroxide-cured gumstock EPDM. Most types of interactions yield relatively good CS$_{23}$, but CS$_{70}$ is significantly higher in all cases. In this respect, all current materials have a significant disadvantage compared to irreversibly cross-linked EPDM as well as PP/EPDM TPVs. All interactions result in
materials that are reprocessable via compression molding, which gives them a distinct processing advantage over irreversibly cross-linked EPDM. The best property-processing balance for the current materials is obtained for some of the multiple hydrogen bonding arrays (ATA and IM) and hydrogen bonds combined with ionic interactions, although their elastic behavior at elevated temperatures (CS70) is rather poor. This balance is unfortunately significantly less preferable than for TPVs. Finally, optimized compounding with processing oil and reinforcing fillers may improve this balance, similarly to conventional elastomers.

8.5. References

5 Product folders for Sarlink® 3140, 3150 and 4155N.
Chapter 9

Approaches to Improve the Melt Processability

In this chapter, two different approaches to improve the (re)processability of thermoreversibly cross-linked maleated ethylene/propylene copolymers (MAn-g-EPM) were discussed, namely the addition of processing oil and a reduction of the anhydride content, both with the objective to make these materials (better) suitable for thermoplastic processing techniques, such as extrusion or injection molding. Multiple hydrogen bonding arrays and reversible covalent cross-links were used for the cross-linking of MAn-g-EPM. Oil addition lowers the hardness, the modulus and the tensile strength, due to the dilution of the cross-linked network, but does not really affect the elongation at break, since the chain segment length between functional groups remains similar. The elasticity of the oil compounds with relatively strong cross-links is not affected, but becomes poorer for relatively weak interactions. The potential of the materials with strong cross-links to be filled with large amounts of processing oil without affecting the elasticity is demonstrated, which may be beneficial in certain applications. A reduction of the anhydride content from 2.1 up to 0.5 wt% results in significantly weaker aggregates, although they remain at similar network density within this range. This causes a lower modulus, poorer elasticity and a large increase of the elongation at break. The melt viscosity of the hydrogen-bonded materials, which were already suitable for thermoplastic processing techniques, decreases with both approaches, but at the expense of the properties. Both approaches do not improve the suitability of the covalently cross-linked materials for thermoplastic processing techniques, since the covalent network remains with its too long characteristic lifetimes.
9.1. Introduction

In the previous chapters, TPEs were developed based on maleated ethylene/propylene copolymer (MAn-g-EPM) using several different thermoreversible cross-linking methods, including ionic interactions with metal (Chapter 2) and ammonium (Chapter 6) cations, “non-organized” hydrogen bonds (Chapters 3 and 4), hydrogen bonds combined with ionic interactions (Chapter 3), multiple hydrogen bonding arrays (Chapter 4) and reversible covalent cross-links (Chapters 5 and 6). Several multiple hydrogen bonding arrays known from literature, i.e., ureido-pyrimidone (UPy)\textsuperscript{1}, (bis)urea\textsuperscript{2,3}, triazole (ATA)\textsuperscript{4} and imidazolidone (IM) groups\textsuperscript{5}, were introduced into MAn-g-EPM. Finally, for thermoreversible covalent cross-linking of MAn-g-EPM, the temperature-dependent equilibrium reactions of cyclic anhydride groups with alcohols and amines\textsuperscript{6,7} were used.

All cross-linked materials are repeatedly processable via compression molding and are hence intrinsically recyclable. Several types of interactions, including ionic interactions with metal cations, covalent cross-links and some of the multiple hydrogen bonding arrays (urea, bisurea and UPy) were shown to be not suitable for thermoplastic processing techniques (Chapter 7). The rheological experiments suggested that ionic interactions with ammonium cations, “non-organized” hydrogen bonds, hydrogen bonds combined with ionic interactions and the ATA and IM multiple hydrogen bonding arrays are suitable for these processing techniques. Unfortunately, these interactions generally yielded poorer mechanical properties than the former series of materials (Chapter 8). This demonstrated that the balance between the properties and the processability is not so good for the current materials.

This chapter discusses two different approaches to improve the property-processing balance for thermoreversibly cross-linked MAn-g-EPM, mainly with the aim to improve their suitability for thermoplastic processing techniques. In the first approach, various amounts of a standard EP(D)M processing oil are added to the materials prior to cross-linking. Hydrocarbon oils are generally used to lower the viscosity of rubber compounds for improved processability, lower hardness and lower rubber compound costs\textsuperscript{8,9}. In the second approach, the anhydride groups of the MAn-g-EPM precursor are partially converted with primary amines to N-alkylimides\textsuperscript{10,11} in order to lower the anhydride content, which may eventually result in the disappearance of the aggregates below a certain threshold\textsuperscript{12,13} since the resulting N-alkylimide groups are significantly less polar. It was shown in Chapter 3 that complete conversion of the anhydride groups of MAn-g-EPM to N-alkylimide indeed results in the complete disappearance of the aggregates. Of course, this approach is not completely similar to simply using a MAn-g-EPM with a lower anhydride content, since the N-alkylimide groups may still have an influence. This approach may improve the processability, since the aggregates play an important role in the rheological behavior (Chapter 7).

Both the dilution with processing oil and the partial conversion of the anhydride groups to imides, as well as the subsequent (thermoreversible) cross-linking reactions, are carried out in the melt on an internal mixer. These procedures are performed for materials that are already suitable for thermoplastic processing techniques, viz. multiple hydrogen bonding arrays (ATA\textsuperscript{4} and IM\textsuperscript{5} arrays), and materials that are not suitable for these techniques, namely covalently cross-linked materials with diamines (HDA) and amino-alcohols (MAE), as shown in Scheme 9.1. The chemical structures
and anhydride conversions of the cross-linked materials are evaluated with Fourier transform infrared (FTIR) spectroscopy. Small-angle X-ray scattering (SAXS) and dynamic mechanical thermal analysis (DMTA) are used to determine the effects of both approaches on the morphology. Finally, their influence on the mechanical properties (hardness, tensile properties and compression set) and the (re)processability, as studied with Mooney viscometry and oscillatory shear experiments, is investigated to determine whether these approaches result in an improved property-processing balance.

**Scheme 9.1.** Chemical structures of MAn-g-EPM cross-linked with multiple hydrogen bonding arrays (ATA and IM) and reversible covalent cross-links (HDA and MAE).

### 9.2. Experimental Section

#### 9.2.1. Materials

Maleated ethylene/propylene copolymer (MAn-g-EPM, 49 wt% ethylene, 49 wt% propylene, 2.1 wt% maleic anhydride (MAn), $M_n = 40 \text{ kg/mol, } M_w = 90 \text{ kg/mol}$) was provided by DSM Elastomers. It was dried for 1 h at 170 ºC under reduced pressure with a low N$_2$-flow prior to use to convert all carboxylic acid groups, formed upon hydrolysis, back to anhydride. N-decylamine (Aldrich), 3-amino-1,2,4-triazole (ATA, Aldrich), 1-(2-aminoethyl)imidazolidin-2-one (IM, Arkema France), N,N’-dimethyl-1,6-hexanediamine (HDA, Aldrich), 2-(methyl-amino)ethanol (MAE, Aldrich) and paraffinic processing oil (Sunpar 2280, Sunoco Holland B.V.) were used as received. HDA was used instead of the N,N’-dimethylethylenediamine used for solution cross-linking (Chapter 6), in view of the relatively low boiling point of the latter diamine, which makes it less suitable for melt cross-linking.

#### 9.2.2. Cross-linking of MAn-g-EPM

For the oil compounds, the required amount of MAn-g-EPM was charged to a 50 g scale Haake Rheomix OS internal mixer at a rotation speed of 60 rpm at 80 ºC for the modifications with HDA and MAE and at 175 ºC for those with IM and ATA. The required amount of processing oil (0, 25, 50 and 80 weight parts of Sunpar 2280 per 100 weight parts of rubber [phr]) was added stepwise to the mixer to achieve continuous mixing. The total amount of material (MAn-g-EPM and processing oil) was kept constant at 45 g. The rotation speed was increased to 100 rpm after mixing for 1 min, followed by addition of the required amount of the cross-
linker (one mol of functional group per mol anhydride) and further mixing for 5 min. The oil was added prior to cross-linking, since crumbling during covalent cross-linking prevents proper mixing after cross-linking.

The anhydride content of the MAn-g-EPM precursor was partially lowered from 2.1 wt% to 0.5, 1.0 and 1.5 wt% via the following procedure. Typically, 45 g of MAn-g-EPM was charged to the internal mixer at a rotation speed of 60 rpm at 150 °C and mixed for 1 min. The required amount of N-decylamine (0.25, 0.5 or 0.75 mol per mol anhydride) was added, followed by mixing for 5 min. Then, the required amount of cross-linker, calculated from the remaining amount of anhydride groups, was added, followed by mixing for 5 min.

The materials were compression molded for 20 min between Teflon sheets in a Collin press at 175 °C.

9.2.3. Characterization techniques

Fourier transform infrared (FTIR) spectroscopy. Compression-molded films were analyzed on a BioRad Excalibur 3000 spectrometer equipped with a Specac Golden Gate attenuated total reflection (ATR) setup over a spectral range from 650 to 4000 cm\(^{-1}\) at a resolution of 4 cm\(^{-1}\), co-adding 20 scans.

Small-angle X-ray scattering (SAXS). SAXS experiments were performed on compression-molded samples at the DUBBLE beamline (BM26) at the European Synchrotron Radiation Facility (ESRF) in Grenoble (France). The data were collected using a 2D multiwire gas-filled detector with pixel array dimensions of 512 x 512. The detector was positioned at 2.5 m from the sample and the q-scale was calibrated using the positions of diffracted peaks of a silver behenate sample. The exposure time for each sample was 300 s and a wavelength of 1.2 Å was used. The experimental data were corrected for background scattering and transformed into 1D-plots by azimuthal angle integration using the FIT2D program developed by Dr. Hammersley. The profiles were scaled for the sample thickness to allow a comparison of intensities.

Dynamic mechanical thermal analysis (DMTA). Rectangular samples with dimensions of around 10 x 3 x 1 mm were measured over a temperature range from -100 to 250 °C at a heating rate of 3 °C/min and a frequency of 1 Hz on a DMA Q800 (TA Instruments) with film tension clamps.

Hardness. The hardness was measured on 6 mm thick samples using a Shore A durometer according to ASTM D2240-91.

Tensile testing. Dumbbell-shaped tensile bars with dimensions of 35 x 2 x 1 mm and a parallel specimen length of 17.5 mm were punched from compression-molded films. Tensile tests were performed at room temperature with a constant speed of 0.5 mm/s on a Zwick Z010 tensile tester equipped with a 20 N force cell using TestXpert v7.11 software. All materials were tested in at least five-fold.

Compression set (CS). Cylindrical samples with a diameter of 13 mm and a thickness of approx. 6 mm were compressed for 22 h between two parallel plates with a linear deformation of 25 % at room temperature (CS\(_{23}\)) or at 70 °C (CS\(_{70}\)). CS was determined after a relaxation time of 30 min at room temperature using:

\[
CS = \left( t_0 - t_f \right) / \left( t_0 - t_n \right) \times 100\%
\]

where \( t_n \) is the thickness of the spacer and \( t_0 \) and \( t_f \) are the initial and final sample thickness, respectively.

Mooney viscosity measurements. Mooney viscosities were measured at 200 °C using a Mooney MV 2000vs (Alpha Technologies). Samples were preheated for 3 min, after which the ML(3+4) values were determined at a rotation speed of 2 rpm for 4 min.
Oscillatory shear experiments. Disk-shaped samples with a diameter of 25 mm and a thickness of approximately 1 mm were measured at 200 °C on a strain-controlled Rheometrics RMS 800 rheometer with a 25 mm parallel plate geometry. Dynamic frequency sweeps were performed over an angular frequency range from 10² to 500 rad/s with a constant strain of 5 %. Strain sweeps confirmed that the response of the materials at this strain level is within the linear viscoelastic regime.

9.3. Results

9.3.1. Chemical structures

Compounds with oil (0, 25, 50 and 80 phr) were prepared with two multiple hydrogen bonding arrays (ATA and IM) and with two types of covalent cross-links (HDA and MAE), whereas the series with lowered anhydride contents (0.5, 1.0, 1.5 and 2.1 wt%) were obtained for only the IM and MAE materials (Scheme 9.1). FTIR spectroscopy is a suitable technique to study the chemical structures of the cross-linked materials, since the position and intensity of the carbonyl (C=O) stretching vibration bands of the cyclic anhydride groups of MAn-g-EPM change upon reaction. The absorption bands at 1865 and 1785 cm⁻¹ from the anhydride groups ¹²,¹⁴ disappear almost completely for all cross-linked materials, indicating that high conversions are achieved. The assignments of the new absorption bands after cross-linking were extensively discussed for solution-cross-linked materials and are summarized in Table 9.1. The reader is referred to the respective chapters for more details. The FTIR spectra are similar before and after compression molding at 175 °C for all materials (not shown here), indicating that no significant chemical changes occur during sample preparation.

Table 9.1. Characteristic absorption bands and their assignment for the cross-linked materials.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Wavenumber (cm⁻¹) (Assignment)</th>
<th>Wavenumber (cm⁻¹) (Assignment)</th>
<th>Wavenumber (cm⁻¹) (Assignment)</th>
<th>Chapter</th>
</tr>
</thead>
<tbody>
<tr>
<td>ATA</td>
<td>1725 (imide)</td>
<td></td>
<td></td>
<td>4</td>
</tr>
<tr>
<td>IM</td>
<td>1705* (imide)</td>
<td></td>
<td></td>
<td>4</td>
</tr>
<tr>
<td>HDA</td>
<td>1712 (acid)</td>
<td>1633 (amide(I))</td>
<td></td>
<td>6</td>
</tr>
<tr>
<td>MAE</td>
<td>1739 (ester)</td>
<td>1712* (acid)</td>
<td>1634 (amide (I))</td>
<td>6</td>
</tr>
</tbody>
</table>

* For the series with lower anhydride contents, these bands overlap with the imide band around 1705 cm⁻¹.

For all cross-linking methods, the intensities of the characteristic absorption bands decrease with increasing amounts of oil, due to the lowered concentrations of the functional groups. The band positions are not affected by the presence of oil, which indicates that oil addition does not significantly influence the cross-linking reactions. Calculations of the conversions of the anhydride groups based on the band around 1785 cm⁻¹ are not possible for the oil compounds, because the intensities of the reference bands are also affected by the addition of oil. After partial conversion of the anhydride groups of MAn-g-EPM with N-decylamine, the presence of the new absorption band at 1705 cm⁻¹, originating from the C=O stretching vibration of the imide,¹¹,¹² indicates the formation
of the desired N-alkylimide structure (Scheme 8.2). The conversions of the anhydride groups are equal to the targeted conversions (± 1 %) for all levels of modification (25, 50 and 75 %), so the desired reduced anhydride contents (1.5, 1.0 and 0.5 wt%) are indeed obtained. After cross-linking, the characteristic absorption bands are again present for the IM and MAE materials, indicating the success of the cross-linking reactions.

Scheme 9.2. Modification of MAn-g-EPM with N-decylamine to obtain N-decylimide groups.

9.3.2. Morphology

SAXS experiments demonstrated the presence of microphase-separated, anhydride-rich domains for the MAn-g-EPM precursor, due to the polarity difference between the polar anhydride groups and the apolar EPM chains (Chapter 2). It was also shown that the aggregates remain present after cross-linking with any of the studied methods, while DMTA suggested that the network density does not change upon cross-linking (Chapters 2-6). In this section, the effects of oil addition and reduced anhydride contents on the morphology are discussed.

The influence of oil addition on the morphology. Figure 9.1 shows the scattering profiles for the ATA and MAE compounds, while the IM and HDA compounds are not shown here in view of their similar trends. The intensity of the scattering peak decreases with increasing oil content for all compounds, due to the lower concentration of aggregates per volume unit, while the position of the maximum shifts to lower q-values, because of the larger distance between the aggregates. The apolar oil is not expected to affect the aggregates themselves, which explains the unaffected peak shape. Note that the relative peak intensities are much higher for the ATA compounds compared to the MAE compounds, because of the higher electron density difference with the EPM matrix.

The temperature-dependent behavior of the oil compounds was studied with DMTA experiments. Figure 9.2 shows the storage modulus as a function of temperature for the ATA and HDA compounds. The trends for the IM and MAE compounds are similar to those for the HDA compounds and are not shown here. For all compounds, the glass transition temperature (Tg) around -50 °C increase slightly with increasing oil content, which is related to the higher Tg of the processing oil compared to the Tg of the EPM backbone. The transition around 0 °C for some materials is the melting of traces of absorbed water. The rubber plateau modulus decreases significantly upon increasing the amount of oil, since the network is diluted with oil, resulting in a decreased resistance against deformation. Oil addition does not change the width of the rubber plateau for the IM, MAE and HDA compounds within the experimental temperature range, while the plateau becomes less broad for the ATA compounds with increasing oil content. Note that the apparent narrower rubber plateau for the ATA compound with 25 phr oil is most probably related to
problems with the sample during the measurement instead of a true transition. The different behavior of the ATA compounds is related to the relative weakness of the ATA array compared to the other materials, especially at elevated temperatures (Chapter 4).

(a)  
(b)  
Figure 9.1. SAXS profiles of (a) the ATA and (b) the MAE oil compounds.

(a)  
(b)  
Figure 9.2. Storage modulus as a function of temperature for (a) the ATA and (b) the HDA compounds.

The influence of lower anhydride contents on the morphology. The scattering profiles of the IM and MAE materials with lower anhydride contents are shown in Figure 9.3. The higher intensities for the IM materials than for the MAE materials are caused by the higher electron density difference with the EPM matrix. The scattered intensity decreases significantly upon lowering the anhydride content, while the peak maximum shifts to higher q-values and the peak becomes broader. Note that this behavior is different from series with varying anhydride conversions (Chapters 4 and 5), for which the intensity are always higher than for the MAn-g-EPM precursor. The scattering peak is still present at the lowest applied anhydride content, i.e., 0.5 wt% (inserts in Figure 9.3), albeit with a very low intensity. This demonstrates that even lower anhydride contents are required to fully prevent aggregate formation, which occurred upon full conversion of the anhydride groups to N-alkylimides (Chapter 3). The N-alkylimide groups are significantly less polar than the functional
groups that they replace, although a (very low) polarity difference with the EPM matrix remains. The electron density difference between the aggregates and the matrix is lower at lower anhydride contents, which explains the decreased intensity. The weakening of the aggregates at lower anhydride contents results in weaker anchoring of polymer chain segments to the aggregates. This causes a decreased size of the restricted mobility layer surrounding the aggregates, which explains the shift of the peak maximum to higher q-values and the peak broadening.\textsuperscript{12,15}

Figure 9.3. SAXS profiles for MAn-g-EPM with lower anhydride contents for (a) the IM and (b) the MAE materials. The profiles for the 0.5 wt\% samples are enlarged in the inserts.

Figure 9.4. Storage modulus as a function of temperature for (a) the IM and (b) the MAE materials with lowered anhydride contents.

Figure 9.4 shows the storage modulus as a function of temperature for the IM and MAE materials with lowered anhydride contents. For both series, the network density is unaffected even at the lowest anhydride content, as indicated by the similar rubber plateau modulus. This suggests that the number of aggregates remains similar and that the imide groups are still participating in the aggregation process. The aggregates become much weaker for the lower anhydride contents, since they contain less hydrogen bonds or covalent cross-links, resulting in a more pronounced gradual decrease in the rubber plateau at lower anhydride contents for the IM materials and the lowest
content for the MAE materials. Additionally, the rubber plateau for the IM materials becomes less broad at the lowest content.

### 9.3.3. Mechanical properties

It was shown in the previous section that the morphology of the cross-linked MAN-g-EPM is significantly affected by both oil addition and lower anhydride contents, albeit with completely different trends. Now the effects of both approaches on the mechanical properties are discussed.

*The influence of oil addition on the mechanical properties.* Average values of the hardness, the tensile strength (TS), the elongation at break (EB) and the modulus at 200 % strain (M\textsubscript{200}) and the compression sets (CS) at room temperature (CS\textsubscript{23}) and at 70 °C (CS\textsubscript{70}) are shown as a function of the oil content in Figures 9.5 and 9.6 for the ATA and MAE compounds, respectively. An overview of the properties of all oil compounds is given in Table 9.2. Note that the Mooney viscosities are discussed in the next section. The hardness, TS and M\textsubscript{200} decrease with increasing oil content for all cross-linkers. The oil does not bear stress and dilutes the network, resulting in a decreased resistance against deformation and, hence, a lower hardness and M\textsubscript{200}. In addition, lower stress levels are required to deform the materials up to failure, which explain the lower TS. These changes are larger for the ATA compounds than for the other compounds, due to the relative weakness of the ATA arrays (Chapter 4). No clear trends are observed in EB, which is most probably related to the relatively large experimental variations (EB ± 40 % strain) and the large influence of the sample quality on EB. Overall, EB is more or less unaffected upon oil addition for all compounds, since the chain segment length between the functional groups and, thus, between the aggregates remains similar independent of the oil content.

![Figure 9.5](image-url)  
*Figure 9.5.* (a) Tensile properties and (b) hardness, CS\textsubscript{23} and CS\textsubscript{70} as a function of the oil content for the ATA compounds.

CS\textsubscript{23} increases significantly with increasing oil content for the ATA compounds, while it remains constant for the IM compounds and even improves somewhat for the HDA and MAE compounds. CS\textsubscript{70} increases for the ATA, IM and HDA compounds, but improves for the MAE compounds. For materials containing (thermo)reversible interactions, CS is determined by two (relaxation) processes, namely plastic deformation during compression and elastic recovery after removal of the
compressive pressure. Oil addition increases the mobility of the EPM chains and, hence, influences the extent of these relaxation processes. For materials with relatively weak interactions, such as for the ATA arrays (Chapter 4), oil addition promotes plastic deformation during compression, thus resulting in increased CS23 and CS70. In the case of strong network junctions, the elastic recovery after removal of the compression becomes faster\(^{16}\), while the extent of plastic deformation remains similar. This explains the trends in CS23 for the IM, HDA and MAE compounds.

![Graph](image1.png)

*Figure 9.6. (a) Tensile properties and (b) hardness, CS23 and CS70 as a function of the oil content for the MAE compounds.*

<table>
<thead>
<tr>
<th>Cross-linker</th>
<th>Oil content (phr)</th>
<th>Hardness (Shore A)</th>
<th>TS (MPa)</th>
<th>EB (%)</th>
<th>M200 (MPa)</th>
<th>CS23 (%)</th>
<th>CS70 (%)</th>
<th>ML(3+4) at 200 °C (MU)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>ATA</td>
<td>0</td>
<td>51</td>
<td>2.3</td>
<td>520</td>
<td>1.3</td>
<td>42</td>
<td>88</td>
<td>25</td>
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<tr>
<td></td>
<td>25</td>
<td>40</td>
<td>1.6</td>
<td>640</td>
<td>0.8</td>
<td>54</td>
<td>96</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>30</td>
<td>1.1</td>
<td>620</td>
<td>0.5</td>
<td>52</td>
<td>100</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>22</td>
<td>0.8</td>
<td>590</td>
<td>0.3</td>
<td>65</td>
<td>100</td>
<td>4</td>
</tr>
<tr>
<td>IM</td>
<td>0</td>
<td>55</td>
<td>2.6</td>
<td>410</td>
<td>1.8</td>
<td>43</td>
<td>80</td>
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<td></td>
<td>25</td>
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<td>1.8</td>
<td>260</td>
<td>1.7</td>
<td>40</td>
<td>85</td>
<td>47</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>39</td>
<td>1.7</td>
<td>360</td>
<td>1.3</td>
<td>44</td>
<td>92</td>
<td>33</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>32</td>
<td>1.4</td>
<td>290</td>
<td>1.2</td>
<td>45</td>
<td>99</td>
<td>21</td>
</tr>
<tr>
<td>MAE</td>
<td>0</td>
<td>54</td>
<td>2.1</td>
<td>290</td>
<td>1.6</td>
<td>31</td>
<td>67</td>
<td>x</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>43</td>
<td>1.8</td>
<td>320</td>
<td>1.2</td>
<td>30</td>
<td>68</td>
<td>x</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>39</td>
<td>1.9</td>
<td>380</td>
<td>1.1</td>
<td>23</td>
<td>57</td>
<td>x</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>30</td>
<td>1.4</td>
<td>270</td>
<td>1.0</td>
<td>26</td>
<td>49</td>
<td>x</td>
</tr>
<tr>
<td>HDA</td>
<td>0</td>
<td>55</td>
<td>2.8</td>
<td>420</td>
<td>1.6</td>
<td>29</td>
<td>68</td>
<td>x</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>42</td>
<td>2.1</td>
<td>390</td>
<td>1.2</td>
<td>27</td>
<td>72</td>
<td>x</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>33</td>
<td>1.6</td>
<td>490</td>
<td>0.7</td>
<td>26</td>
<td>77</td>
<td>x</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>26</td>
<td>1.3</td>
<td>470</td>
<td>0.6</td>
<td>25</td>
<td>86</td>
<td>x</td>
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</tbody>
</table>

*An x indicates extensive melt fracture during Mooney viscosity measurements.*
The increase in $CS_{70}$ for the IM and HDA compounds is related to more pronounced plastic deformation at elevated temperatures, most probably because of significant weakening of the hydrogen bonds for the IM compounds and the relatively fast exchange between anhydride and amide-acid groups for the HDA compounds. This exchange remains rather slow for the MAE compounds, due to the relatively slow anhydride/hemi-ester equilibrium compared to the anhydride/amide-acid equilibrium (Chapter 6), which explains the beneficial behavior in $CS_{70}$. Note that the behavior in CS for the IM, HDA and MAE oil compounds may be advantageous for certain applications, due to their potential for the addition of relatively large amounts of (low-cost) processing oil with unaffected or even improved elastic behavior.

The influence of lower anhydride contents on the mechanical properties. The mechanical properties of the thermoreversibly cross-linked MAn-g-EPM with reduced anhydride contents are shown as a function of the anhydride content in Figures 9.7 and 9.8 and in Table 9.3 for the IM and MAE series, respectively. For both types of cross-links, the hardness and $M_{200}$ decrease almost linearly with decreasing anhydride content, while $CS_{23}$ and $CS_{70}$ increase continuously and $EB$ increases dramatically. Finally, TS decreases with decreasing anhydride content for the IM series, but increases after an initial decrease for the MAE series. The cross-links are partially replaced with weaker polar interactions between the imide groups upon lowering the anhydride content, resulting in a decreased resistance against deformation and, hence, a decreased hardness and $M_{200}$.

![Figure 9.7.](image)

The trends in EB, TS and CS can be explained with the help of the so-called “hopping” process, as originally proposed by Cooper$^{17}$ for ionomers. This mechanism allows reversible interactions to disconnect under stress conditions. The corresponding chain segments can relax the applied stress, which prevents premature failure and results in a higher EB. Free groups can re-connect upon entering other aggregates and contribute to the network again, resulting in a higher TS. For the current materials, this hopping process is possible for the imide groups and the IM arrays, but not for the covalent cross-links in the MAE materials, because the exchange between cross-linked and “free” groups is extremely slow at room temperature (Chapter 6). Therefore, chemical bonds have to be broken for the MAE materials once the stress level becomes too high. Hopping is obviously...
much easier for the extremely weak polar interactions between the imide groups, which explains the large increase in EB upon increasing the amount of imide groups and, hence, lowering the anhydride content. For the IM series, it is reasonable to assume that hopping of the hydrogen bonds is also facilitated for the weaker aggregates at lower anhydride contents, which results in lower stress levels required for failure and explains the decrease in TS. The trends in TS for the MAE series are rather surprising and are yet not fully understood. Finally, the poorer CS₂₃ and CS₇₀ at lower anhydride contents are caused by more pronounced plastic deformation in the compressed state via this hopping process.

![Graph](a) Tensile properties and (b) hardness, CS₂₃ and CS₇₀ as a function of the anhydride content for the MAE materials.

**Figure 9.8.** (a) Tensile properties and (b) hardness, CS₂₃ and CS₇₀ as a function of the anhydride content for the MAE materials.

**Table 9.3.** Mechanical properties and Mooney viscosity of the IM and MAE materials with lowered anhydride contents.

<table>
<thead>
<tr>
<th>Cross-linker</th>
<th>Anhydride content (wt%)</th>
<th>Hardness (Shore A)</th>
<th>TS (MPa)</th>
<th>EB (%)</th>
<th>M₂₀₀ (MPa)</th>
<th>CS₂₃ (%)</th>
<th>CS₇₀ (%)</th>
<th>ML(3+4) at 200 °C (MU)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>IM</td>
<td>2.1</td>
<td>55</td>
<td>2.6</td>
<td>410</td>
<td>1.8</td>
<td>43</td>
<td>80</td>
<td>76</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>51</td>
<td>1.4</td>
<td>340</td>
<td>1.1</td>
<td>56</td>
<td>81</td>
<td>61</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>48</td>
<td>1.0</td>
<td>700</td>
<td>0.6</td>
<td>72</td>
<td>97</td>
<td>40</td>
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<tr>
<td></td>
<td>0.5</td>
<td>41</td>
<td>0.5</td>
<td>1060</td>
<td>0.3</td>
<td>83</td>
<td>98</td>
<td>12</td>
</tr>
<tr>
<td>MAE</td>
<td>2.1</td>
<td>54</td>
<td>2.1</td>
<td>290</td>
<td>1.6</td>
<td>31</td>
<td>67</td>
<td>x</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>50</td>
<td>1.6</td>
<td>300</td>
<td>1.1</td>
<td>36</td>
<td>80</td>
<td>x</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>48</td>
<td>1.5</td>
<td>490</td>
<td>0.7</td>
<td>38</td>
<td>81</td>
<td>x</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>46</td>
<td>1.9</td>
<td>810</td>
<td>0.5</td>
<td>49</td>
<td>90</td>
<td>x</td>
</tr>
</tbody>
</table>

*An x indicates extensive melt fracture during Mooney viscosity measurements.

**9.3.4. Rheological behavior**

So far, the effects of oil addition and lower anhydride contents on the morphology and the mechanical properties were discussed. In this section, the effects of both approaches on the melt
(re)processability are studied to determine whether improvements in the property-processing balance are achieved. Independent of the oil content, all materials could be easily compression molded into homogeneous films at 175 °C, indicating that the cross-links are thermoreversible.

An indication of the reprocessability of these materials via the desired thermoplastic processing techniques is obtained via Mooney viscosity measurements. Mooney viscosities below 80 Mooney units (MU) are taken as a guidance for processability. The Mooney viscosities ($ML(3+4)$) were determined at 200 °C after a preheat time of 3 min instead of the common 1 min to give the temperature-dependent interactions sufficient time to reach an equilibrium state, as confirmed by the constant torque levels at the end of the experiments. In addition, the rheological behavior was studied in more detail via oscillatory shear experiments.

The influence of oil addition on the (re)processability. Previous work demonstrated that the covalently cross-linked materials, i.e., HDA and MAE, suffer from extensive melt fracture during Mooney viscosity experiments at 200 °C, due to the long characteristic lifetimes of the reversible covalent cross-links in relation to the relative short timescales of these experiments (Chapter 7). This demonstrated that these materials are not suitable for thermoplastic processing equipment, for which the timescales are also relatively short. The processability is not improved for the HDA and MAE compounds upon oil addition, as extensive melt fracture still occurs at any oil content (Table 9.2). This is most probably related to the unaffected aggregate structures. For the ATA and IM materials, the Mooney viscosity at 200 °C decreases with increasing oil content compared to the already processable pure materials (Table 9.2).

The storage ($G'$) and loss ($G''$) moduli from the oscillatory shear experiments are shown as a function of the angular frequency in Figure 9.9 for the ATA and MAE oil compounds. The trends in $G'$ and $G''$ for the IM and HDA compounds with increasing oil content are similar to those for the MAE compounds and are not shown here, although the shapes of the $G'$ and $G''$ curves are different, as discussed in Chapter 7. For all compounds, the dilution of the network with increasing oil content results in lower absolute values of both $G'$ and $G''$ at a given frequency. The rheological behavior of the ATA compounds is significantly affected upon oil addition. The crossover of $G'$ and $G''$, which is an indication of flow of the material at lower frequency, as the viscous response ($G''$) starts to dominate the elastic response ($G'$), shifts to higher frequencies with increasing oil content. This effect is typical for the dilution of polymers with a solvent, in this case oil. This shows that the characteristic relaxation times, for which the inverse of frequency at the crossover is a measure, become significantly shorter for the ATA compounds upon increasing oil content, resulting in a significantly lower Mooney viscosity.

The rheological behavior is similar for the MAE, HDA and IM compounds independent of the oil content, which is evident from the unaffected shapes of the $G'$ and $G''$ curves. The plateaus in $G'$ persist to the lowest frequencies in the current experiments for all oil contents, indicating that the materials still behave as networks. It was shown for the pure MAE material that this plateau persists to frequencies below $10^{-4}$ rad/s, indicating that the characteristic lifetimes of the covalent cross-links are extremely long (Chapter 7). Oil addition does not shorten the characteristic lifetimes of the covalent cross-links within the current experimental frequency range, which explains the
occurrence of melt fracture during Mooney measurements independent of the oil content. The decrease in Mooney viscosity for the IM compounds is related to the lower absolute values of the moduli, despite their unaffected rheological behavior. These results demonstrate that Mooney viscosities may be a fair prediction for processability in practice, although these single point measurements do not describe the full rheological behavior.

These results demonstrate that oil addition does not significantly affect the rheological behavior for the covalently cross-linked MAn-g-EPM, while the melt viscosities decrease for the materials with multiple hydrogen bonding arrays. An alternative approach to improve the (re)processability may be the addition of polar plasticizers, since they will mainly affect (the strength of) the aggregates. For ionomers, typically polar plasticizers, such as zinc stearate, are added to improve the melt processability. However, this may dramatically affect the properties as well. A combination of polar and apolar plasticizers may also be a viable approach.

The influence of lower anhydride contents on the (re)processability. The Mooney viscosity at 200 °C decreases for lower anhydride contents for the IM materials (Table 9.3), again indicating improved (re)processability. Melt fracture still occurs for the MAE materials at any anhydride content, despite the significant weakening of the aggregates. The G’ and G” curves are shown as a function of the frequency in Figure 9.10 for the IM and MAE series.

The absolute values of the moduli decrease for lower anhydride contents for both series of materials, due to the decreased resistance against deformation for weaker aggregates. The rheological behavior of the IM materials is significantly affected upon lowering the anhydride content, as indicated by the steeper slopes of G’ and especially G” at low frequency. The largest changes occur at the lowest anhydride content, for which a crossover of G’ and G” is observed. This explains the decreasing Mooney viscosity for lower anhydride contents. The behavior of G’ and G” is not affected significantly for the MAE series, except for the lowest anhydride content, for which the slopes of G’ and G” become somewhat more steep. This demonstrates that these covalently cross-linked materials still behave network-like within the experimental frequency range, as indicated by the persisting plateau in G’.

Figure 9.9. The storage (G’) and loss (G”) moduli as a function of the angular frequency (ω) for (a) the ATA compounds and (b) the MAE compounds at various oil contents at 200 °C.
lower anhydride contents does not shorten the characteristic lifetimes of these covalent cross-links sufficiently, resulting in melt fracture during Mooney viscometry at any current anhydride content.

![Graphs showing storage (G') and loss (G'') moduli as a function of the angular frequency (ω) for (a) the IM and (b) the MAE materials with lower anhydride contents at 200 °C. Note that the G' curves for the MAE materials with 1.0 and 1.5 wt% overlap.](image)

Figure 9.10. The storage (G') and loss (G'') moduli as a function of the angular frequency (ω) for (a) the IM and (b) the MAE materials with lowered anhydride contents at 200 °C. Note that the G' curves for the MAE materials with 1.0 and 1.5 wt% overlap.

The lower anhydride contents still do not allow the use of short-timescale processing techniques for the MAE materials. Even lower anhydride contents may be necessary to completely remove the aggregates for enhanced (re)processability. However, this will eventually result in too few functional groups per polymer chain for proper network formation and properties. An alternative may be the use of a different, more polar elastomer backbone for grafting of the maleic anhydride, such as nitrile or chloroprene rubbers. This may prevent the formation of aggregates, since the polarity difference between the functional groups and the rubber backbone is lower, while still sufficient functional groups can be introduced to form a network.

### 9.4. Conclusions

In this chapter, two different approaches to improve the (re)processability of the thermoreversibly cross-linked MAn-g-EPM were discussed, namely the addition of processing oil and the reduction of the anhydride content of the MAn-g-EPM precursor by a reaction with N-decylamine, with the aim to make them better suitable for (short-timescale) thermoplastic processing techniques. Multiple hydrogen bonding arrays, i.e., ATA and IM, and covalent cross-links with diamines (HDA) and amino-alcohols (MAE) were used for thermoreversible cross-linking of MAn-g-EPM. High conversions of the anhydride groups confirmed the occurrence of the cross-linking reactions.

Oil addition does not significantly affect the aggregate structure, since the apolar oil mainly resides in the apolar EPM matrix. The addition of liquid oil dilutes the network, resulting in decreased resistance against deformation and, hence, lower hardness, M200 and TS with increasing oil content for all cross-linkers. EB remains more or less unaffected upon oil addition, since the chain segment length between the functional groups is similar. For the ATA compounds, CS23 becomes poorer, due to the relatively weak interactions. For the stronger cross-links, CS23 is unaffected upon oil
addition for the IM materials or even improves somewhat for the HDA and MAE materials. This demonstrates the potential of these materials to be extended with (large amounts of) processing oil without affecting the elastic behavior. The strength of the aggregates decreases significantly upon lowering the anhydride content, since the cross-links are partially replaced with relatively weak interactions between the imide groups, although the aggregates themselves do not disappear. This results in a decreased hardness and M200 and poorer elasticity, while EB increases spectacularly, since hopping-like processes are easier for the weaker aggregates.

Both approaches do not improve the (re)processability of the covalently cross-linked MAn-g-EPM, since the covalent network with its too long relaxation times persists. The (re)processability is improved for the already processable ATA and IM compounds, but at the expense of the properties.

9.5. References

18. Mooney viscosity measurements are generally used for non-cured rubber compounds, for which values below 80 MU are required for applicability in extrusion techniques. These measurements as well as the extrusion steps are typically performed at 100 °C to avoid premature cross-linking reactions. For the current thermoreversibly cross-linked materials, obviously higher temperatures can be used.
Technology Assessment

The main aim of this thesis was to develop thermoplastic elastomers (TPEs) based on maleated ethylene/propylene copolymers (MA-n-g-EPM) using different thermoreversible cross-linking methods, including ionic interactions, hydrogen bonding and covalent cross-links. These methods were compared for their property-processing balance in Chapter 8. Here, their potential for commercial applications is discussed, mainly in comparison to commercial products, such as conventionally cross-linked elastomers and thermoplastic elastomers (TPEs). Additionally, suggestions to improve the property-processing balance are given.

The results presented so far were obtained for materials synthesized via a small-scale solution route in order to obtain homogeneous products. Melt cross-linking in batch mixers or continuous extrusion is obviously preferred from a commercial viewpoint, since large quantities of cross-linked material can easily be processed, while additional solvent removal and purification steps are avoided, resulting in lower product costs. Furthermore, melt cross-linking allows compounding with processing oils and reinforcing fillers during the same processing step. In principle, the grafting of maleic anhydride onto EPM could even be combined with the cross-linking procedure.

Most types of cross-linked materials could be successfully produced in the melt on laboratory scale, including multiple hydrogen bonding arrays, covalent cross-links and ammonium ionomers, as discussed in Chapter 7, as well as the amide-acids and -salts. The chemical structures and anhydride conversions are comparable to those of the solution-cross-linked materials (confirmed by Fourier transform infrared (FTIR) spectroscopy), as well as the mechanical properties. The only exceptions are potassium and zinc ionomers, due to non-homogeneous melt neutralization with metal acetates. This problem may be avoided by using better soluble metal salts, such as stearates. This shows that melt cross-linking is in principle possible for these thermoreversibly cross-linked materials. Several types of interactions prevent the use of thermoplastic processing techniques after cross-linking (Chapter 7), which may require subsequent shaping in a separate processing step with low shear rates and relatively long timescales, such as compression molding.

Optimized compounding with rather large amounts of processing oil, which was shown to be possible in Chapter 9, and reinforcing fillers, such as carbon black, may be used to improve the property-processing balance and the cost perspective of the current materials similarly to conventionally cross-linked elastomers. The effect of reinforcing fillers is an outstanding issue.

The following advantages and disadvantages can be distinguished based on the comparison of the current materials with peroxide-cured gumstock (i.e., no additives) EPDM:

Advantages:

- Repeated processing is possible via compression molding for all types of interactions, while some interactions even enable processability via thermoplastic processing techniques, such as extrusion and injection molding. Conventionally cross-linked elastomers are intrinsically not processable after cross-linking.
• Most materials have a (much) higher tensile strength and elongation at break compared to non-filled, cross-linked elastomers.

Disadvantages:

• The elastic behavior of the current materials is significantly poorer compared to sulfur and peroxide cross-linked elastomers, especially at elevated temperatures.

• The effect of compounding with reinforcing fillers has yet to be studied and may be less beneficial than for cross-linked elastomers, as it may influence the aggregate formation.

Possible fields of application in competition with conventional elastomers may include applications that require a high elongation at break, which is generally rather low for conventional elastomers even after compounding, and/or a high tensile strength, without high requirements on the elasticity.

For TPE-applications, the current materials have to compete with existing, commercialized TPEs. The comparison with thermoplastic vulcanizates (TPVs) based on EPDM and poly(propylene), although not completely fair as discussed in Chapter 8, shows the following advantages and disadvantages of the current materials.

Advantages:

• Similar or even better tensile properties, especially elongation at break, can be obtained without any additives. This advantage may be further exploited by proper compounding.

• Compounding with processing oil results in a significantly lower hardness (down to 20-30 Shore A) without affecting the elastic behavior for some types of interactions (Chapter 9). These low hardness values are currently not available for commercial TPEs.

• The current materials are transparent, contrary to TPVs. Of course, this advantage is lost upon the addition of reinforcing fillers, such as carbon black.

Disadvantages:

• For several types of interactions, reprocessing is only possible via compression molding, whereas TPVs can be processed via injection molding and extrusion.

• The elastic behavior at elevated temperatures is significantly poorer than for TPVs, despite the comparable elasticity at room temperature for most types of interactions.

This demonstrates that TPVs have a superior property-processing balance compared to the newly-developed materials. Possible applications for the current materials have to be found in areas that require good tensile properties (especially high elongation at break) or certain specific properties, such as low hardness and/or transparency.

Last but not least, the product costs are important, since they generally are decisive for the application of a material. Product costs are determined by the raw material costs, including the elastomer, (low-cost) processing oil and reinforcing fillers, and the grafting and cross-linking chemicals, as well as the production costs, which mainly depend on the type(s) of processing equipment. The cost perspective is therefore not so beneficial for expensive cross-linkers, such as certain multiple hydrogen bonding arrays (UPy and (bis)urea).
To conclude this chapter, some suggestions for improvements of the non-optimum property-processing balance of the newly-developed materials are given. Two approaches were explored in Chapter 9, i.e., the addition of processing oil and lower anhydride contents, but did both not improve this balance for covalently cross-linked materials. Other possible approaches include:

- Alternative MAn-g-EPM precursors with different molecular weight (distribution) and/or degree of grafting of anhydride groups may improve the property-processing balance, since these parameters affect both the properties and the processability, as demonstrated during previous work on MAn-g-EPM based ionomers\(^5\).

- The addition of polar plasticizers will mainly affect the strength and structure of the polar aggregates, but hardly the EPM matrix, which may be beneficial for this balance.

- The use of a more polar backbone may prevent aggregate formation by lowering the polarity difference between the functional groups and the elastomer matrix. For this purpose, for instance nitrile or chloroprene rubbers may be suitable, which are unfortunately more expensive than EPM rubbers. A main issue with this approach is whether it is possible to graft the maleic anhydride groups to a sufficiently high level.

- The property-processing balance may be significantly improved by using alternative thermoreversible interactions that yield a sharper decrease in relaxation times at elevated temperatures. For this purpose, the use of semi-crystalline polymer tails may be interesting, for instance via a reaction of MAn-g-EPM with NH\(_2\)-functional poly(amides)\(^6\).

References

1. The amide-acids and -salts were prepared according to the melt procedure discussed in Chapter 9, resulting in comparable chemical structures and mechanical properties as for the solution-cross-linked materials from Chapter 3.


Appendix

Thermoreversible Cross-linking with $\pi-\pi$ Interactions

In this thesis, different methods for the thermoreversible cross-linking of maleated ethylene/propylene copolymer (MAn-g-EPM) were discussed, including ionic interactions, hydrogen bonds and chemical cross-links. Additionally, some experiments were performed to introduce $\pi-\pi$ interactions between aromatic rings into MAn-g-EPM, but the limited amount of data did not warrant a separate chapter. These groups were introduced as stable imides via the reaction of their amine-functionalities with the anhydride groups of MAn-g-EPM, using N-phenyl-p-phenylenediamine (NPPDA) and 1-naphthalenemethylamine (NMA), as shown in Scheme A.1.

Scheme A.1. Reaction scheme for the introduction of $\pi-\pi$ interactions into MAn-g-EPM.

Modification reactions

The NMA material was obtained via the following procedure. Typically, 45 g of dried MAn-g-EPM (49 wt% ethylene, 49 wt% propylene, 2.1 wt% maleic anhydride (MAn), $M_n = 40$ kg/mol, $M_w = 90$ kg/mol, DSM Elastomers) was charged to a 50 g scale Haake Rheomix OS internal mixer at 180 °C and mixed for 1 min at 60 rpm. Next, an equimolar amount of 1-naphthalenemethylamine (NMA, Aldrich) was added, followed by mixing for 5 min at a rotation speed of 100 rpm. The NPPDA material was provided by DSM Elastomers and was obtained via modification of the same MAn-g-EPM with a small molar excess of N-phenyl-p-phenylenediamine (NPPDA) in the melt.

The resulting materials were compression molded for 20 min at 180 °C. Details on the characterization techniques can be found in the previous chapters.
Results

Fourier transform infrared (FTIR) spectroscopy was used to study the chemical structure and anhydride conversion of the reactions products. The anhydride bands around 1785 and 1865 cm\(^{-1}\) disappear almost completely for both the NPPDA and NMA materials (not shown here), indicating high conversions. A new sharp band is observed at 1725 cm\(^{-1}\) for NPPDA, originating from the carbonyl (C=O) stretching vibration of the aromatic imide, and at 1705 cm\(^{-1}\) for NMA, which originates from the C=O stretching vibration of the aliphatic imide. Small-angle X-ray scattering (SAXS) and dynamic mechanical thermal analysis (DMTA) demonstrate that microphase-separated aggregates are still present upon modification and that the network density is not affected (not shown here), similarly to all cross-linked materials (Chapters 2-6).

Average values of the hardness, the tensile strength (TS), the elongation at break (EB), the modulus at 200 % strain, and the compression sets (CS) at room temperature (CS\(_{23}\)) and at 70 °C (CS\(_{70}\)) are given in Table A.1. The hardness and M\(_{200}\) increase upon introduction of the phenyl rings, due to the increased resistance against deformation. TS increases, while EB is not really affected, which is related to the occurrence of ion hopping-like processes for physical interactions, such as π-π interactions, as discussed previously in this thesis. Finally, only slightly improved CS\(_{23}\) and CS\(_{70}\) values are obtained for the modified materials, due to the increased resistance against plastic deformation during compression.

These results demonstrate that the properties are improved compared to the MAn-g-EPM precursor and suggest that π-π interactions are indeed formed, though not supported by spectroscopic evidence. However, the changes in the properties are relatively small compared to effects for the other types of interactions (Chapter 2-6), which demonstrates that, as expected, the π-π interactions are relatively weak. The modified materials can be repeatedly compression molded, while the low Mooney viscosities suggest their applicability for thermoplastic processing techniques.

Table A.1. Mechanical properties of MAn-g-EPM modified with phenyl-rings.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Hardness (Shore A)</th>
<th>TS (MPa)</th>
<th>EB (%)</th>
<th>M(_{200}) (MPa)</th>
<th>CS(_{23}) (%)</th>
<th>CS(_{70}) (%)</th>
<th>ML((3+4)) at 200 °C (MU)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MAn-g-EPM</td>
<td>38</td>
<td>0.4</td>
<td>560</td>
<td>0.4</td>
<td>88</td>
<td>100</td>
<td>3</td>
</tr>
<tr>
<td>NPPDA</td>
<td>51</td>
<td>0.7</td>
<td>520</td>
<td>0.8</td>
<td>82</td>
<td>91</td>
<td>2</td>
</tr>
<tr>
<td>NMA</td>
<td>52</td>
<td>1.0</td>
<td>680</td>
<td>0.8</td>
<td>70</td>
<td>100</td>
<td>3</td>
</tr>
</tbody>
</table>
**Samenvatting**

Vernetten, in de Angelsaksische literatuur aangeduid met crosslinken, van elastomeren is noodzakelijk om typische rubbereigenschappen zoals hoge elasticiteit, taaiheid en oplosmiddelresistentie te verkrijgen. De belangrijkste industriële technieken hiervoor, zijnde zwavel en peroxide vulkanisatie, resulteren in de vorming van permanente chemische crosslinks. Dit verhindert (her)verwerking in de smelt na crosslinken en zorgt voor tijdrovende en relatief dure productieprocessen. Dit heeft geleid tot de ontwikkeling van thermoplastische elastomeren (TPEs); materialen die rubbereigenschappen combineren met de verwerkbaarheid van thermoplasten. TPEs zijn gebaseerd op thermo-reversibele crosslinks, welke zich gedragen als permanente crosslinks bij de gebruikstemperatuur, maar verzwakken of verdwijnen bij hogere temperaturen. Dit maakt het gebruik van technieken als extruderen en spuitgieten mogelijk.

Het hoofddoel van dit proefschrift is het vergelijken van verschillende methoden om hetzelfde basismateriaal thermo-reversibel te crosslinken, namelijk een etheen-propeen co-polymeer met daarop geënte malëinezuur anhydride groepen (MAn-g-EPM). De bestudeerde methoden zijn ionische interacties, (meervoudige) waterstofbruggen en covalente crosslinks. De relaties tussen de structuur, de eigenschappen en de verwerkbaarheid zijn onderzocht om te bepalen voor welke crosslink methode(n) de beste balans tussen eigenschappen en verwerkbaarheid verkregen wordt. De bestudeerde materialen zijn op laboratoriumschaal gemaakt via een oplosmiddelroute om goed gedefinieerde en homogeen gecrosslinkte materialen te verkrijgen. Er zijn geen additieven zoals olie en versterkende vulstoffen toegevoegd om de analyse zo eenduidig mogelijk te houden.

Kleine-hoek Röntgenverstrooiing (SAXS) heeft aangetoond dat het grote verschil in polariteit tussen de anhydride groepen en de EPM ketendelen resulteert in de vorming van kleine fasegescheiden aggregaten voor het uitgangsmateriaal (MAn-g-EPM). Deze aggregaten gedragen zich als multifunctionele fysische crosslinks en verhogen de netwerkdichtheid in vergelijking met EPM. De aggregaten blijven intact na crosslinken met elke onderzochte crosslink methode. Dynamische mechanische thermische analyse (DMTA) heeft aangetoond dat de netwerkdichtheid niet verandert na crosslinken, wat aangeeft dat de crosslinks alleen in de aggregaten gevormd worden. De aggregaten worden sterker door het crosslinken en houden stand tot hogere temperaturen in vergelijking met het uitgangsmateriaal MAn-g-EPM.

Ionische interacties met metaal kationen zijn verkregen na neutralisatie van gehydrolyseerd MAn-g-EPM met kalium (K) en zink (Zn) acetaat, resulterend in ionomen met di-carboxylaat functionaliteiten. Het type metaal kation heeft een belangrijke invloed op de uiteindelijke structuur, omdat de specifieke coördinatie van zink met di-carboxylaten voor een relatief slecht gedefinieerde aggregaatstructuur zorgt. De treksterkte, de rek bij breuk en de elasticiteit verbeteren met toenemende neutralisatiegraad en zijn veel beter voor K-ionomen dan voor Zn-ionomen.
Samenvatting

Ionomeren met relatief zwakke ammonium kationen zijn gemaakt door neutralisatie met tertiaire amines en hebben slechtere rubbereigenschappen dan de K- en Zn-ionomeren.

Amide-zuren, die waterstofbruggen kunnen vormen, zijn gemaakt via de reactie van MAn-g-EPM met een equimolaire hoeveelheid primaire amine. Een overmaat amine resulteert in de vorming van amide-zouten die waterstofbruggen combineren met ionische interacties. De treksterkte en de elasticiteit zijn enigszins verbeterd voor de amide-zuren ten opzichte van MAn-g-EPM, maar worden pas significant beter voor de amide-zouten, vanwege de additionele ionische interacties. De materialen kunnen meerdere malen geperst worden bij 80 °C, terwijl temperaturen hoger dan 120 °C vermeden moeten worden in verband met irreversibele imide vorming.

Verschillende meervoudige waterstofbruggen, d.w.z. imide-diaminopyridine, triazol, imidazolidon, (bis)ureum en 2-ureido-4-pyrimidon (UPy) groepen, zijn geïntroduceerd in MAn-g-EPM en zijn vergeleken met “niet-georganiseerd” waterstofbruggen (o.a. de amide-zuren en het gehydrolyseerde MAn-g-EPM). Het type (meervoudige) waterstofbrug heeft een grote invloed op de uiteindelijke rubbereigenschappen, die verbeteren in de volgorde: MAn-g-EPM << “niet-georganiseerd” < triazol < imidazolidon < ureum < bisureum < UPy. Ureum en bisureum materialen hebben een betere elasticiteit dan de andere materialen, vooral bij hogere temperaturen, wat veroorzaakt wordt door de specifieke organisatie van de waterstofbruggen.

Materialen met covalente crosslinks zijn gemaakt via de evenwichtsreactie van de anhydride groepen van MAn-g-EPM met diolen, diamines en amino-alcoholen. Een evenwichtsverschuiving bij hogere temperaturen zou kunnen zorgen voor een (gedeeltelijke) verdwijning van de crosslinks. Hoge conversies zijn mogelijk bij relatief lage temperaturen (50-75 °C) voor alle typen crosslinkers, hoewel een geschikte katalysator (p-tolueen sulfonzuur) toegevoegd moest worden voor de diolen. De treksterkte en elasticiteit verbeteren behoorlijk met toenemende conversies, terwijl het type crosslinker relatief weinig invloed heeft. De materialen zijn herhaaldelijk verwerkbaar via persen bij 175 °C als alleen alcohol en secundaire amine groepen gebruikt worden. De herverwerkbaarheid van deze materialen blijkt niet het gevolg te zijn van de gewenste evenwichtsverschuiving, maar van een continue dynamische uitwisseling tussen gecrosslinkte en vrije groepen.


De vergelijking van de verschillende thermo-reversibele crosslink methoden toont aan dat een breed scala aan mechanische eigenschappen en elasticiteit verkregen kan worden door middel van de
keuze van het type crosslink. De sterkte van de aggregaten en de “overspring”-processen zijn verantwoordelijk voor deze verschillen in de rubbereigenschappen. Enkele van de meervoudige waterstofbruggen (triazol en imidazolidon) en de amide-zouten geven de beste balans tussen eigenschappen en verwerkbaarheid. Helaas hebben de andere goed verwerkbare materialen relatief slechte rubbereigenschappen en zijn de materialen met goede eigenschappen slecht verwerkbaar met thermoplastische verwerkingstechnieken.

Twee methoden ter verbetering van deze balans zijn bestudeerd, namelijk de toevoeging van olie en het gebruik van lagere anhydride gehaltes. Beide methoden verbeteren de verwerkbaarheid van de covalent gecrosslinkte materialen niet, omdat de relaxatietijden van het covalente netwerk nog steeds te lang zijn. Het is wel aangetoond dat deze materialen gevuld kunnen worden met grote hoeveelheden olie zonder de elasticiteit te veranderen, wat zeer voordelig kan zijn in bepaalde toepassingen. De smeltviscositeit daalt behoorlijk voor de reeds goed verwerkbare materialen met meervoudige waterstofbruggen, hetgeen echter ten koste gaat van de rubbereigenschappen.

Tot dusver zijn de resultaten besproken van een academische studie over het thermo-reversibel crosslinken van MAN-g-EPM via een oplossingsroute. Crosslinken in de smelt heeft natuurlijk de voorkeur vanuit een industriële standpunt. De meeste reacties kunnen inderdaad uitgevoerd worden via de smelt met een kneder. Echter, geoptimaliseerd compouderen van deze materialen met onder andere olie en versterkende vulstoffen zoals roet is noodzakelijk voor daadwerkelijke commerciële toepassingen. Dit valt echter buiten het doel van dit proefschrift. Sommige van de nieuwe materialen zonder additieven hebben een superieure treksterkte en/of rek bij breuk in vergelijking met ongevulde, peroxide gecrosslinkte EPDM rubber en thermoplastische vulkanisaten gebaseerd op dispersies van gecrosslinkte EPDM in poly(propyleen). De elasticiteit is helaas aanzienlijk slechter, vooral bij hogere temperaturen. De huidige materialen hebben uiteraard een voordeel ten opzichte van conventioneel gecrosslinkte elastomeren omdat ze (her)verwerkbaar zijn na crosslinken. Helaas is de balans tussen de eigenschappen en verwerkbaarheid minder goed dan voor TPVs. Methoden om deze balans te verbeteren zijn het gebruik van andere MAN-g-EPM startmaterialen of relatief polaire elastomeren of het toevoegen van polaire weekmakers. Mogelijke commerciële toepassingen kunnen gevonden worden in toepassingen waarbij goede mechanische eigenschappen (vooral hoge rek bij breuk) vereist zijn zonder al te hoge eisen aan de elasticiteit.
De laatste pagina’s van dit proefschrift wil ik gebruiken om de mensen te bedanken die een bijdrage aan dit werk hebben geleverd. Uiteindelijk staat er één naam op dit proefschrift, maar zonder hulp van anderen was dit resultaat niet mogelijk geweest.

Allereerst wil ik mijn promotor prof. Piet Lemstra bedanken voor de mogelijkheid om dit project binnen SKT uit te voeren. De grote vrijheid die je Aio’s binnen hun project geeft heb ik erg gewaardeerd. De sarcastische opmerkingen die je zo nu en dan plaatste vond ik niet altijd even prettig, maar uiteindelijk heb ik er wel veel van geleerd. Tenslotte ook nog bedankt voor je correcties. Han Goossens ben ik veel dank verschuldigd voor de grote betrokkenheid en de directe begeleiding. Vooral je uitgebreide kennis van karakteriseringstechnieken heeft een grote toegevoegde waarde voor dit werk gehad. Ook bedankt voor het uitgebreid doorlezen van mijn hoofdstukken; je sabbatical in Zurich is de correcties zeer ten goede gekomen, omdat je het daar niet zo druk had als in Eindhoven. Martin van Duin wil ik bedanken voor je betrokkenheid bij dit project gedurende deze 4½ jaar en je onuitputtelijke enthousiasme. Onze samenwerking heb ik als erg prettig ervaren, ondanks de soms behoorlijke felle discussies. Ook jou wil ik bedanken voor de vele correcties, die niet altijd even duidelijk, maar wel grondig en constructief waren.

Ook wil ik de overige leden van mijn promotiecommissie bedanken. Prof. Christian Bailly wil ik bedanken voor de betrokkenheid bij dit project in de latere fase, de discussies over het rheologische gedrag van mijn materialen en de correcties van mijn proefschrift. Prof. Rint Sijbesma ben ik erg dankbaar voor de discussies, de samenwerking met betrekking tot de meervoudige waterstof-bruggen en het corrigeren van de relevante hoofdstukken. I also want to thank prof. Ludwik Leibler for the interesting and enthusiastic discussions about my work, in particular about the hydrogen bonding units, and the corrections of my thesis. Tenslotte wil ik prof. Jacques Noordermeer bedanken voor de kritische commentaren, ook tijdens DPI meetings en congressen.

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Mark
Curriculum Vitae

The author of this thesis was born in Schijndel on May 18th 1979. After finishing his secondary education at Gymnasium Beekvliet in Sint Michielsgestel in 1997, he studied Chemical Engineering at the Eindhoven University of Technology. He obtained his Masters’ degree cum laude in 2003 after completion of his thesis ‘The influence of ionic groups on the morphology and mechanical properties of poly(methyl methacrylate)’ in the ‘Polymer Technology’ group of prof.dr. P.J. Lemstra. In March 2003, he started his PhD-study in the same group. During his PhD study, the author completed four modules of the course ‘Registered Polymer Scientist’ (RPK) organized by the ‘National Dutch Graduate School of Polymer Science and Technology’ (PTN).