Kinetics of cross-linking and de-cross-linking of EPM rubber with thermoreversible Diels-Alder chemistry

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ABSTRACT

The kinetics of the Diels-Alder (DA) cross-linking and retro-Diels-Alder (rDA) de-cross-linking reactions have been studied for furan-containing EPM rubber thermoreversibly cross-linked with a bismaleimide. Cross-linking conversions obtained from spectroscopic methods deviate from rheological methods as the former take into consideration both the intermediate DA adduct and complete cross-links, while the latter only determine the formation and decomposition of complete cross-links. The thermoreversibility of the system was shown by a combination of equilibrium swelling and rheological measurements. Dynamic time sweeps of the rubber at different temperatures were used to determine the Arrhenius activation energies of 7.04 and 57.9 kJ/mol for the DA and the rDA reactions, respectively. \( E_{a,DA} \) is relatively low and suggests a diffusion limitation while \( E_{a,rDA} \) correspond to values reported in literature. Both values were used to simulate cross-link density profiles as a function of time and temperature that correspond well with the experimental data.

1. Introduction

Elastomeric materials are usually cross-linked to form 3D networks that give rubbers their characteristic elasticity and strength. Traditionally, the main techniques to cross-link rubbers on an industrial scale are sulfur vulcanization and peroxide curing [1]. Unfortunately, these techniques yield irreversible cross-links that prevent reprocessing of the production scrap and after-life waste [2]. During the last two to three decades much attention has been paid to rubber devulcanization technology [3,4], albeit with different degrees of success. Recently, the complete reworkability of cross-linked elastomers has gained more interest due to current societal trends towards sustainability and \textit{cradle-to-cradle} products. Alternatives for devulcanization of cross-linked rubbers include the introduction of reversible cross-links in the form of hydrogen bonds [5–7], ionic interactions [8] or even covalent bonds [9], that respond to an external stimulus such as temperature [10–13]. The processability of a reversibly cross-linked product should be similar to that of a thermoplastic at high temperatures, while retaining the physical properties of a thermoset cross-linked product at the application temperature. Chemically modified elastomers such as maleated ethylene/propylene rubbers (EPM-g-MA) [14] or epoxidized butyl rubber [15] can be cross-linked in such a reversible manner using covalent Diels-Alder (DA) chemistry. To do so, an electron-rich diene such as furan has to be attached onto the polymer backbone [16–19]. This can be achieved via copolymerization [20] or chemical modification [6,9,18,19]. The pendant furan groups can then be coupled with an electron-poor cross-linker, like bismaleimides (BM) [21–23]. Thermoreversible DA cross-linking and retro-DA (rDA) de-cross-linking of polymers in general allows for relatively fast kinetics and mild reaction conditions [24–27]. Especially the low coupling (< 50 °C) and high decoupling...
(> 100 °C) temperatures between a furan and a (bis)maleimide make DA chemistry a very attractive route for thermoreversible polymer cross-linking [28–31]. The kinetics of the DA reaction between furan and maleimide in solution is a second order, while the \( rDA \) reaction obeys a first order kinetics [32,33]. The formation of the final, thermoreversible cross-links (F-MM-F) between pendant furan groups (F) and BM cross-linkers (MM) is preceded by the formation of an intermediate DA adduct (F-MM) (Scheme 1).

The (reversible) cross-linking kinetics of polymeric systems can be studied by several spectroscopic characterization techniques such as UV–Vis [33,34] and FT-IR spectroscopy [33]. In most investigations on DA kinetics in polymeric systems the focus is on the formation and decomposition of the DA adduct [34,35]. A major drawback of these methods is that they cannot discriminate between the intermediate adducts and the final cross-links (i.e. F-MM and F-MM-F in Scheme 1). Therefore, these spectroscopic methods do not provide any information regarding the network properties or elasticity of the material gained by the formation of such cross-links. NMR relaxometry does provide an insight in the formation (and breakage) of the active cross-links [33,36–38], but the response time is too slow compared to the relatively fast \( rDA \) kinetics to be studied here. In rubber technology the kinetics of cross-linking are typically studied using rheological measurements [39–41]. These yield so-called rheometer curves that present the torque as a measure for the extent of cross-linking versus time at a specific cure temperature. In rheometer curves the cross-link density generally builds up rather slowly, because the first cross-links formed upon heating the sample are not elastically active, since they convert the polymer chains to an insoluble gel. Once the gel point is passed, the cross-link density increases steeply [42]. Typically, the optimum cure time is determined from such curves as the time required to reach 90% of the maximum torque [40].

The goal of this study is to use such rheological measurements in a quantitative approach to study the kinetics of \( rDA \) (de-)cross-linking. Equilibrium swelling tests and infrared measurements are used to obtain a better understanding of the chemistry of the thermoreversible cross-links in the rubber network. Analogous EPM-g-MA precursors that are cross-linked with diamines are used as an irreversibly cross-linked reference [43]. The combination of analytical methods and dynamic time sweeps allow for the discrimination between the formation and rupture of the intermediate DA adduct and the final cross-links. The kinetic rate coefficients of the DA cross-linking and the retro DA de-cross-linking reactions can be obtained from the low temperature (60–80 °C) and the high temperature experiments (130–150 °C), respectively. The activation energies (\( E_A \)) and the pre-exponential factors (\( k_0 \)) corresponding to these reactions can then be determined from Arrhenius plots. To the best of our knowledge this is the first time the kinetics of DA cross-linking and \( rDA \) de-cross-linking in a thermoreversible network is described on the basis of rheological measurements. This will give more insight in the processes taking place on a molecular level when recycling or reprocessing such materials in the bulk.

2. Experimental

2.1. Materials

Maleated EPM (EPM-g-MA, Keltan DE5005, 49 wt% ethylene, 2.1 wt% MA, \( M_n = 50 \text{ kg/mol} \), polydispersity index = 2.0) was kindly provided by ARLANXEO Performance Elastomers. EPM-g-MA is amorphous, i.e. it is homogeneous polymers at room temperature and higher and, thus, enables the kinetic approach followed in this study. Furfurylamine (FFA, Aldrich, ≥ 99%) was freshly distilled. An aliphatic bismaleimide (MM) was synthesized from 1,12-diaminododecane (Sigma-Aldrich, > 98%) and maleic acid anhydride (MA, Sigma-Aldrich, > 99%) according to a reported procedure [44]. Octadecyl-1-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate (Sigma-Aldrich, 99%), tetrahydrofuran (THF, Sigma-Aldrich, > 99.9%), decahydronaphthalene (decalin, mixture of cis + trans, Sigma-Aldrich, > 98%) and acetone (Sigma-Aldrich, > 99.5%) were used as received as antioxidant and solvents, respectively.
2.2. Methods

2.2.1. Functionalization with furan

Prior to the reaction, EPM-g-MA was dried in a vacuum oven for one hour at 175 °C to convert present diacids into anhydride. The EPM-g-MA precursor was converted with FFA into EPM-g-furan according to a reported procedure [9]. Typically, 45.0 g EPM-g-MA rubber (9.6 mmol MA) was dissolved in 500 mL THF at room temperature. 2.8 g of freshly distilled FFA (28.9 mmol; 3.0 eq. based on MA content in EPM-g-MA) was then added to the 10 wt% rubber solution. The reaction mixture was stirred for 5 h in a closed system at room temperature and then precipitated by pouring it slowly into a tenfold amount of acetone (5 L) under mechanical stirring, yielding the polymer product as white threads. The product (EPM-g-furan) was dried to constant weight in an oven at 35 °C. Subsequently, the now slightly yellowish product was briefly compression molded at 175 °C and 100 bar for 15 min to ensure the conversion of all intermediate maleimide acid products to imide products.

2.2.2. Bismaleimide cross-linking

Typically, 40.0 g of EPM-g-furan rubber (8.6 mmol furan) and 1000 ppm phenolic anti-oxidant were dissolved in 500 mL THF. Subsequently, 0.1–1.0 eq. (based on furan content of EPM-g-furan) of BM was dissolved in THF and added to the 10 wt% rubber solution while stirring. The majorit of the solvent was evaporated in the fume hood by blowing over air. The residual solvent was removed in a vacuum oven at 50 °C and the resulting product was compression molded at 160 °C and 100 bar for 30 min. The resulting products were thermally annealed in an oven at 50 °C for 7 days.

2.2.3. Diamine cross-linking

EPM-g-MA was also cross-linked with 1,12-diaminododecane as an irreversibly cross-linked reference. 15.0 g of EPM-g-MA and 1000 ppm of phenolic antioxidant were dissolved in 120 mL THF. Subsequently, an equimolar amount (based on MA content in EPM-g-MA) of 1,12-diaminododecane was dissolved separately in approximately 20 mL THF. The diamine solution was added to rubber solution under stirring, resulting in a viscous gel that cannot be stirred anymore after a few seconds. The viscous gel is transferred to a petri-dish and the majority of the solvent is evaporated in the fumehood by blowing over air. The residual solvent was removed in a vacuum oven at 35 °C and the resulting product was compression molded at 160 °C and 100 bar for 15 min to yield test samples with the desired dimensions.

2.3. Characterisation

The rubber samples were analyzed by Fourier transform infrared spectroscopy (FT-IR). Spectra were recorded using a Perkin-Elmer Spectrum 2000. Rubber films of 0.1 mm thickness were compression molded at 160 °C and 100 bar for 30 min, annealed for 3 days in an oven at 50 °C and measured in a KBr tablet holder (transmission). Measurements were performed over a spectral range from 4000 to 400 cm⁻¹ at a resolution of 4 cm⁻¹, co-averaging 16 scans. Deconvolution was performed using PeakFIt 4 from Systat software. The area under the individual deconvoluted FT-IR peaks (R² > 0.95) were quantified and the differences in relative peak areas were used to calculate the reaction conversions.

The bands at 1464 cm⁻¹ (CH₂ scissoring), 1395 cm⁻¹ (CH₂ wagging), 1361 cm⁻¹ (CH₂ twisting) and 723 cm⁻¹ (CH₃ in-plane bending, δCH₃) are assigned to the EPM backbone and remain unchanged upon cross-linking. δCH₃ was used as an internal reference (A₂23). Unfortunately, the band at 1190 cm⁻¹ (in-plane bending of the DA ring, δDAring) that is associated with the formation of a DA adduct [16,45] has some overlap with neighboring rubber peaks. The relative decrease of the characteristic furan peak at 1013 cm⁻¹ (symmetric C-O-C vibration νCOC, A₁013) was, therefore, used to calculate the cross-linking conversion (XIR) (Eq. (1)). The concentration of cross-links [F-MM-F]IR is determined from XIR (Eq. (2)).

\[
X_{IR} = \left(1 - \frac{[F]}{[F]_i} \right) \times 100% = \left(1 - \frac{A_{1013}/A_{223}}{A_{1013}^{XL}/A_{223}^{XL}} \right) \times 100%
\]

(1)

\[
[F-MM-F]_{IR} = \frac{1}{2} X_{IR} [F]_i
\]

(2)

A^XL area under absorption peak in non-cross-linked EPM-g-furan.

A^IR area under absorption peak in cross-linked EPM-g-furan.

The concentration of F-MM-F as determined from equilibrium swelling experiments ([F-MM-F]eo in mol/mL) in the rubber was also determined from equilibrium swelling experiments in decalin [46]. Approximately 500 mg of dried, cross-linked sample was immersed in 15 mL decalin until equilibrium swelling at room temperature (3 days) was reached. The surface of the sample was then dabbed with a tissue and the swollen weight was measured (W₁). Subsequently, the swollen sample was dried in a vacuum oven at 80 °C until a constant weight was obtained (W₂). The weights of the swollen and dried samples were used to calculate the cross-link density using the Flory-Rehner equation (Eq. (3)) [47,48]. Additional equilibrium swelling tests were performed over a temperature range of −20 to 125 °C.
\[
[F-MM-F]_0 = \frac{[F-MM-F]}{[MM]_0} = \frac{\ln(1-V_R) + V_R + \chi V_F^2}{2V_F(0.5V_R - V_F^2/2)}
\]

with \(V_R = \frac{W_2}{W_2 + (W_2 - W_1)\frac{\rho_{EPDM} \cdot \Delta V_{FM}}{\rho_{decalin}}}
\]

\(V_R\) volume fraction of swollen rubber sample.

\(V_F\) molar volume of solvent (decalin: 154 mL/mol at room temperature).

\(\chi\) Flory-Huggins interaction parameter (decalin-EPDM: 0.121 + 0.278\(V_R\)) [49].

\(\rho\) density (0.860 g/mL for EPM-g-furan and 0.896 g/mL for decalin)

The samples used for dynamic mechanical measurements were prepared by compression molding 4 g of rubber into 5 mm wide and 2 mm thick squares at 160 °C and 100 bar for 30 min and punching out cylindrical disks of 8 mm in diameter. Frequency sweeps were performed on a strain-controlled ARES-LS2 rheometer with home-made parallel plates of 7.9 mm in diameter with an imposed strain of 0.2%. Time sweeps were performed on a stress-controlled Anton Paar MCR300 rheometer with home-made, parallel serrated plates of 8 mm in diameter with an imposed strain of 0.2% and a frequency of 1 Hz. The storage \((G'')\) and loss \((G''')\) moduli of the thermoreversibly cross-linked rubber samples were determined from time sweeps. Sample preparation by de-cross-linking at 150 °C (DA peak at 1190 cm\(^{-1}\) was not observed in IR spectrum) was followed by time sweeps at 60, 70 and 80 °C, starting with a completely de-cross-linked system, i.e. no furan peak at 1013 cm\(^{-1}\) observed on IR spectrum. Dynamic time sweeps were performed at temperatures of 130, 140 and 150 °C after cross-linking the samples at 60 °C. The amount of cross-links formed over time can be related to the plateau modulus of the rubber via \(G' = \frac{\rho F}{M} \) with \(M\) the molecular weight between cross-links [50,51], but this method takes into consideration both chemical cross-links and trapped entanglements. To account for the non-ideal character of the network and to eliminate the effect of any dangling ends or loops, the cross-linking conversion \(x_{\text{theo}}\) was calculated from the ratio of the different moduli instead (Eq. (4)) [52].

\[
x_{\text{theo}} = \frac{G^* - G_0^*}{G_{\text{max}} - G_0^*}
\]

\(G^*\) complex modulus determined from \(\sqrt{(G''^2 + G'''^2)}\) with \(\sigma G^* = \sqrt{\frac{1}{G^*} (G''^2 \frac{\rho F}{M} + G'''^2 \frac{\rho F}{M})}
\]

\(G_0^*\) initial complex modulus

\(G_{\text{max}}\) complex modulus at equilibrium

It is noted that \(G_{\text{max}}\) is equilibrium conversion at the temperature considered and not based on the (theoretical) maximum concentration of cross-links. While (differential) equations corresponding to the kinetics of the equilibrium reaction between a single furan and a single maleimide group can be solved analytically, the DA cross-linking reaction of a polymer requires a double reaction equilibrium (Eqs. (5) and (6)). Two assumptions were made in order to be able to perform a kinetic study on thermoreversible cross-linking of EPM-g-furan with MM difunctional cross-linker. First, it is assumed that the two kinetic rate coefficients for the DA reaction towards F-MM and F-MM-F are equal and the same assumption was made for the two kinetic rate coefficients for the retro DA reactions. This assumption might be disputable for densely cross-linked thermoset resins. However, the low degree of functionalization of EPM-g-furan (1 furan unit per 150 monomers) results in an average distance between functional groups of 335 Å along the polymer backbone. This is well above the characteristic Kuhn length of a typical EPM segment (18 Å) [53,54]. This implies the presence of highly mobile chain segments between cross-links [55-58]. As a consequence, it is safe to assume that the presence of a cross-link point will not significantly influence the chain mobility and, thus, will not affect the chemical reactivity of “neighboring” furan groups. For this reason, it is safe to assume an average (constant) reactivity over time for this system at both low and high cross-linking density. The second assumption is more general for kinetic studies on reversible reactions [33,34,59-61]. The initial stage of the thermoreversible DA equilibrium is assumed to be dominated by the DA cross-linking reaction at low temperatures and by the retro DA de-cross-linking reaction at high temperatures [32-34]. For kinetic studies on the thermoreversible DA reaction, a simplified power law reaction model is often used to determine the corresponding kinetics equations (Eq. (7)) with \(k\) being an apparent kinetic coefficient that is a function of the actual kinetic constant multiplied with the initial concentration of the starting reagents to the power \(n\) [33,62,63]. The initial part of \(x_{\text{theo}}\) (the first three minutes), determined from low-temperature rheological measurements, \(y\) fitted to a second order DA kinetics equation to obtain an apparent \(k_{DA}\) in mol L\(^{-1}\) s\(^{-1}\) which includes the initial concentration of the starting reagents (Eq. (8)). The initial part of \(x_{\text{theo}}\) determined from high-temperature rheological measurements was fitted to a first order retro DA kinetics equation to obtain \(k_{DA}\) (Eq. (9)). Subsequently, both sets of kinetic rate coefficients resulting from these two fits at different (low and high) temperatures are individually fitted to the Arrhenius equation (Eq. (10)) in order to determine the pre-exponential factors \(k_0\) and the activation energies \(E_a\), corresponding to the DA and the retro DA reactions. The resulting parameters can be used to determine the kinetic rate coefficients for both reactions at every temperature via the Arrhenius equation. Doing so allows for the determination of the equilibrium constant \(K_{eq}\), which is related to the change in standard Gibbs free energy for the reaction \((\Delta G)\) and, ultimately, to the change in enthalpy \((\Delta H)\) and entropy \((\Delta S)\) of the reaction (Eqs. (11) and (12)).

\[
[F] + [MM] \xrightarrow{k_{DA}} [F-MM]
\]
\[
[F-MM] + [F] \xrightleftharpoons[k_{DA}]{k_{rDA}} [F-MM-F]
\]  
(6)

\[
\frac{dX}{dt} = k(1-X)^n
\]
(7)

\[
k_{DA} = \frac{1}{1-X_{F-MM-F}}
\]
(8)

\[
k_{rDA} = \ln(1-X_{F-MM-F})
\]
(9)

\[
k_{0,DA} = k_{0,DA}e^{-\frac{E_a,DA}{RT}}
\]
(10)

\[
K_{eq} = \frac{k_{DA,T}}{k_{rDA,T}}
\]
(11)

\[
\Delta G = -RT\ln K_{eq} = \Delta H - T\Delta S
\]
(12)

\(k_{0,DA}\) pre-exponential factors of DA (\(k_{0,DA}\)) and rDA (\(k_{0,rDA}\)) reactions, respectively.

\(E_a,DA\) activation energies of the DA (\(E_a,DA\)) and rDA (\(E_a,rDA\)) reactions, respectively.

\(k_{DA,T}\) kinetic rate coefficients at a specific temperature of DA (\(k_{DA,T}\)) and rDA (\(k_{rDA,T}\)) reactions, respectively.

The pre-exponential factors and activation energies of the DA cross-linking and the retro DA de-cross-linking reactions should provide a good insight into the kinetics of this thermoreversible network. There parameters can be inserted into the set of four differential equations that fully describes the equilibrium reactions involved in the DA cross-linking and rDA de-cross-linking of the polymer (Eqs. (13)-(16)). Simultaneously solving this set of four differential equations can be used not only to check whether the resulting fit parameters match with the experimental data, but also to predict the concentrations of the species involved at other conditions.

\[
\frac{d[F]}{dt} = -k_{DA}[F][MM] + k_{DA}[F-MM] - k_{DA}[F-MM][F] + k_{rDA}[F-MM-F]
\]
(13)

\[
\frac{d[MM]}{dt} = -k_{DA}[F][MM] + k_{DA}[F-MM]
\]
(14)

\[
\frac{d[F-MM]}{dt} = k_{DA}[F][MM] - k_{rDA}[F-MM+M] + k_{rDA}[F-MM-F] - k_{DA}[F-MM][F]
\]
(15)

\[
\frac{d[F-MM-F]}{dt} = k_{DA}[F-MM][F] - k_{DA}[F-MM-F]
\]
(16)

Fig. 1. FT-IR absorption spectra of EPM-g-furan with BM. A: after thermal annealing at 50 °C for 70 h and after subsequent heating at 150 °C for 1 h and B: with different amounts of BM after thermal annealing at 50 °C for 70 h.
3. Results and discussion

3.1. Thermoreversible cross-linking

FT-IR spectra of EPM-g-furan confirm the thermoreversible character of DA cross-linking (Fig. 1A). Characteristic furan peaks, such as ν_C=C and ν_C=O at 1504 and 1013 cm\(^{-1}\), respectively, can be seen to decrease upon cross-linking at low temperature (70 h at 50 °C) and to increase after de-cross-linking at high temperature (1 h at 150 °C). The DA adduct formation in samples with different amounts of BM was also followed by transmission FT-IR after thermal annealing to determine XIR and their final [F-MM-F]IR (Fig. 1B). It is clear how the characteristic absorption band corresponding to the unreacted furan group (1013 cm\(^{-1}\)) decreases, as expected, with the amount of BM used up to 0.6 equivalents.

At the same time [F-MM-F]IR and [F-MM-F]es both increase with the amount of MM added (Table 1). Although the values determined via both types of measurements have the same curvatures and are in the same order of magnitude, comparing them in more detail confirms that there is a significant discrepancy between [F-MM-F]IR and [F-MM-F]es. The reason is that IR takes into account the disappearance of all furan groups as a consequence of the formation of both the intermediate and the final cross-link (F-MM and F-MM-F, respectively). Meanwhile, equilibrium swelling determines exclusively the formation of active cross-links (Scheme 1). The same is true for the rheological measurements. For this reason, only the concentration of final cross-links, as determined from swelling tests and rheological measurements, will be used to determine the cross-linking kinetics.

The reversible character of the cross-links was shown for samples with different cross-link densities by performing a series of rheology experiments at different temperatures (Fig. 2). The shear storage modulus (G') at 30 °C increases linearly (R\(^2\) > 0.9) with the cross-link density. At 180 °C G' remains constant, regardless of the initial cross-link density of the samples and decreases with respect to the value determined at 30 °C. This is evidence for the de-cross-linking of the samples via the rDA reaction. When decreasing the temperature from 180 °C to 30 °C, G' regains 90% of its initial value after 1 h of re-cross-linking. This confirms the thermoreversible character of the network at different cross-link densities, while at the same time also providing an estimated time scale for the reformation of the network at the given temperature (approximately 1 h at 30 °C).

3.2. Equilibrium

The effect of an increase in temperature on the cross-link density in irreversibly (diamine) and thermoreversibly (BM) cross-linked

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Table 1

<table>
<thead>
<tr>
<th>Molar ratio BM:furan</th>
<th>[F-MM-F] + [F-MM]IR (mol/mL)</th>
<th>[FMMF]es (mol/mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3 eq.</td>
<td>0.9 · 10(^{-5})</td>
<td>4.6 · 10(^{-5}) ± 0.5 · 10(^{-5})</td>
</tr>
<tr>
<td>0.4 eq.</td>
<td>2.6 · 10(^{-5})</td>
<td>9.2 · 10(^{-5}) ± 0.7 · 10(^{-5})</td>
</tr>
<tr>
<td>0.5 eq.</td>
<td>4.1 · 10(^{-5})</td>
<td>8.2 · 10(^{-5}) ± 0.6 · 10(^{-5})</td>
</tr>
<tr>
<td>0.6 eq.</td>
<td>10.2 · 10(^{-5})</td>
<td>13.7 · 10(^{-5}) ± 0.9 · 10(^{-5})</td>
</tr>
</tbody>
</table>

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Fig. 2. Shear storage modulus of thermoreversibly EPM-g-furan samples cross-linked with different amounts of MM cross-linker, measured at a frequency of 10 rad/s and an imposed strain of 0.2% at 30 °C (filled black squares), at 180 °C (red dots) and at 30 °C after 1 h of thermal annealing at 50 °C (empty black squares). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
EPM rubbers was investigated by performing equilibrium swelling tests at different temperatures (Fig. 3A). It must be noted that the influence of the temperature on the polymer/solvent interaction parameter $\chi$ and the densities of the rubber and the solvent was neglected for making this comparison (assuming the influence of these parameters is the same for irreversibly and reversibly cross-linked rubbers) and, thus, data are presented as apparent cross-link density. When increasing the temperature of the equilibrium swelling, a large decrease of the apparent cross-link density is observed for the BM cross-linked EPM-g-furan, whereas for the diamine cross-linked EPM-g-MA the apparent cross-link density only slightly decreases, which is probably due to the neglected temperature effects mentioned above. This difference clearly indicates that increasing the temperature shifts the equilibrium concentration of cross-links for the EPM-g-furan/BM system. A similar effect is observed when measuring the shear storage moduli ($G'$) of (BM cross-linked) EPM-g-furan and diamine cross-linked EPM-g-MA at different temperatures (Fig. 3B). The strong decrease in $G'$ with temperature that is observed for the non-cross-linked EPM-g-furan corresponds to disentanglements. Standard rubber elasticity theory predicts that for cross-linked rubbers, $G'$ should increase linearly with temperature [1, 64]. However, the decrease in $G'$ observed for the diamine cross-linked EPM-g-MA is characteristic for loosely cross-linked, rubbery networks, as a result of the disentanglement of dangling ends which have a higher mobility at elevated temperatures [65, 66]. For the BM cross-linked EPM-g-furan, however, the decrease in $G'$ with temperature is much steeper, which is direct proof of the retro DA de-cross-linking. To the best of our knowledge this is the first time that such relevant differences are reported between two network systems that are (almost) perfectly equal in chemical structure and differing only in the nature (irreversible vs thermoreversible) of the cross-linking points.

The cross-linking density was also measured during thermal annealing of compression molded samples (Fig. 4A). For the diamine cross-linked EPM-g-MA no significant change in cross-link density was observed upon thermal annealing. During sample preparation of the BM cross-linked EPM-g-furan sample via compression molding at 160 °C for 30 min, the cross-link density strongly decreases from $\sim 1.2 \cdot 10^{-4}$ to $\sim 5.10^{-4}$ mol/mL, i.e. de-cross-linking via the rDA reaction takes place. During subsequent thermal annealing at 50 °C the cross-link density slowly increases over time to $\sim 1.1 \cdot 10^{-4}$ mol/mL, indicating that re-cross-linking via the DA reaction results in almost complete recovery to the original cross-link density. Similar effects are observed when performing time sweeps with
the BM cross-linked EPM-g-furan at high temperatures (Fig. 4B). At 160 °C G′ decreases rapidly as a function of time due to de-cross-linking. After approximately 2 h, the modulus reaches a plateau at 0.3 MPa. A subsequent decrease in temperature from 160 to 50 °C results in an increase in G′ over time. This increase is attributed to re-cross-linking via the DA reaction. After 1 h the modulus reaches a new plateau at 0.6 MPa, which is at 90% of the initial value at the start of this experiment. A very small, continuing increase in modulus was observed for at least another 14 h. These rheological observations and the large difference between the time scales at which cross-linking appears to take place in a static (equilibrium swelling, plateau reached after ~50 h) and a dynamic (rheology measurement, plateau reached after ~1 h) experiment both indicate that the mobility of BM in the rubber matrix is limited. The high shear force applied to the sample in a rheometer experiment appears to increase the mobility of the BM in the rubber matrix, evidently resulting in a faster cross-linking reaction than in a swelling experiment. During the cross-linking reaction in the rheometer a more tight rubber network is formed over time. This may, again, limit the mobility of BM as is evident from the slow but steady increase of the shear modulus towards the initial plateau value. For the remainder of this study it is assumed that such diffusion limitations do not play a significant role during the initial stages of cross-linking during a rheometer experiment and that they do not influence the rDA de-cross-linking reaction at all.

3.3. Diels-Alder cross-linking kinetics

The cross-linking conversion was determined from the complex modulus G″ of the thermoreversibly cross-linked EPM-g-furan samples (Eq. (4)), as measured by time sweeps at 60, 70 and 80 °C (after de-cross-linking at 150 °C) and at 130, 140 and 150 °C (after cross-linking at 60 °C). The kinetic rate coefficients of the DA and the rDA reactions are determined from the initial parts (the first 60 data points) of the conversion data (Fig. 5). In this approach it is assumed that the reaction kinetics for the non-cross-linked material at low temperatures are initially dominated by the forward DA cross-linking reaction and for the fully cross-linked material at high temperatures by the backward rDA de-cross-linking reaction. This assumption may be disputed, as 60, 70 and 80 °C are not particularly low temperatures and 130, 140 and 150 °C are not particularly high temperatures. Nevertheless, Differential Scanning Calorimetry and Dynamic Mechanical Thermal Analysis measurements on the same material performed in previous studies showed that the rDA reaction only starts to take place above 120 °C [9]. The difference in temperature between the low and high temperature experiments is small because the material does not allow for a reliable dynamic time sweep at lower temperatures and may show some degradation at very high temperatures. Having noted these caveats, kDA at 60, 70 and 80 °C was determined by fitting the cross-linking conversions at these temperatures to second order reaction kinetics (Eq. (8), Fig. 5A). Likewise, kDA at 130, 140 and 150 °C was determined by fitting the corresponding conversion data to first order reaction kinetics (Eq. (9), Fig. 5B; rate coefficients and R² values given in box). The linear fits are almost perfect (R² close to unity). As expected, the rate coefficients for both the DA and rDA reactions increase with temperature.

Next, the rate coefficients were fitted in Arrhenius plots to determine the k0 and Ea of the DA and rDA reactions (Fig. 6). The values for k0,DA, Ea,DA, k0, rDA, and Ea, rDA were found to be 0.491 mL mol⁻¹ s⁻¹, 7.04 kJ mol⁻¹, 57.9 s⁻¹ and 35.0 kJ mol⁻¹, respectively. These parameters were used to determine the kinetic rate coefficients for both reactions at different temperatures via the Arrhenius equation. The resultant kinetic rate coefficients were used to determine the equilibrium constants at those temperatures. These equilibrium constants were used in a Van’t Hoff plot to find the change in enthalpy and the change in entropy of the reaction (Fig. 6B). These were found to be −27.9 MJ mol⁻¹ and −39.6 kJ K⁻¹ mol⁻¹, respectively.

The Ea of the exothermic DA reaction is, thus, indeed found to be lower than that of the endothermic rDA reaction. Even so, the Ea found for the DA cross-linking reaction (7.04 kJ/mol) is relatively low compared to values found in literature for the DA reaction in polymeric systems (~30 kJ/mol) [62,63]. Such a low activation energy is characteristic for a reaction with a diffusion limitation and further confirms the discrepancy between cross-link densities determined from spectroscopic and rheological methods. In this work
the kinetics of the formation and breakage of cross-links are determined on the basis of rheological measurements. This way, only the concentration of complete cross-links is taken into consideration. Meanwhile, the activation energies for the DA reaction found in literature were determined from spectroscopic measurements and, thus, represent the single reaction between a furan and a maleimide group \[62,63\]. The reason why \(E_{a,DA}\) determined from rheological measurements is lower is the concentration of reactant for the DA cross-linking reaction is \([F-MM]\), which is significantly lower than \([MM]_0\) during the entire reaction (MM is also used for the formation of a DA adduct as measured by spectroscopic methods). The second order dependency of these reactant concentrations on the DA reaction rate results in the determination of higher DA rate coefficients and, therefore, a lower \(E_{a,DA}\). This appears not to significantly affect the rDA de-cross-linking reaction. The \(E_a\) found for this endothermic rDA de-cross-linking reaction is found to be comparable to values found in scientific literature (values ranging from 41 to 161 kJ/mol have been reported for \(E_{a,rDA}\) \[35,60,67–71\]). The change in enthalpy and the change in enthalpy of the reaction were both found to be negative. This means that de DA cross-linking reaction is indeed an exothermic process that results in a decrease of entropy of the reaction as the reagents combine to form a single network.

### 3.4. Model validity

The determined rate coefficients were used to generate the concentration of cross-links over time at the different temperatures using the differential equations (Eqs. (13)(16)) corresponding to the DA cross-linking reaction at 60, 70 and 80 °C (Fig. 7A) and to the rDA de-cross-linking reaction at 130, 140 and 150 °C (Fig. 7B). An initial BM concentration of \(1.35 \cdot 10^{-4}\) mol/mL (0.5 eq. based on furan content of EPM-g-furan) was used for the cross-linking reactions and the same initial cross-link density (concentration of F-MM-F) was used for the de-cross-linking reactions. These generated cross-linking concentration profiles over time were compared with the
experimental data by converting the cross-linking conversions into cross-link densities using the same initial concentration of BM and cross-links for the cross-linking and de-cross-linking reactions, respectively.

The experimental data for the DA cross-linking reaction show a more steep increase in cross-link density over time at higher temperatures and ultimately a lower cross-link density at their equilibrium plateau. Although the predicted data for these reactions follow these initial trends, they increasingly deviate from the experimental data at larger reaction times and the equilibrium plateaus appear to be in a reverse order with the temperature. Assuming that the rDA de-cross-linking reaction is insignificant with respect to the DA cross-linking reactions at these relatively low temperatures therefore appears to be incorrect and the complete system of differential equations should be considered when modelling such reactions. As the predicted data seem to correlate better with the experimental data for the rDA de-cross-linking reaction, the assumption that the DA cross-linking reaction is insignificant with respect to the rDA de-cross-linking reactions at these relatively high temperatures appears to be correct.

The present work is unique in the sense that it is a study on the reaction kinetics of this cross-linking/de-cross-linking system based on rheological measurements in the solid state as opposed to in a solution [72]. Polymers in general and cross-linked polymers in particular, are well known to impose diffusion limitations to molecules in their matrix, resulting in a less homogeneous dispersion of BM and even lower local concentrations [73,74]. This is particularly evident when considering the low activation energy for the DA cross-linking reaction (7 kJ/mol in the solid state and 30 kJ/mol in solution) and the deviation of the predicted data from the experimental data at the corresponding cross-linking equilibrium plateaus. The chemistry of cross-linking and de-cross-linking is strongly dependent on the chemical and physical properties of the polymeric system used, the experimental conditions and the occurrence of side reactions [35]. When the DA reaction is used for the cross-linking of (rigid) polymers, diffusion of the reactants has to be considered since the mobility of groups can be limited by their attachment to the polymer. This low mobility results in a relatively slow thermal annealing process compared to the molecular DA reaction between furans and maleimides. Moreover, the effect of the diffusion limitation changes over time as the polymers become more and more viscous upon cross-linking. Furthermore, when decoupling a maleimide from one end, the cross-link is broken, but the BM is still attached to the polymer on one side, making it more likely to reconnect at the pending furan moiety that is still in close vicinity because of the limited chain mobility. All these aspects should be taken into account when considering the cross-linking/de-cross-linking kinetics of such a system in the solid state as it appears that the reaction kinetics cannot simply be deduced from the situation in a solution.

4. Conclusions

The kinetics of the Diels-Alder cross-linking and retro-Diels-Alder de-cross-linking reactions in a thermoreversibly cross-linked EPM rubber have been studied on the basis of the formation and deformation of cross-links. The observed deviation between the concentration of cross-links as determined by spectroscopic analysis (infrared) and physical methods (rheology and swelling tests) confirmed that the former also measures of the formation of the initial DA adduct whereas the latter only determines the formed cross-links. The appropriate choice of a reference material (in this case a diamine cross-linked EPM-g-MA) allowed for appreciating the thermoreversible behavior by clearly distinguishing the stability of the cross-links as function of temperature. A combination of equilibrium swelling and dynamic time sweeps was used for getting more insight into the kinetics of the equilibrium reactions taking place in the thermoreversibly cross-linked system at hand. From swelling tests, it was qualitatively shown that the equilibrium between the DA and rDA reaction shifts at every temperature. Dynamic time sweeps performed at different temperatures were used to determine the kinetic rate coefficients for the DA cross-linking and the rDA de-cross-linking reaction at several low and high temperatures, respectively. The resulting kinetic rate coefficients were fit to the Arrhenius equation to determine $k_0$ and $E_a$ of both reactions. These parameters were therefore used to determine the equilibrium constants at different temperatures and the change in enthalpy and the change in entropy of the reaction were determined using those. Finally, the activation energies and pre-exponential factors were used to generate the concentration of cross-links over time at different temperatures using the system of ordinary differential equations. $E_a$ was found to be $7.04$ kJ mol$^{-1}$, which is relatively low compared to values found in literature and suggests a diffusion limitation. $E_a$ was found to be $57.9$ kJ mol$^{-1}$, which is in line with values found in literature. These findings correspond with the generated concentration profiles that have a better fit with the experimental data for the rDA de-cross-linking reaction than for the DA cross-linking reaction. The most important conclusion that can be drawn from this work is that the rheological behavior of a material at different temperatures can be used to quantitatively characterize reversible cross-linking in the bulk, which is in striking contrast with spectroscopic methods that only provide information at the molecular level.

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References


