Depth-sensing Indentation
and High-Throughput Experimentation
on Polymers and Elastomers

PROEFSCHRIFT

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Depth-sensing Indentation  
and High-Throughput Experimentation  
on Polymers and Elastomers

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Chapter 1

Introduction to depth-sensing indentation and high-throughput experimentation

Abstract
Polymers and elastomers are extensively used in daily life. The large choice of possible monomers and polymer architectures results in a large variety of possibilities for the development of new materials. Also for elastomers, the number of variables in the cross-linking chemistry offers the opportunity to optimize the material performance. New polymers and elastomers can meet future or current material demands by offering a better trade-off between various properties such as elastic stiffness, strength, biodegradability and low production costs than can be achieved using conventional materials. Therefore, the research and development of new polymers is an ongoing and highly attractive field of research.

High-throughput experimentation (HTE) represents an experimental strategy that can be adopted to speed up the development of new polymeric materials and to manage the large number of parameters influencing the properties. This chapter reviews HTE-investigations into mechanical properties of polymers. A crucial element to the HTE-investigation is the matching of various HTE steps: The HTE-characterization should combine well with the synthesis and the sample preparation step, for instance in terms of the amounts of material needed. The total HTE-workflow should offer labor-extensive sample handling and characterization.

Depth-sensing indentation offers the opportunity to perform high-throughput screening of mechanical properties of polymers, as small amounts of material suffice and the technique allows convenient automation. The sample preparation for depth-sensing indentation can be performed by depositing the polymer from a solution. The requirements and the challenges for the preparation of suitable polymer films are discussed. HTE-equipment helpful to this deposition, as well as HTE-equipment for spectroscopic characterization, are described. In this chapter also the aim of the thesis is formulated.

Part of this chapter has been submitted for publication: J. M. Kranenburg, C. A. Tweedie, K. J. Van Vliet, U. S. Schubert, Challenges and progress in high-throughput screening of polymer mechanical properties by indentation.
1.1 Motivation

Applications for polymers and elastomers range from consumer goods, additives in paints, automobile parts, (smart) packaging materials and personal care products to biomedical applications such as degradable scaffolds.\(^{1a}\) This list could be extended with applications where mechanical properties are not that important, such as display components,\(^{1b}\) drug delivery systems\(^{1c}\) and surfactants. The mechanical properties required for the various applications span a large range. One illustration: the material stiffness ranges from 10 MPa for rubber sealants to 100 GPa for reinforcing polymer fibers.

Requirements to the materials, such as minimal use of supplies during production, solubility in environmentally friendly solvents,\(^{1d}\) mechanical stiffness, strength, toughness and degradability or recyclability at the end of the product life become more and more demanding. Furthermore, possible new applications will pose additional requirements. The variation in polymer building units, chain length and chain architecture has been expanded considerably by the ongoing progress in synthetic polymer chemistry. Due to these variations, also the phase-segregation behavior can be influenced. Tunability of the chemical and physical characteristics of the polymer opens the way to meet current and future requirements.

Research on structure-property relationships in polymer science is therefore both intriguing from the fundamental point of view, as well as important with respect to possible future application.

A promising and challenging approach for accelerated development of new materials, as well as for an efficient investigation of structure-property relationships\(^{2-4}\) is high-throughput experimentation (Section 1.3). For mechanical characterization in a high-throughput approach, depth-sensing indentation (Section 1.2) may be employed. Also outside such a context, depth-sensing indentation constitutes a helpful technique to investigate mechanical properties of (new) polymeric materials.

1.2 Depth-sensing indentation

In contrast to older indentation techniques such as Vickers, Brinell and Knoop hardness measurements, where the residual imprint after indenting the material of interest is measured, depth-sensing indentation is based on analyzing the load on an indenter probe and the displacement of that probe into the material of interest (Figure 1.1).\(^{5,6}\) The load and the displacement are recorded continuously during the indentation experiment. From these experimental data and knowledge of the indenter probe geometry, information on the mechanical properties of the material can be evaluated. Depth-sensing indentation (DSI) is also called instrumented indentation, or load and depth-sensing indentation. The displacements during indentation experiments range from several nanometers\(^{7}\) into the millimeter range.\(^{8}\) If indentation is conducted in order to probe the bulk material properties,
the maximum indentation depth has to be sufficient to sample a representative material volume.\textsuperscript{[9]} Related to the employed maximum indentation depths, alternative names for the technique are microindentation,\textsuperscript{[10]} ultra microindentation\textsuperscript{[11]} or nanoindentation.\textsuperscript{[6,12]} Strictly speaking, nanoindentation refers to DSI for which the maximum load or maximum displacement is less than 100 nN or 100 nm, respectively.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{load_displacement_response.png}
\caption{Load-displacement response obtained upon indenting polystyrene using a Berkovich indenter geometry.}
\end{figure}

DSI is a very suitable technique in the field of thin film or coating technology. Mechanical properties of thin polymeric or hybrid films deposited on a substrate, as well as mechanical property gradients within the film, can be investigated by indenting either on the surface of the film or along cross-sections of the film.\textsuperscript{[13,14]} In case the amount of material available for testing is limited, due to either limited material supply or prohibitive material cost, DSI is a suitable choice as well. Such limited availability of material may arise when it is convenient to produce only small amounts of new materials during classical chemical synthesis or during rapid analysis of new property correlations via combinatorial or high-throughput experiments.\textsuperscript{[15-17]} The high-throughput approach is discussed in more detail in the next section.

\subsection{1.3 High-throughput experimentation}

High-throughput experimentation (HTE) and combinatorial materials research in the field of polymer science aim to speed up the design and preparation of new materials as well as the elucidation of relations between structure, processing conditions and resulting properties.\textsuperscript{[2,3,18]} In a combinatorial experiment, a relatively large number of chemically distinct, but related, compositions are prepared and analyzed for their key properties.\textsuperscript{[4]} In order to improve the time efficiency, a combinatorial experiment is usually carried out using high-throughput
techniques, which enable the preparation and screening of multiple materials in a single experiment.\[4\] These multiple materials together are called a ‘library’. In order to minimize the amount of effort per sample, high-throughput techniques are usually highly automated, giving the potential advantage of reduced random variation in the results arising from, for instance, operator-variability.

Optimal understanding of the structure-property relationships present in the combinatorial library and optimal time efficiency can be realized by implementing the following steps in the combinatorial workflow:\[2\]

1. Design of experiment: to choose the experimental variables for the different members of the library such that the experiment maximizes the gained knowledge, while the number of members is kept to a minimum. Advanced methods exist to make use of prior knowledge to optimize the choices for the experimental variables.\[19\]

2. Automated (parallel) synthesis and/or formulation;

3. Deposition of the materials as thin films or as dots;

4. High-throughput investigation of those films or dots by spectroscopy, DSI, or other characterization methods;

5. Advanced data handling allowing facile visualization and/or mathematical description of the structure-processing-property relationships present in the dataset.\[20\]

After performing these five steps, one may use the obtained knowledge, the questions remaining and/or the new questions that rose during these steps to design the next combinatorial experiment.\[2\] Alternatively, one can ‘zoom in’ into a parts of the parameter space that showed interesting ‘leads’ or ‘hits’ to identify even more optimal results during a finer-meshed investigation into those parts of the parameter space.\[21,22\] Design of experiment (step 1), advanced data handling (step 5) and proper integration of all steps of the combinatorial workflow significantly improve the results of the experiment.\[20\] During combinatorial experiments, many different materials are prepared (step 2) at, generally, small amounts for each material. During high-throughput experiments, typically 100 mg (an example from a polyolefin catalyst optimization study by Boussie et al.\[22\]) to 500 mg (sequential robot-assisted cationic ring-opening polymerization by Hoogenboom et al.\[23\]) of polymer are synthesized. Therefore, high-throughput characterization techniques have to be capable of providing reliable information on the property of interest while using only small amounts of material.
1.4 HTE investigation of mechanical properties of polymers

Various HTE techniques are employed to screen the mechanical properties of polymers. One of these is indentation. Krupicka et al.\textsuperscript{[13]} investigated whether indentation and scratch testing are suitable tools to evaluate the performance of organic coatings. They found that in a limited time, reproducible data on indentation modulus, elastic recovery, and scratch depth was generated, and rupture could be identified, together with the load at which the rupture occurred. Such indicators may help in understanding coating performance such as mar resistance. Tweedie et al.\textsuperscript{[15]} synthesized, in triplicate, 576 unique polyacrylate compositions by printing 70:30 and 70:30 mixtures (by volume) of 24 different acrylates followed by photopolymerization (combination of steps 2 and 3). Each polymer spot weighed only approximately 1 µg. The 576 unique polymer compositions were subsequently tested by depth-sensing indentation (step 4) in 24 hours. The authors observed that the modulus obtained for the copolymers (Figure 1.2) was not always the value expected from the volume fraction and modulus of its pure constituents, because microstructural and phase changes influenced the stiffness, as well. HTE is a suitable technique to investigate the effect of such complex and not yet quantitatively understood factors on the resulting properties.

![Figure 1.2: Elastic moduli obtained for a polymer library with 576 members by automated indentation (reprinted from ref. 15).](image)

Simon et al.\textsuperscript{[17]} deposited a gradient library starting from two solutions, one containing poly(L-lactic acid) and the other containing poly(D,L-lactic acid). Subsequently, the composition as a function of location along the deposited film was verified by Fourier
transform-infrared spectroscopy, and also the stiffness was probed as a function of location, i.e., as a function of composition. A higher poly(L-lactic acid) content resulted in a higher crystallinity (as observed by polarized optical microscopy) and a higher modulus. Lin-Gibson et al.\cite{24} studied photopolymerization of dimethacrylate networks using 2-dimensional gradient samples varying in monomer composition and light exposure time. A good correlation was found between the conversion (determined by near-infrared spectroscopy) and the mechanical properties obtained by dynamic DSI measurements for the cross-linked networks.

Depending on the application one has in mind, the combinatorial experiment involves the screening of more than just the mechanical properties. Therefore, step 4 in the protocol mentioned above may involve several sub-steps. Anderson et al.\cite{16} screened a library for both bio-degradability and mechanical stiffness. The latter property was determined by DSI. They showed that it is possible to tune both properties independently. Brocchini et al.\cite{25} established relationships between the chemical structure of 112 distinct polyarylates and their properties such as glass transition temperature, air-water contact angle and cell proliferation, and subjected selected polyarylates to miniaturized tensile testing, as well. Such a combinatorial study not only helps to identify structure-property relations for complex and poorly understood phenomena such as cell adhesion, but also provides a large reference dataset that helps to identify the right material exhibiting the desired combination of properties.

Apart from indentation, other experimental approaches to high-throughput mechanical property investigation of polymers exist as well; Stafford et al.\cite{26} developed a method to obtain the elastic modulus of polymer films from the buckling wavelength of bilayers consisting of a stiff, thin polymer film with known thickness, coated onto a relatively soft, thick substrate. In case a composition gradient is present in the film, this technique provides the modulus as a function of composition.\cite{27} Another instrument for high-throughput mechanical characterization probes the force exerted by a clamped polymer membrane onto a pin.\cite{28} Discrete polymer samples were generated by clamping a temperature or composition gradient film between perforated plates and performing the experiment at each hole. This set-up allows for high-strain rate or low strain-rate testing by either letting the sample plate impact onto the pin, or moving it towards the pin using a motorized actuator (Figure 1.3), respectively. A film thickness of 25 µm and a hole diameter of 3 mm were reported,\cite{29} indicating that at least 200 µg of material is required for each library-member. In agreement with analytical modeling, the moduli obtained via this (biaxial) test are 35% higher than the uniaxial moduli for the same materials.\cite{28} The film buckling-method and the pin-on-film method both require a good control of the film thickness over relatively large distances or, at least, good knowledge on the film thickness as function of location.\cite{27,28} The sample-preparation for DSI seems less demanding. Furthermore, both methods start from a gradient library. Therefore, an accurate conversion from property as function of location, to property
as function of composition is necessary. The accuracy of this conversion, which was rather good for the materials investigated by Simon et al.,\textsuperscript{[17]} depends strongly on the (spectroscopic) technique used, and the spectra of the components in the library. For discrete libraries, the conversion from sample identity to composition is more straightforward.

Kossuth et al.\textsuperscript{[31]} measured the complex modulus of elasticity and the loss tangent for 96 samples with the 'standard' HTE format (8 × 12 samples, spaced 9 mm apart) in parallel. Polystyrene-block-polybutadiene-block-polystyrene was deposited on a polyimide substrate, and on each spot a pin imposed a displacement oscillation while the force was measured. The sample properties could be determined for a temperature range from −120 to 200 °C from the mechanical response of the sample-polyimide ‘composite’. Apart from a reproducibility study, also the specific softening of the polystyrene phase upon addition of a plasticizer, and the effect of tackifier addition was demonstrated. Parallel experimentation provides a potentially higher throughput than DSI, which is performed sequentially. However, the parallel approach did cause non-negligible variation in the modulus as a function of the location of the position on the sample-plate.\textsuperscript{[31]} Using the same probe for all the members of the HTE-library improves the sensitivity of the combinatorial experiment for variations in stiffness through the library. In this context it is noted that the testing rate attainable by DSI is sufficiently fast for most combinatorial experiments. For instance, Tweedie et al.\textsuperscript{[15]} reported testing 576 distinct polymers within 24 hours.

\textbf{Figure 1.3:} High-throughput characterization device for multiple clamped polymer films (reprinted from ref. 28).
1.5 Sample preparation

A convenient sample preparation method for indentation is to print or pipet a solution of the polymer onto a substrate and to dry the polymer subsequently. Usually, a stiff substrate such as glass is chosen\textsuperscript{[15,17]} to avoid extra compliance that needs to be corrected for. This approach allows the preparation of both discrete\textsuperscript{[15]} and gradient libraries.\textsuperscript{[17,24]} The deposited polymer spot or film needs to be thick enough. For too thin samples, the indentation load-displacement response and, therefore, the obtained material properties, will be influenced by the properties of the substrate, \textit{i.e.}, the ‘substrate effect’ occurs. Influence from the substrate on the obtained hardness can generally be ignored if the film thickness is more than approximately ten times the maximum indentation depth (the exact factor depends on the film and substrate properties\textsuperscript{[32-34]}), while for the elastic property a somewhat larger factor should be used as the elastic strain field extends deeper into the material than the plastic strain field.\textsuperscript{[35]} Models are developed to correct for the substrate influence if the thickness is precisely known\textsuperscript{[33,34]} but such corrections encompass a significant amount of extra work, namely measuring the thickness, repeating the indentation experiments to various depths and extra data-processing, that should be avoided during HTE experimentation.

Upon depositing films or dots from a solution, the so-called ‘coffee-drop effect’ may occur. This means that during drying, material collects at the rim of the spot, leaving only a thin film at the middle of the spot (Figure 1.4a).\textsuperscript{[36,37]} In the center, the film can be too thin to perform accurate measurements due to the substrate effect.\textsuperscript{[35]} Furthermore, extensive coffee-drop effect results in height variations on individual samples and between samples of the same library. This significantly increases the time necessary to program and perform a measurement run. Several approaches can be followed to decrease the coffee-drop effect:

- Using a mixture of two solvents with a difference in boiling temperatures and solubility with respect to the polymer (Figure 1.4),\textsuperscript{[38]}
- Increasing the polymer concentration in the polymer solution;
- Increasing the substrate temperature onto which the solution is dropcast or printed;
- Changing the substrate surface-energy,\textsuperscript{[37]} or confining the solution.

Another consideration relating to the sample preparation is that the surface should not be tilted, \textit{i.e.}, the sample surface should be perpendicular to the indentation axis. Actually, a moderate degree of coffee-drop effect may be beneficial, as in that case, indenting somewhat off the center of the drop results in a smaller tilt than if no coffee-drop effect occurred at all.
The removal of the solvent, including the high-boiling solvent that one may have used to optimize the dot shape (as discussed above), from the polymer dot is a crucial factor, as residual solvent may have a significant influence on the mechanical properties. Assurance that all solvent is removed can only be obtained if the sample is heated above the glass transition temperature of the polymer, although drying at temperatures below the glass transition temperature in vacuum will already suffice for thin films or dots deposited using low-boiling solvents. Depending on the solvent used, it may be necessary to perform the annealing above the boiling temperature of the solvent and/or in vacuum. The thermal treatment can influence the mechanical properties. Therefore, indentation and differential scanning calorimetry (DSC) experiments may be repeated to improve the understanding of the relation between molecular architecture, phase behavior and mechanical properties.

It should be realized that the effects of the same thermal treatment on the degree of crystallization, yield stress increase,\textsuperscript{39} removal of the solvent, etc. will vary within the library, as the distance of the annealing temperature to the crystallization temperature or the glass transition temperature differs for different library-members. Repeating the high-throughput experiment after multiple thermal histories opens the way to obtain structure-processing-property relationships for the materials studied.
1.6 Selected high-throughput techniques

This section describes three high-throughput instruments used for the work described in this thesis. A pipetting robot (Figure 1.5a) can be used to create mixtures of various starting solutions, or to dispense a solution containing a polymer onto glass slides. In particular for larger sets of solutions to be dispensed, a pipetting robot is more convenient than pipetting by hand. Furthermore, it offers in principle better positional accuracy than manual pipetting. For some polymer-solvent combinations, heating the substrate (Figure 1.5b) improved the thickness profile of the polymer dots remaining after drying (Figure 1.5c and d) due to the suppression of the ‘coffee-drop effect’ (Section 1.5). Several liquid handling systems, with various possibilities and options, are commercially available.[40-42]

![Figure 1.5:](a) The pipetting robot; (b) pipetting onto a heated glass slide; (c) thickness profile resulting for a PS-toluene solution pipetted at room temperature and at (d) 95 °C (dashed segments were too steep for the optical interferometry measurement). The higher substrate temperature reduced the ‘coffee-drop’ effect.
A Raman instrument suitable for HTE is shown in Figure 1.6. The spectrometer is equipped with an automated sample stage and software to measure multiple locations subsequently in one run. As this technique requires a monochromatic light source, Raman spectroscopy became more popular when lasers came available. Upon irradiation, a molecule is excited into a virtual state. Usually, relaxation to the ground state occurs, but a small fraction of the excited molecules relaxes to a different vibrational energy state. Relaxation to the ground state is called ‘Rayleigh scattering’ and gives radiation of the same wavelength as the source. Relaxation to a different state results in scattered light with a (usually) lower energy than the incident light. The energy difference is the Stokes shift. Raman spectra show the intensity of the scattered light as a function of this energy difference. The vibrational energy range probed by Raman spectroscopy and by infrared spectroscopy overlap. In contrast to infrared spectroscopy, Raman spectroscopy is in particular sensitive to apolar molecular vibrations that cause a change in polarizability, while infrared spectroscopy is especially sensitive to vibrations that cause a change in the polarity.

![Figure 1.6: A Raman instrument equipped with a stage and software that facilitate high-throughput experiments; a thin aluminum sheet serves to fix the (cured elastomer) samples at specified locations.](image)

The depth-sensing indentation instrument used for most of the experiments in this thesis is shown in Figure 1.7a. Various tip geometries can be mounted to the transducer, such as a conospherical indenter (Figure 1.7b) or a Berkovich. The transducer (left in Figure 1.7a) is capable of accurately applying loads as small as several μN (load noise floor is ~0.1 μN) up to 10 mN. The indentation depths used in the current work ranged from 50 nm up to several μm, but both smaller and larger indentation depths are accessible as well. The load and displacement noise floor and range depend on the transducer. A second transducer was used, as well, that offered the possibility to apply a force oscillation on top of the quasistatic load. From the resulting displacement oscillation and the phase lag between both, visco-elastic properties can be obtained. Furthermore, the residual indents can be imaged by scanning the indenter tip over the surface. An overview of commercially available indenter systems with their specific possibilities can be found in ref. 35.
A custom-built sample stage was used, where vacuum could be applied under the substrates to ensure low compliance between the slides containing the samples and the stage (Figure 1.7a). In total, ten sample slides could be located on this sample stage.

![Figure 1.7: (a) The depth-sensing indentation system used for most of the indentation experiments in this thesis; the transducer with the indenter probe is located at the left, the top-down optics to select the measurement locations is located at the right; the vacuum lines in the sample stage are visible below the glass slides; (b) scanning electron microscopy image of the conospherical indenter tip that was used for part of the work described in the thesis.](image)

### 1.7 Scope and outline of this thesis

The work described in this thesis aims to investigate mechanical properties of polymers and elastomers using high-throughput experimentation concepts. In order to understand the relations between structure, processing and mechanical properties of the materials studied, their molecular characteristics, phase behavior and other relevant properties were to be examined as well. Furthermore, the relatively small-scale measurement techniques employed in this thesis for HTE characterization are also very well-suited for the investigation of materials that are synthesized in small amounts only, as well as coating systems that are deposited as thin layers. Therefore, investigations on these (co)polymers are included in this thesis as well.

The thesis starts with reviewing the molecular origins of mechanical properties of polymers, as well as the analysis methods employed to obtain mechanical properties from the DSI experiment. Factors influencing the obtained mechanical properties of polymers are identified. Subsequently, chapter three presents a HTE study on the elastic properties of copoly(oxazoline)s. Poly(oxazoline) chemistry offers the opportunity to control the side-group and the chain-length distribution, as well as to prepare block copolymers. Because of this, tailoring material properties, such as solubility in environmentally friendly solvents, surface energy and material stiffness is feasible and poly(oxazoline)s may be used for several new applications. The chapter reports a systematic study on the influence of the side-group
attached to the oxazoline units and the side-group distribution along the polymer chain on the mechanical properties.

The size of the probed volumes makes DSI well-suited for mechanical testing of compounds that, in the early research stage, are synthesized in small amounts only. This is the case for the supramolecular materials investigated in chapter four of this thesis. The current interest in this new class of materials stems from the ability of the supramolecular interactions to incorporate interesting optical, responsive as well as self-repairing properties into the material.

Chapter five of the thesis describes an HTE-sample preparation approach for elastomer materials. Furthermore, the applicability of Raman spectroscopy and DSI as tools to quantify the conversion of reactive sites and the cross-link density of ethylene-propylene-diene rubber (EPDM), respectively, are discussed. For EPDM prepared without fillers, a good correlation was found between indentation depth at fixed loading conditions and Shore A hardness, which is a common industrial measure for the material hardness.

Exposure of coatings and paints to sunlight and humidity results in chemical changes of protective and decorative organic coating materials. These chemical changes influence the mechanical properties, and finally lead to failure (cracking, delamination) of the coating. The investigated polyester coatings exhibited an increase of the hardness when exposed to UV light. The increases in hardness could be related to the ageing conditions, and to the chemical changes in the material (polar group formation, chain-scission and cross-linking reactions) that were observed with infrared spectroscopy, gel permeation chromatography and gel fraction measurements.

1.8 Abbreviations and symbols used in this thesis

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<tr>
<th>Abbreviation</th>
<th>Symbol</th>
<th>Definition</th>
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<tr>
<td>AFM</td>
<td></td>
<td>atomic force microscopy</td>
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<tr>
<td>BPPB</td>
<td></td>
<td>bis(t-butylperoxy-i-propyl)benzene</td>
</tr>
<tr>
<td>BPPB MB</td>
<td></td>
<td>bis(t-butylperoxy-i-propyl)benzene masterbatch</td>
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<tr>
<td>DSI</td>
<td></td>
<td>depth-sensing indentation</td>
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<td>DSC</td>
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<td>differential scanning calorimetry</td>
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<td>EPM</td>
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<td>ethylene-propylene rubber</td>
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<tr>
<td>EPDM</td>
<td></td>
<td>ethylene-propylene-diene rubber</td>
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<tr>
<td>EHe</td>
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<td>poly(2-(3-ethylheptyl)-2-oxazoline)</td>
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<td>Et</td>
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<td>poly(2-ethyl-2-oxazoline)</td>
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<td>FT-IR</td>
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<tr>
<td>Non</td>
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<td>poly(2-nonyl-2-oxazoline)</td>
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Chapter 1

phr  parts per hundred parts rubber, i.e., grams per 100 g rubber
PBA  poly(butyl acrylate)
PC  polycarbonate
PDI  polydispersity index
PDM  $N,N'$-m-phenylene dimaleimide
PEG  poly(ethylene glycol)
PNI  poly(neopentyl-isophthalate)
PNT  poly(neopentyl-terephthalate)
PS  polystyrene
POM  polarized optical microscopy
Phe  poly(2-phenyl-2-oxazoline)
TAC  triallyl cyanurate
TGA  thermal gravimetric analysis
UV  ultraviolet

$A_c$  contact area
$\varepsilon$  strain
$E_r$  reduced modulus
$E_i$  modulus of elasticity obtained by indentation
$E$  Young’s modulus (modulus of elasticity obtained via standardized macroscopic measurements such as uniaxial tensile testing)
$H$  hardness
$h$  displacement
$h_c$  contact depth
$h_{max}$  maximum indentation depth
$M_n$  number averaged molar mass
$P$  load
$S$  slope at the start of the unloading

1.9 References


Introduction to depth-sensing indentation and high-throughput experimentation


[38] P. J. Lyon, J. C. Carter, J. C. Bright, M. Cacheiro, WO Patent 02(069119) A1, **2002**.
Chapter 2

Mechanical properties of polymers

Abstract
The standards for the measurement of mechanical properties are set by macroscopic tests. This chapter highlights the challenges involved in obtaining various mechanical properties of polymers (elastic modulus, yield stress, creep parameters, etc.) by indentation. Several approaches for the analysis of depth-sensing indentation data, such as the ‘Oliver and Pharr’ and the ‘Field and Swain’ protocol, and dynamic indentation analysis, are discussed together with their limitations.
The molecular origin of the mechanical properties of glassy polymers is discussed as well. Furthermore, influences of the processing of the materials on the material properties, notably the yield stress, are briefly described in order to identify potential influences from the sample preparation on the indentation results.

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2.1 Elastic modulus

The modulus of elasticity of materials, also called E-modulus or Young’s modulus, describes the material stiffness at small strains or the resistance of the material to reversible deformation. The Young’s elastic modulus is defined as the initial slope of a stress-strain diagram obtained during a uniaxial tensile test. Polymers are viscoelastic, meaning that the elastic properties depend on the time of observation and time of loading, but the initial or rapid response of polymers is often still characterized by an elastic modulus. The Young’s elastic modulus of glassy polymers is governed principally by inter-chain interactions.\cite{1} Usually the relatively weak Van-der-Waals interaction is the most important inter-chain interaction, and the resulting Young’s elastic modulus of glassy polymers typically ranges from 2.5 to 4.5 GPa.\cite{2} Extensive thermal annealing may result in local rearrangement of small parts of the macromolecule and, therefore, in a slight increase of the inter-chain interactions and, thus, in the modulus of the elasticity.\cite{3} However, such changes are usually not so large that editors of standard data tables on elastic moduli of glassy polymers would include the thermal history information.\cite{4,5}

The relations between contact load and displacement for flat-punch, spherical or conical indenters into a linear-elastic solid were derived by Boussinesq, Hertz and Sneddon.\cite{6-8} For a flat punch, a sphere (with a radius much larger than the indentation depth) and a cone (or Berkovich, which is a pyramid with a triangle as a base and a center to face angle of 65.3° \cite{9}), the force and the displacement are related by a simple power-law relation with the pre-factor depending on the Young’s elastic modulus and the geometry, and the power depending also on the indenter geometry.\cite{9} Therefore, for linear-elastic materials not showing any plasticity, $E$ can be evaluated when the load and displacement are measured and the indenter geometry is known.

Based on load-displacement relationships derived by Sneddon, Oliver and Pharr developed an analysis method to obtain the Young’s elastic modulus from the indentation experiment that is well suited for elastic-plastic materials.\cite{10-12} This analysis method is widely applied in the HTE-studies employing DSI\cite{13,14} as it offers facile, HTE-compatible data handling. In this analysis, the reduced modulus $E_r$ is calculated from the stiffness at the onset of the unloading $S$ and the projected area of contact between the probe and the material $A$. (The coefficient $\beta$ is related to the indenter geometry, and is slightly larger than 1.\cite{11})

$$E_r = \frac{\sqrt{\pi}}{2\beta} \cdot \frac{S}{\sqrt{A(h_c)}} \quad (2.1)$$

The area of contact depends on the contact depth $h_c$ which is calculated as shown in Figure 2.1. The initial unloading slope $S$ is obtained by fitting the unloading load-displacement response. The fit function, and the relation of the parameters $m$ and $\varepsilon$ to the shape of the indent, are discussed elsewhere.\cite{11,12,15,16} As elastic displacements occur both in the specimen
Mechanical properties of polymers

(with modulus of elasticity $E_{\text{sample}}$ and Poisson’s ratio $\nu_{\text{sample}}$) and in the indenter, the elastic modulus of the sample is therefore calculated from $E_r$ using:

$$E_{\text{sample}} = \left(1 - \nu_{\text{sample}}^2\right) \left(\frac{1}{E_r} - \frac{1 - \nu_{\text{indenter}}^2}{E_{\text{indenter}}^2}\right).$$  \hspace{1cm} (2.2)

Figure 2.1: Load-displacement response obtained upon indenting polystyrene with a Berkovich indenter, showing the fit applied in the Oliver & Pharr method to obtain the slope $S$ at the onset of the unloading step. $P_{\text{max}}$ and $h_{\text{max}}$ are the load and indentation depth just prior to unloading, respectively.

For polymers, the modulus obtained by the Oliver and Pharr method is significantly higher than the macroscopic Young’s elastic modulus: the reported differences range from 70% for polystyrene (PS) and polycarbonate (PC),\cite{17} to 67% for polymethyl methacrylate (PMMA) and 46% for PC\cite{18} to 20% for poly(benzocyclobutene)\cite{16} (all using a Berkovich indenter). Several factors contribute to the discrepancy between $E$ obtained by the Oliver and Pharr method and the macroscopic Young’s elastic modulus:

- The Oliver and Pharr analysis assumes that the unloading is elastic,\cite{10} while viscoelasticity applies for polymers. An additional complication is the non-linearity of the visco-elastic deformation that occurs when polymers are strained to above 1 to 2%.\cite{16,19} Experimentally, one observes that when the indent is reloaded directly after the unloading, the reloading does not coincide with the unloading response, indicating that the unloading is not simply elastic. The slope of the load-displacement response at the onset of unloading is higher than at the end of the reloading.
- The creep influences the obtained $S$, and thereby $E$ (Equation 2.1). Procedures are proposed to correct $S$ for the creep rate based on the creep rate prior to the
unloading.\cite{15,20} For polymers, quick unloading is recommended to ensure that the unloading is predominantly elastic.\cite{21}

- In the Oliver and Pharr procedure, also \( A_c \) depends on the initial unloading slope \( S \), see Figure 2.1. As different unloading rates result in different \( S, A_c \) (which should depend on what happened prior to the unloading) mathematically depends on the unloading itself. Cheng \textit{et al.}\cite{21} proposed an approach to calculate \( h_c \), and thus \( A_c \), from the maximum displacement \( h_{\text{max}} \) only. However, that procedure requires that the (visco-)elastic deformation is linear and that no plastic deformation occurs.\cite{21}

- At the indent perimeter, material may pile-up. This results in a larger contact area \( A_c \) than inferred from the Oliver and Pharr procedure. As a consequence, a too low \( A_c \) is used in the calculation and \( E \) is overestimated (Equation 2.1). For elastic-plastic materials it was shown that the Oliver and Pharr method underestimates the real contact area significantly if the material has a low yield stress compared to the elastic modulus, and has little or no capacity to work-harden (in this calculation, no strain softening prior to the strain hardening was incorporated in the model while that often occurs for polymers, see Section 2.4). As the yield stress, the strain softening and the strain hardening (see below) may vary throughout a HTE-library, the ratio between the real projected contact area and \( A_c \) obtained by the Oliver and Pharr method may also vary to some extent. In extreme cases, this might even obscure the trends in elastic properties within the HTE-library; therefore, it is advisable to image some of the residual indents by AFM or by scanning the indenter over the indented surface. Based on the ratio of the final depth to the maximum indentation depth, Tranchida \textit{et al.}\cite{17} expected the influence of the pile-up on \( E \) to be modest for most glassy polymers.

- A last factor is that for shallow indents (up to 100 nm) the Young’s elastic modulus may differ from the bulk due to confinement effects.\cite{22} If a material is compressed in one direction, it expands in the orthogonal directions. Impeding that expansion may increase the material’s resistance to deformation up to 35%, 60% or 114% for a material with a Poisson’s ratio of 0.3, 0.35 or 0.4, respectively.\cite{17} The shallower the indent, the more effective this impediment may be, due to intrinsic length scales of the material such as the chain length.\cite{22} For HTE-experiments, this confinement effect is an undesired complicating factor. In some non-HTE studies, however, this effect may constitute an opportunity to study polymer chain dynamics, which may result in nano-structured materials with improved properties.\cite{22}
From the loading branch of the load-displacement response obtained with a flat punch indenter (Figure 2.2), $E$ can be derived in a way that circumvents some of the problems mentioned above.\cite{23} This probe geometry has the advantage that the contact area is constant and independent of the indentation depth, that no assumptions on the contact perimeter are required and that, initially, plasticity is negligible.\cite{23} Unfortunately, this geometry is very sensitive to tip-sample misalignment: $1^\circ$ misalignment results in approximately 10% difference in $E$. It is possible to minimize the misalignment.\cite{23} However, performing an alignment procedure for all members of the HTE-library is time-consuming and is therefore not HTE-compatible.

The Field & Swain method is another approach to obtain $E$.\cite{24} In this method, which has also been used in a HTE context,\cite{25} indentation experiments are performed using a relatively large radius sphere. The method assumes elastic or elastic-plastic material behavior and makes use of partial unloading. The load and displacement before and after partial unloading are analyzed using a modified version of the Hertz equation. Due to the relatively large radius of the sphere, linear visco-elasticity can be assured relatively easily. The Field & Swain method is numerically not as sensitive to errors in initial surface detection as the original Hertz analysis.

Other approaches modified the Hertz or Boussinesq analysis to account for the viscous response, and determine both the initial elastic modulus and the material viscosity from the loading response of the material.\cite{18,26-28} This allows studying the time-dependent polymer properties.
2.2 Creep and relaxation properties

Visco-elasticity (or visco-plasticity) is often probed by applying a constant load and measuring over a long time period the deformation of the test specimen.\cite{29} A simplified mathematical description of the displacement increase with time can be obtained by the Voigt or Kelvin model, which consists of a spring and a dashpot in parallel.\cite{1,29} Alternatively, one could impose a sudden uniaxial deformation and measure the stress, which will decrease with time due to relaxation of the polymer chains. The Maxwell model, consisting of a spring and a dashpot in series, provides a simple description for this stress decrease.\cite{1,29} Other models exist that describe the creep and relaxation behavior more accurately at the expense of using more parameters.

To determine visco-elastic properties, typically a flat punch\cite{26,28} or a large radius spherical indenter\cite{19,28,27} is used in order to prevent plasticity and non-linear elasticity, although also studies were conducted using a Berkovich indenter.\cite{18,30,31} The latter indenter geometry causes higher strain levels, as discussed in Section 2.4. Apart from analytical approaches to discriminate between viscous, elastic and (visco-)plastic deformation,\cite{28,30,31} numerical approaches are developed as well.\cite{3,21,32} Another challenge for obtaining visco-elastic and visco-plastic properties from indentation creep or relaxation experiments originates from the (thermal) drift in the experiment, which could become a significant error source during lengthy experiments. Furthermore, for larger tip radius (chosen to avoid non-linearity and plasticity), the measurement becomes more sensitive to tip-sample adhesion, surface roughness and surface detection uncertainties.\cite{9,33}

Good agreement was found between the time-dependent relaxation modulus $G(t)$ and Poisson’s ratio $\nu$ determined by microindentation (in combination with strain measurements) and by uniaxial test for PMMA and epoxy,\cite{28} while less good agreement was observed for experiments performed with ‘sharper’ indents due to non-linear deformation behavior.\cite{33}

2.3 Loss tangent and storage modulus

When an oscillating force or displacement is imposed on a material, the imposed mechanical energy is partly dissipated and partly stored. The first response is typical for a fluid, while the latter is typical for an elastic solid. The loss tangent indicates the ratio between both responses.\cite{1,2,29} Superposing a small oscillation to the quasistatic load or displacement profile (‘dynamic DSI’), allows extraction of frequency-dependent visco-elastic properties.\cite{9,34} It is noted that in most dynamic indentation analysis protocols, the contact depth, and thus the contact area, is calculated from the ‘stiffness’ (the ratio of the load amplitude to the displacement amplitude) measured during the oscillation.\cite{9} As this stiffness depends on the frequency, the contact depth mathematically depends on the frequency, which is not physically true.\cite{35} This issue was already addressed in Section 2.1 on the elastic modulus. In
addition, the dynamic DSI loading conditions differ from those in standard macroscopic rheological techniques.[36] Nevertheless, the storage modulus derived from dynamic indentation matches its macroscopic counterpart reasonably well, as observed for PMMA and two types of PDMS.[36]

In contrast to the storage modulus, the loss tangent obtained by dynamic DSI is not dependent on the contact area and therefore not affected by inaccuracies in the contact depth determination.[37] Hayes et al.[37] established a mastercurve for the loss tangent by dynamic indentation, making use of the time-temperature superposition principle. The glass transitions of poly( cyanurate) and epoxy resin obtained from these mastercurves were in agreement with the glass transitions found by DMTA at the same test frequency (Figure 2.3).

![Figure 2.3: The glass transition temperature of an epoxy resin, as identified by a peak in the loss tangent during dynamic mechanical thermal analysis (DMTA), correlated well with that identified by dynamic indentation (reproduced from ref. 37).](image)

### 2.4 Yielding, strain softening and strain hardening

Yielding of a glassy polymer can be considered as mechanically passing the glass transition: the polymer segment mobility is increased due to the applied mechanical stress.[38] In analog to the time-temperature correspondence that states that at a shorter time-scale, i.e., a higher test frequency, one finds a higher $T_g$, also a time-load correspondence (a higher strain rate results in a higher yield stress)$^{[38-40]}$ and a temperature-load correspondence (a higher temperature results in a lower yield stress)$^{[40,41]}$ exist.

The magnitude of the yield stress depends on the thermal history of the sample (Figure 2.4). A long thermal treatment just below the glass transition induces local rearrangement of small parts of the macromolecule, thereby increasing the inter-chain interactions and thus increasing the yield stress. Compressive testing can be used to study the stress and strain behavior of the material beyond the yield point, as, in contrast to tensile testing, localization of the
deformation phenomena is minimized.\textsuperscript{[42-44]} As the load-displacement response and the contact area development during the indentation experiment depend on the yield stress, the strain softening and the strain hardening,\textsuperscript{[3]} several findings from uniaxial compression tests combined with modeling are summarized here:

- After yielding, the polymer often shows a stress decrease (strain softening), followed by a stress increase (strain hardening). This strain hardening originates from the resistance to deformation of the entanglement network.\textsuperscript{[42]}
- The yield stress can be quantitatively described as a function of the annealing time and temperature. Mechanical rejuvenation, for instance by cold rolling, erases the thermomechanical history of the material and reduces the yield stress, sometimes even so much that after yielding the material does not strain-soften.\textsuperscript{[39]}
- For larger plastic strains, the relation between stress and strain does not depend on the thermal history (as long as the thermal history was not so rude that it caused cross-linking or degradation). Therefore, the strain softening guides the stress-strain curve from the yield point to the same strain hardening curve for all thermal histories.
- The strain hardening relates to the entanglement density.\textsuperscript{[42,44]} A material with a low entanglement density (many repeat units between entanglements, \textit{e.g.}, polystyrene) exhibits less strain hardening than a material with a higher entanglement density (\textit{e.g.}, polycarbonate).

\textbf{Figure 2.4:} Compressive stress-strain curves for polycarbonate. The yield stress and the amount of strain softening after yielding strongly depend on the thermal history of the sample (reproduced from ref. 44).
Yielding occurs when the stress and the strain exceed critical values. The typical strains during the indentation experiment for various indenter geometries can be assessed using the representative strain $\varepsilon_{\text{repr}}$ as a rough descriptor. For conical indenters, the representative strain depends on the effective cone angle $\alpha$. A sharper cone induces higher strains in the sample material.[9]

$$\varepsilon_{\text{repr}} = \frac{0.2}{\tan \alpha} \quad (2.3)$$

A Berkovich indenter results in a moderate representative strain level of approximately 8%.[9] Considering that typical strains at yield for glassy polymers range from 1 to 8%,[5] plasticity occurs right from the start of the indentation experiment for Berkovich indenters. For spheres with radius $R$, a representative value for the strain is[9]

$$\varepsilon_{\text{repr}} = 0.2 \frac{a}{R} \quad (2.4)$$

where $a$ describes the radius of the circle of the tip-sample contact perimeter. With increasing load, the contact radius and, thus, the contact strain increase. Therefore, plasticity sets in gradually for indentations performed with a spherical indenter. For flat punch indentations, the transition from (visco-)elastic to (visco-)plastic deformation shows up as a sudden decrease in the slope of the load-displacement response (Figure 2.2). With increasing yield stress, this bending of the loading response occurs at higher indentation load and displacement, and the slope of the post-yield branch of the loading curve is increased.[3]

The yield stress of glassy polymers is not (yet) easily deducible from the indentation data via simple equations. Via (non-HTE) finite element modeling employing an elastic-viscoplastic material model, Pelletier[3] found a good agreement between experimental and modeled load-displacement responses for the loading step of indentation experiments for flat punch and spherical indentations on polycarbonate with different yield stresses. For experiments employing a spherical indenter, a slightly larger contact area was found, both experimentally and by modeling, for shallow indents on the polycarbonate with the lower yield stress, as more plasticity takes place. For deeper indents, the contact area was somewhat smaller for the low yield stress material, due to larger strain softening (that causes pile-up) for the high yield stress material.[3]

### 2.5 Hardness

The hardness is a measure for the resistance to local deformation of a material. The hardness of the material depends on a combination of the elastic modulus, yield strength and strain-hardening capacity of the material.[45] Various hardness measurement methods exist: the Shore hardness, which is developed for elastomers and soft polymers, is calculated from the penetration depth of a spring-loaded indenter,[46] while the Rockwell hardness (usually applied for ‘harder’ plastics such as nylon, polycarbonate and polystyrene) is calculated from
the depth of the residual impression.\textsuperscript{[45,47]} For Shore and Rockwell hardness tests, various scales exist employing different loads and indenter geometries. The Vickers and Brinell hardness are calculated from the lateral dimensions of the residual impression, that are measured by optical microscopy after removing the indenter.\textsuperscript{[45]} The Vickers geometry is a pyramid with a square as the base plane, while in the Brinell experiment a 10 mm diameter spherical indenter is used.\textsuperscript{[45]} The Berkovich indenter, which is often used in depth-sensing indentation, has a triangle as the basal plane and opening angles such that its ratio of projected area $A_c$ to depth $h_c$ is the same as for the Vickers probe.\textsuperscript{[9]} The Berkovich probe is more suited for small-scale indentation, as a three-sided indenter allows better convergence to a point at the tip apex, while a four-sided Vickers probe in practice converges to a line.\textsuperscript{[9]}

The mean contact pressure at the onset of unloading in the DSI experiment is often taken as a measure of the hardness $H$ of the material. It is calculated from the load at the start of the unloading $P_{\text{max}}$ and the total projected contact area $A_c$ (which is obtained from the contact depth $h_c$ and the indenter shape): \[
H = \frac{P_{\text{max}}}{A(h_c)} \quad \text{(2.5)}
\]

For metals, usually a good correlation exists between Brinell\textsuperscript{[48]} or Vickers\textsuperscript{[49,50]} hardness and either the yield-stress or the tensile strength, thus presenting the hardness as a measure for plasticity. The hardness of polymers obtained by DSI, however, does not reflect the resistance to plastic deformation only, but is substantially influenced by the elastic deformation.\textsuperscript{[51]} The hardness is not a real material property for polymers and depends strongly on the loading history.\textsuperscript{[35,52]} Visco-elasticity influences the measured hardness: elastic deformation that does not recover quickly enough upon unloading results in a higher contact depth $h_c$ and, thus, a higher contact area $A_c$, thereby reducing the hardness $H$ (Equation 2.5). However, in a relative sense, this metric can be used to compare different polymers.

## 2.6 Various considerations on DSI on polymers

By imaging the indented surface using the indenter probe or using an AFM mounted on the indenter system, topographic information can be obtained. Such topographic information provides the opportunity to obtain more parameters or better quality parameters from the indentation experiments.\textsuperscript{[53]} For instance, insight in the surface tilt or the amount of pile-up helps to evaluate the quality of the obtained elastic modulus. The drawback is, of course, that this imaging step greatly reduces the experimental throughput.

Another consideration regarding indentation on polymers relates to orientation and (semi-)crystallinity. The crystallites in semi-crystalline polymers are anisotropic: their properties differ for the various crystallographic directions. If the crystallites are small (compared to the length-scale of testing) and distributed as well as oriented randomly, the overall material is still isotropic. In this case, the stiffness obtained by DSI still provides a
suitable average for the elastic property of the material. However, some processing steps (e.g., extrusion) can introduce orientation. For materials exhibiting orientation, indentation can be combined with post-test imaging to study the degree of orientation. However, some of the standard analysis methods may be inaccurate, as they assume an isotropic mechanical response.

If the indentation experiments are performed under load control conditions, the same load function results in differences in the unloading rate (nm/s) and in the indentation contact depth between various members of the HTE-library investigated. If experimental factors, such as the unloading rate$^{[54,55]}$ or indentation contact depth$^{[56]}$ cause variation in the obtained results, this variation should end up in the standard deviation describing the uncertainty in the obtained property for each library member, rather than as a difference between library members. This can be ascertained by performing the experiment employing several maximum loads $P_{max}$.

In case indentation is used for HTE testing of ‘bulk’ polymer properties, it is recommended to indent more than 100 nm into the material, as in this case the response originating from the top 10 nm of the polymer film, which is reported to have a different $T_g$$^{[57]}$ and different mechanical properties$^{[22,58]}$ is minimized. An extra advantage of not using very shallow indents is that the initial surface detection ($h_0$) and the tip apex defect become less critical as well.

### 2.7 Conclusions

A short introduction into mechanical properties of polymers, their molecular origins and common mechanical tests was presented. The applicability and versatility of DSI to probe mechanical properties of polymers was discussed. The discussion in this chapter provides a background to evaluate the accuracy of the obtained results. Convenient HTE-compatible DSI analysis protocols are available to obtain the elastic properties of polymers. Due to pile-up, non-linear elasticity, visco-elasticity and other factors discussed in this chapter, the material stiffness obtained for polymers by DSI is somewhat higher than the modulus of elasticity obtained by macroscopic testing. Also the loss tangent can easily be obtained by DSI, and the storage modulus matches better with the macroscopic counterpart than expected from theoretic considerations.
2.8 References

Mechanical properties of polymers

Chapter 3

An HTE study of the elastic properties of poly(2-oxazoline)s

Abstract

Using depth-sensing indentation, the elastic moduli $E$ of 2-oxazoline copolymers were investigated in order to establish structure-property relationships. The adopted experimental procedure, dropcasting of the copolymer materials followed by depth-sensing indentation, could be incorporated into a high-throughput experimentation workflow. The elastic modulus of the investigated materials depended strongly on the side-group. Materials containing poly(2-nonyl-2-oxazoline) exhibited a lower modulus than materials without any poly(2-nonyl-2-oxazoline) block as poly(2-nonyl-2-oxazoline) is at room temperature above its glass transition temperature $T_g$, while the other homopolymers in this study are glassy at room temperature. The elastic modulus also depends on the relative humidity (RH) of the testing environment; the stiffness of poly(2-ethyl-2-oxazoline) and poly(2-methyl-2-oxazoline) decreased significantly due to water absorption from the air. At lower RH, hydrogen bonding or polar interactions among the polymer chains resulted in a surprisingly high modulus for the poly(2-methyl-2-oxazoline). In addition, the elastic moduli of AB diblock copolymers were bounded by those of the A and B homopolymers, both at high and at low RH. Furthermore, the elastic moduli of ABA triblock copolymers were between those of the respective AB diblock copolymers and A homopolymers, at constant total degree of polymerization. The elastic moduli of these copolymers depended on the interplay between phase-separation, crystallization and hygroscopicity, and can be adjusted by tailoring the composition. Variation in polymer architecture, i.e., monomer distribution over the polymer chain, resulted in different phase segregation behavior and different transition temperatures. This was shown for 2-ethyl-2-oxazoline:2-nonyl-2-oxazoline block and random copolymers by differential scanning calorimetry (DSC). The observed elastic moduli and loss tangents, which differed considerably between random and block copolymers with identical overall chemical composition, were well explained by the phases identified through DSC.


Chapter 3

3.1 Introduction

A large number of differently substituted 2-oxazolines that are well-suited monomers for living cationic ring-opening polymerizations can be prepared relatively easily, by reacting nitriles with 2-aminoethanol.[1,2] ‘Living’ polymerization implies that the growth of all polymer chains starts at the same time, that all polymer chains grow with uniform speed and that chain transfer reactions, terminating reactions, as well as other side-reactions are absent. Therefore, the molecular weight distribution of the resulting polymer is narrow. Furthermore, the reaction centers remain active after the complete consumption of the first type of monomer, allowing the subsequent incorporation of a second or a third type of monomer into the polymer chains. Thus, diblock or triblock copoly(2-oxazoline)s with a narrow molecular weight distribution can be obtained in a multi-step procedure. A schematic representation of the cationic ring opening polymerization is given in Scheme 3.1.

Recently, it was shown that the long reaction times for the polymerization of 2-oxazolines, which has often been a major concern in this research area, can be reduced by performing the reactions at higher temperatures.[3-5] Utilizing 2-methyl-, 2-ethyl-, 2-nonyl- and 2-phenyl-2-oxazoline as monomers, a 16-membered library of 12 diblock copolymers and 4 chain-extended homopolymers was synthesized in a microwave reactor.[3] Also triblock copolymers[6] and ethyloxazoline:nonyloxazoline block and random copolymers[7] were synthesized with the same total degree of polymerization. Nearly all of these compounds showed only slight deviations from the targeted composition, and had narrow molecular weight distributions, as indicated by the polydispersity index (PDI) being smaller than 1.2. Differential scanning calorimetry (DSC) demonstrated that the glass transition temperature \( T_g \) of these materials depended on the side group,[3,6,7] as will be discussed in more detail later in this chapter. The surface energy, determined by contact angle measurements of diiodomethane and ethyleneglycol droplets on spin-cast films of these copolymers, was 43 to 46 mN/m if the polymers did not contain any poly(2-nonyl-2-oxazoline).[8] For polymers that contained (at least) one block of poly(2-nonyl-2-oxazoline), the surface energy was lower (19 to 23 mN/m). In agreement with other work,[9-11] this lower surface energy was attributed to segregation of the nonyl side-chains to the surface.[8] Atomic force microscopy (AFM) imaging of spin-cast
films demonstrated a higher roughness if the polymers contained at least one block of poly(2-nonyl-2-oxazoline), as compared to films without any poly(2-nonyl-2-oxazoline), which could be related to crystallization of the nonyl side-chains at the surface.\textsuperscript{[12]}

The synthesis, the thermal characterization as well as the surface energy measurements of the library of diblock copolymers were performed in a manner compatible with high-throughput experimentation.\textsuperscript{[3,8]}

The control over the molecular weight, the side groups, and side group distribution within the chains, which is typical for these polymers and this synthesis method, provides tunability of the physical properties. Additionally, this control over molecular structure and the narrow molecular weight distribution make them suitable materials to study quantitative structure-property relationships. In view of potential application of poly(oxazoline)s as, \textit{e.g.}, active component in hair dressing formulation or impregnant for paper or textiles,\textsuperscript{[13-15]} the mechanical properties deserve to be studied, as well. Until recently, the study of the mechanical properties of poly(oxazoline)s has been limited to peel tests that use mechanical force to separate a film from the underlying substrate,\textsuperscript{[9,16,17]} as well as a few rheological measurements of complex shear moduli,\textsuperscript{[18]} dynamic mechanical analysis, and uniaxial tensile tests of freestanding films.\textsuperscript{[19]} For poly(2-ethyl-2-oxazoline), the brittleness of the material impeded obtaining the mechanical properties.\textsuperscript{[19]}

In this chapter, $E$ of copoly(oxazoline)s is studied using depth-sensing indentation and structure-property relationships are discussed. As the relative humidity (RH) of the testing environment influenced $E$, measurements were repeated on selected materials at three RH levels. The current study expands the applicability of depth-sensing indentation for high-throughput experimentation by combining the freedom in the selection of the starting materials in the approach of Tweedie \textit{et al.}\textsuperscript{[20]} with the concept of preparing the samples from a polymer solution of Simon \textit{et al.}.\textsuperscript{[21]}

3.2 Homopoly(2-oxazoline)s and diblock copoly(2-oxazoline)s

3.2.1 Materials, sample preparation and indentation experiments

An overview of the homopoly(2-oxazoline)s and diblock copoly(2-oxazoline)s discussed in the current section is given in Table 3.1, together with their abbreviations. Their synthesis was described elsewhere.\textsuperscript{[3]} In brief, by living cationic ring opening polymerization at a monomer to initiator ratio of 50, the first block of 50 units was prepared. Subsequently, the second block was polymerized, resulting in block copolymers of in total 100 units. Differential scanning calorimetry (DSC) showed that all polymers that contained (at least) one block of poly(2-nonyl-2-oxazoline) had a melting temperature $T_m$ in the range of 146 to 151 °C, whereas all other polymers were fully amorphous to the extent detectable via DSC.\textsuperscript{[3]}

The observed glass transition temperatures are shown in Table 3.1. The occurrence of a single
The glass transition for the Me/Et, Me/Phe and Et/Phe combinations indicates the presence of only one amorphous phase, which is attributed to the modest degree of polymerization. No glass transition was observed for the chain extended poly(2-nonyl-2-oxazoline). Due to the proximity of the melting peak of the nonyl(2-oxazoline), no $T_g$ could be determined for PheNon and NonPhe, either.

**Table 3.1:** Overview of the 16-membered set of diblock copoly(2-oxazoline)s and chain extended homo poly(2-oxazoline)s, showing the abbreviation, the degree of polymerization for the first and the second block, and the glass transition temperature for each compound (data from ref. 3).

<table>
<thead>
<tr>
<th>second block →</th>
<th>first block ↓</th>
<th>poly(2-methyl-2-oxazoline)</th>
<th>poly(2-ethyl-2-oxazoline)</th>
<th>poly(2-nonyl-2-oxazoline)</th>
<th>poly(2-phenyl-2-oxazoline)</th>
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</thead>
<tbody>
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<td>50°C</td>
<td>79°C</td>
<td>79°C</td>
</tr>
<tr>
<td></td>
<td>MeEt</td>
<td>50:49</td>
<td>63°C</td>
<td>MeNon</td>
<td>50:52</td>
</tr>
<tr>
<td></td>
<td>MeNon</td>
<td>50:52</td>
<td>MePhe</td>
<td>50:52</td>
<td>88°C</td>
</tr>
<tr>
<td><strong>poly(2-ethyl-2-oxazoline)</strong></td>
<td>EtMe</td>
<td>50:50</td>
<td>50°C</td>
<td>50°C</td>
<td>60°C</td>
</tr>
<tr>
<td></td>
<td>EtEt</td>
<td>50:50</td>
<td>59°C</td>
<td>EtNon</td>
<td>50:50</td>
</tr>
<tr>
<td></td>
<td>EtNon</td>
<td>50:50</td>
<td>EtPhe</td>
<td>50:52</td>
<td>89°C</td>
</tr>
<tr>
<td><strong>poly(2-nonyl-2-oxazoline)</strong></td>
<td>NonMe</td>
<td>50:50</td>
<td>50°C</td>
<td>50°C</td>
<td>50°C</td>
</tr>
<tr>
<td></td>
<td>NonEt</td>
<td>50:46</td>
<td>56°C</td>
<td>NonNon</td>
<td>50:50</td>
</tr>
<tr>
<td></td>
<td>NonNon</td>
<td>50:50</td>
<td>NonPhe</td>
<td>50:45</td>
<td>-</td>
</tr>
<tr>
<td><strong>poly(2-phenyl-2-oxazoline)</strong></td>
<td>PheMe</td>
<td>50:48</td>
<td>50°C</td>
<td>50°C</td>
<td>50°C</td>
</tr>
<tr>
<td></td>
<td>PheEt</td>
<td>50:46</td>
<td>84°C</td>
<td>PheNon</td>
<td>50:50</td>
</tr>
<tr>
<td></td>
<td>PheNon</td>
<td>50:50</td>
<td>PhePhe</td>
<td>50:50</td>
<td>107°C</td>
</tr>
</tbody>
</table>

The block copolymers were dissolved in chloroform (with the exception of MeMe, which was dissolved in demineralized water). Approximately 5 μL of each solution was pipetted onto a glass slide. The diameter and the height of the resulting spots ranged from approximately 2 to 3.5 mm, and from 100 to 400 μm, respectively. Four such glass slides were prepared, one of
which is shown in Figure 3.2. After drying (see Experimental section), indentation experiments were performed on the polymer spots.

Figure 3.1: One of the four prepared glass slides with drop cast samples. The first three rows and the first spot of the fourth row form the diblock copolymer library that is discussed in this section.

As examples, load-displacement responses obtained with a Berkovich indenter on the EtPhe and the EtNon diblock copolymers are shown in Figure 3.2a. These load-displacement responses were analyzed using the method proposed by Oliver and Pharr.\textsuperscript{[23,24]} The unloading responses were fitted with a power law equation

$$P = a(h - h_f)^m$$ (3.1)

to obtain the slope at the start of the unloading \(S\). From the slope \(S\) and the maximum depth \(h_{max}\), the contact depth \(h_c\) is determined using

$$h_c = h_{max} - 0.75 \frac{P_{max}}{S}$$ (3.2)

As the tip shape was determined, the projected tip-sample contact area \(A\) can be calculated from the area function and the contact depth \(h_c\). With \(\beta = 1\), the reduced modulus \(E_r\) is then calculated as

$$E_r = \frac{\sqrt{\pi}}{2\beta} \frac{S}{\sqrt{A(h_c)}}$$ (3.3)

From the reduced modulus, the elastic modulus of the polymer as obtained via indentation \(E_i\) is calculated, where 0.4 is taken as the Poisson’s ratio of the polymer \(v_{sample}\). When indenting stiff materials, it is important to realize that also the indenter is elastically deformed, as well.

$$E_{i,\text{sample}} = \left(1 - v_{sample}^2\right) \left(\frac{1}{E_r} - \frac{1 - v_{indenter}^2}{E_{indenter}}\right).$$ (3.4)

The analysis results of the load-displacement responses in Figure 3.2a are shown in Figure 3.2b. Key parameters from Equations 3.2 and 3.3 are indicated for one load-displacement response of EtNon. The EtPhe responses are much stiffer (have a higher \(E_i\), see Figure 3.2b) than the EtNon. At higher RH the stiffness of EtPhe is reduced, as can be observed visually in the loading response. The creep during the hold time increases as well.

The combination of sufficiently long hold time and rapid unloading rate proved to be appropriate to achieve (unless stated otherwise) a predominantly elastic unloading response for all materials described in this section, which is a necessary requirement for applying the Oliver & Pharr method.
Figure 3.2: (a) Indentation load-displacement responses (Berkovich indenter) and (b) analysis results for EtPhe at two different humidities (5.4% and 40% RH) and for the EtNon copolymer, showing that higher humidity lowers the stiffness of the material, and that EtPhe is stiffer than EtNon; for clarity, only four of the EtPhe responses are shown; key parameters for the calculation of $E_i$ are displayed.

Figure 3.3 shows results on reference materials that were processed such that the material contained no solvent: PheEt was annealed above its $T_g$ and NonNon was melt processed. The $E_i$ of these samples corresponded well with those on the corresponding samples from the HTE library. This shows that the chloroform from the dropcasting is absent or its amount is so reduced that its effect on $E_i$ is negligible. The thick NonNon reference sample appeared white due to crystallization, while the corresponding sample from the library was transparent, due ostensibly to the smaller crystallite size. Nevertheless, the moduli of both poly(2-nonyl-2-oxazoline) samples were nearly identical ($E_{i,meltprocessed} = 0.81$ GPa; $E_{i,library} = 0.87$ GPa).
Figure 3.3: Comparison of the library samples with solvent-free reference samples (Berkovich tip, TriboIndenter, 5.4% RH).

For some of the tested materials (for instance EtEt), sample preparation and tensile testing are rather difficult due to the brittleness of these materials.\cite{19} However, DSI measurements could be performed successfully, resulting in small standard deviations in measurements on the same sample, and in good agreement between duplicate samples (Figure 3.4). The high-throughput nature of the measurements is illustrated using a measurement series performed with the TriboIndenter: ten measurements per copolymer spot were performed on two slides with sixteen copolymer spots each. These 320 measurements were performed in an automated run during 20 hours, of which 11 hours were spent on moving to the next indent position and approaching the sample surface between two indents. These 11 hours may be reduced by performing a ‘quick approach’ to the sample surface at each spot near the indent positions before starting the actual measurement. This run was not fully optimized for this potential increase in experimental throughput.

3.2.2 Chain-extended homopolymers

Indentation moduli obtained for the entire library samples are presented in Figure 3.4 (a, b and c). Their hardness values are briefly discussed in the Appendix. The results in Figure 3.4a and 3.4c are obtained with the TriboIndenter on two sample slides and at two humidity levels, and the results in Figure 3.4b are obtained at an intermediate RH using the NanoTest600. At low RH, the elastic modulus of the nonyloxazoline homopolymer ($E_i = 0.87$ GPa) was lower than $E_i$ of the other homopolymers.

DSC demonstrated that for MeMe, EtEt and PhePhe, $T_g$ is above room temperature (Table 3.1). With increasing side chain length (methyl, ethyl,\cite{3} propyl, pentyl),\cite{25} $T_g$ decreases. No $T_g$ was observed for 2-heptyl-2-oxazoline and 2-nonyl-2-oxazoline homopolymers.\cite{25} Although the exact location of $T_g$ of NonNon could not be determined, it is expected to be lower than the $T_g$ of 2-pentyl-2-oxazoline homopolymer, \textit{i.e.}, lower than 5 °C. 2-Pentyl, 2-heptyl, and 2-
nonyl-2-oxazoline homopolymers exhibit a melting temperature near 150 °C.\textsuperscript{[25]} As NonNon is not glassy, it has a lower modulus than MeMe, EtEt and PhePhe (Figure 3.4a and 3.4b) but the semicrystallinity of the poly(2-nonyl-2-oxazoline) prevents $E_i$ from dropping to the MPa range (the MPa range is typical for $E$ of amorphous polymers above $T_g$). In conclusion, the observed $E_i$ of NonNon is in the range expected for semicrystalline polymers probed at a temperature between $T_m$ and $T_g$.

EtEt ($E_i = 4.3$ GPa, Figure 3.4a) has a lower $E_i$ than MeMe (7.0 GPa) and PhePhe (5.5 GPa). MeMe and EtEt are both hygroscopic.\textsuperscript{[26]} The low elastic modulus of EtEt can be explained by some water that is present in the sample even at 5.4% RH. For hygroscopic polymers, water decreases the $T_g$ and the elastic modulus of the glassy state.\textsuperscript{[27]} The decrease of the modulus is most pronounced when (due to the absorbed water) the $T_g$ is (starts to be) close to the temperature at which the test is performed (\emph{i.e.}, room temperature). The decrease of the modulus due to water is expected to be most pronounced for EtEt, as EtEt (free of water) is at room temperature only 34 °C below its $T_g$,\textsuperscript{[3,19]} compared with 54 °C for MeMe (Table 3.1). Further indication that the difference between the glass transition temperature $T_g$ and room temperature influences the elastic modulus is given by the $E_i$ of the EtPhe and PheEt samples, that are much closer to the $E_i$ of PhePhe than to EtEt, corresponding to a much larger difference between their $T_g$ and room temperature than for EtEt.

Apart from this, differences in intermolecular interactions and the occurrence of secondary glass transitions may result in different elastic moduli for MeMe, PhePhe and EtEt. Due to such a secondary glass transition, the Young’s modulus is for instance $\sim 2.5$ GPa for polycarbonate, compared to $\sim 3.3$ GPa for polystyrene.\textsuperscript{[28,29]} Nuño-Donlucas \emph{et al.}\textsuperscript{[19]} measured \emph{via} differential mechanical thermal analysis (DMTA) a secondary transition for poly(2-ethyl-2-oxazoline) at $-100$ °C. If such transitions are absent for poly(2-methyl-2-oxazoline) and poly(2-phenyl-2-oxazoline) or are less effective in reducing $E_i$, this could be a second explanation as to why EtEt has a lower $E_i$ than MeMe and PhePhe at 5.4% RH.

$E_i$ of MeMe at low RH is surprisingly high (7.0 GPa) – significantly higher than that of PhePhe ($E_i = 5.5$ GPa, PhePhe is at room temperature 80 °C below $T_g$) and much higher than $E_i$ typically measured with depth-sensing indentation on a stiff glassy polymer such as polystyrene.\textsuperscript{[30]} This high elastic modulus of MeMe is not caused by experimental artifacts, as will be discussed in detail in the next paragraph.
An HTE study of the elastic properties of poly(2-oxazoline)s

The high $E_i$ observed for MeMe indicates intermolecular interactions additional to the Van der Waals interactions. Another glassy polymer exhibiting an exceptional high $E_i$ (8 to 12 GPa) is poly(acrylic acid).\cite{31,32} For poly(acrylic acid), these intermolecular interactions may arise from hydrogen bonds, while for poly(oxazoline)s, hydrogen bonds or polar interactions may play a role. Due to steric or chemical factors, for the polymers in this study, these interactions were strongest for poly(oxazoline)s with only a small methyl side group. Protons from water molecules may hydrogen bond with the electronegative oxygen atoms of the poly(oxazoline). These water molecules may be attracted by the material from the surrounding atmosphere (see Section 3.2.4), and may be so tightly bound that they remain in the material even after the rigorous drying procedure. Two hydrogen bonds per water molecule result in intermolecular interaction between polymer chains. Infrared spectroscopy (Figure 3.5) on the dried homopolymers demonstrated that the carbonyl peak of MeMe, EtEt and PhePhe was located at $\sim1626$ cm$^{-1}$, while the carbonyl peak of NonNon was located at 1640 cm$^{-1}$. 1626 cm$^{-1}$ matches the wavenumber attributed to hydrogen-bonded carbonyl in poly((hydroxyalkyl)oxazoline), while the carbonyl peak of NonNon is located close to the

Figure 3.4: Depth-sensing indentation results obtained at different humidities and with two indenter geometries (a and c: Berkovich; b: indenter with spherical apex); symmetry in indentation moduli (5.4% RH) is visualized in the 3D graphic; indents outside the tip shape calibration range and indents with a high creep rate are disregarded.
‘free’ C=O position. Furthermore, a larger signal in the OH-stretching region (3400 to 3600 cm\(^{-1}\)) was observed for the MeMe, EtEt and PhePhe materials than for the NonNon material, indicating that the NonNon contains less moisture than the other three homopolymers.

Alternatively, polar interactions between chains induced by N-C=O ↔ N+=C-O- isomerism can contribute to the enhanced interaction between adjacent chains. Such isomerism is inferred in literature for poly(2-methyl-2-oxazoline)\(^{[18]}\) and for poly(2-isopropyl-2-oxazoline).\(^{[33]}\) In conclusion, the high \(E\) of MeMe is attributed to interchain interactions arising from hydrogen bonding and/or polar interactions.

Figure 3.5: FTIR spectra of the homopolymers at low humidity; the carbonyl vibration is located at 1623, 1628, 1640 and 1626 cm\(^{-1}\) for MeMe, EtEt, NonNon and PhePhe, respectively.

The copoly(oxazoline)s in the current study are rather difficult to measure in macroscopic mechanical tests due to their brittleness. However, using depth-sensing indentation, the materials could be characterized successfully. The elastic modulus from depth-sensing indentation experiments \(E_i\) is for polymers usually somewhat higher than \(E\) determined in macroscopic mechanical tests. This is attributable to deviations from ideal elastic behavior\(^{[34]}\) and pile-up (material heaps up next to the indent and causes an underestimation of the projected contact area, and therefore an overestimation in \(E_i\), Equation 3.3).\(^{[35]}\) These factors result for a reference material like polycarbonate in a difference between \(E\) and \(E_i\) of approximately 0.5 GPa (\(E_i = 3.0\) GPa; \(E \sim 2.5\) GPa\(^{[28]}\)). The amount of pile-up observed during line scanning (NanoTest600) and profilometric imaging (TriboIndenter) of the indents on the MeMe was small (the resulting overestimation in \(E_i\) is < 8%). Substrate effects (\(i.e.,\) the elastic properties of the substrate influencing the obtained results due to insufficient sample thickness with respect to the indentation depth) can safely be ignored: the MeMe sample had a thickness of 50 µm, while the deepest indent for this material in Figure 3.4a was only
An HTE study of the elastic properties of poly(2-oxazoline)s

0.49 µm. Formation of a pre-indent (resulting in an artificially low measured contact depth and therefore an erroneously high $E_i$) can be excluded as well. The residual indentation observed after loading to a magnitude twice that of the preload was insignificant, and $E_i$ of MeMe did not decrease with maximum load applied during the experiment. (The effect of a pre-indent on the calculated $E_i$ will decrease for deeper indents, resulting in a decreasing trend in $E_i$ as a function of maximum load.) In sum, the high modulus $E_i$ for MeMe, as compared to stiff glassy polymers such as polystyrene, appears to accurately reflect the significant stiffness of this polymer.

3.2.3 AB and BA diblock copolymers

The $E_i$ of any AB diblock copolymer in this library is intermediate to that of the chain extended A- and the B-polymers (Figure 3.4). It is observed that $E_i$ of the diblock copolymers with only one poly(2-nonyl-2-oxazoline) block was closer to $E_i$ of NonNon than to that of the other (high-$T_g$) component. Because the volume fraction of Non is large (volume fraction Non is estimated to be > 60% because of its long side chain), the high-$T_g$ block has less influence on the resulting elastic properties. Furthermore, the volume fraction of the glassy phase is lower than the actual volume fraction of the high-$T_g$ component, as poly(2-nonyl-2-oxazoline) chains may surround segments of the high-$T_g$ component and, thus, provide them some freedom to move, resulting in non-glassy behavior of part of the high-$T_g$ segments.

The $E_i$ of pairwise combinations (AB vs. BA) typically agreed very well with each other (Figure 3.4). Only the diblocks with Non as the first block showed (in two out of three cases) a higher $E_i$ than the pairwise combination ($E_{i,NonPhe} > E_{i,PheNon}$ and $E_{i,NonMe} > E_{i,MeNon}$). Chain transfer and chain coupling occurred to some extent during the synthesis of the NonMe, NonEt (and NonPhe). Therefore, the pairwise combinations differ in chain length, chemical composition distribution over the chains, surface morphologies (as observed by AFM on thin films) and mechanical properties. Figure 3.4a shows for nearly all samples a good agreement between duplicate experiments on spots of the same (co)polymer material on two different glass slides. Only for MePhe, this agreement is somewhat poorer. This is thought to be due to slightly poorer surface conditions for one of the MePhe samples. The lower $E_i$ in Figure 3.4a for MePhe, which also shows the lowest standard deviation, is probably most reliable.

3.2.4 Effect of humidity on $E_i$

For all samples considered, $E_i$ decreased with increasing humidity (Figures 3.4 and 3.5), the least humidity-sensitive samples being NonNon, NonPhe and PheNon. PhePhe was somewhat sensitive to humidity (1.3 GPa decrease for the increase in relative humidity from 5.4 to 40% RH). The Et and Me combinations with Non or with Phe were considerably more compliant with increasing humidity. The most humidity-sensitive samples were the EtEt, MeMe, MeEt
and EtMe. At 40% RH for nearly all employed maximum loads, the displacement of the MeMe and EtEt surfaces exceeded the measurable depth range of the TriboIndenter (approximately 4.5 μm at the current settings). Van Caeter\textsuperscript{[18]} reports $G' = 0.002$ GPa and $G''/G' \sim 0.2$ for chain-extended poly(2-methyl-2-oxazoline) from rheometry at 1 Hz and 40 °C. Assuming that Van Caeter conducted his experiments at ambient humidity, this result (particularly the high $G''/G'$ ratio) corresponds qualitatively with the appreciable compliance of MeMe at ambient humidity (Figure 3.4c).

The Oliver and Pharr analysis gives erroneous results if at the end of the hold period the creep, \textit{i.e.}, the displacement at sustained maximum load, is relatively high.\textsuperscript{[36,37]} Therefore, if the ratio of the displacement rate at the start of the unloading to the displacement rate at the end of the hold period was smaller than 5 (an arbitrary criterion adopted here), no results are given. At 40% RH, MeEt, EtMe and NonEt did not meet this criterion and are therefore not shown in Figure 3.4c. Other diblocks that showed an appreciable but lower creep rate than the disregarded diblocks were EtNon, PheEt, EtPhe, PheMe, MePhe, NonMe and MeNon. (Further, for EtNon, NonMe and MeNon the average and standard deviation presented in Figure 3.4c is based on only four load-displacement responses as, due to larger deformation at increased humidity, only those responses remained within the tip area function calibration.) For these samples, the presented $E_i$ may exhibit a small error due to the creep. Also for EtEt at 9% RH, the $E_i$ may be slightly affected, as the displacement rate at the start of the unloading was only 7 times the creep rate at the end of the hold period. For all other results presented in Figure 3.4, this error source can be neglected.

The modulus of diblocks with Et, Me (and Phe) is affected by humidity. This corresponds with the observation that these materials, after equilibrating with ambient humidity, lose weight (Table 3.2) that can be attributed to water loss, when the material is heated during thermal gravimetric analysis (degradation of these polymers typically occurs at much higher temperatures, $> 350$ °C\textsuperscript{[3]}). At 9% RH, and possibly even at 5.4% RH, some moisture is absorbed from the surrounding atmosphere, albeit only a small amount,\textsuperscript{[26]} resulting in softening of the Et-material. The relatively small decrease of $E_i$ for PhePhe with increasing humidity can be explained by the high glass transition temperature; therefore, in spite of the water present, the material remains glassy. The weight loss of the NonNon was much smaller.

The stiffness of MePhe and PheMe decreased much more with increasing humidity than did the stiffness of EtPhe and PheEt (Figures 3.4 and 3.5); this can be explained by their respective water content at ambient humidity (Table 3.2). More detailed gravimetric measurements revealed that the weight gain of dried EtEt\textsuperscript{[38]} and of dried polyethyloxazoline/polyethersulfone blends\textsuperscript{[39]} upon exposure to higher humidity equals the weight loss after subsequent drying. This reversibility supports the statement that water absorption is the cause for the observed softening.
Table 3.2: Weight loss during thermal gravimetric analysis (TGA) between 80 °C and 140 °C on selected (co)polyoxazoline materials that were prior to TGA measurements in approximate equilibrium with ambient humidity.

<table>
<thead>
<tr>
<th>Material</th>
<th>Weight loss (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeMe</td>
<td>6.2</td>
</tr>
<tr>
<td>EtEt</td>
<td>2.3</td>
</tr>
<tr>
<td>NonNon</td>
<td>0.4</td>
</tr>
<tr>
<td>PhePhe</td>
<td>3.6</td>
</tr>
<tr>
<td>MePhe</td>
<td>4.3</td>
</tr>
<tr>
<td>EtPhe</td>
<td>1.4</td>
</tr>
</tbody>
</table>

Figure 3.6 also shows that the type of indenter geometry used during the experiments (sphere or Berkovich) caused only minor differences. The comparison between the two indenter geometries and the two instruments is not explored further, as the current materials are not very suitable for these comparative investigations due to the dependency of the modulus on the humidity.

The number of reports on the effect of humidity on the elastic modulus of glassy polymers is relatively small. This effect is reported for poly(methylmethacrylate) (PMMA) where $E$ decreases by 0.44 GPa with an increase in RH from 0% to 100%,\cite{40} and for polycarbonate (PC).\cite{41} For (semicrystalline) ethylene-vinyl alcohol copolymers (29 mol% ethylene content) a drop in $E$ from 3.0 to 1.9 GPa is reported upon a humidity increase from 0% to 53% RH;\cite{42} for starch a drop from 2.4 to 1.5 GPa is reported for an increase from 32% to 90% RH.\cite{43} Compared to these numbers, some of the drops in $E_i$ reported in this work (for instance for PheMe) are surprisingly large.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3.6.png}
\caption{Comparison of $E_i$ obtained at several humidity levels and with two types of indenters for selected (co)polymers.}
\end{figure}
3.3 Triblock copoly(2-oxazoline)s

3.3.1 ABA copolymers compared to A homopolymers and AB copolymers

In addition to the diblock copolymers, a triblock copoly(2-oxazoline) library was synthesized, as well.\textsuperscript{[6]} On selected members of the triblock copolymer library, indentation experiments were performed.\textsuperscript{[44]} The finer increments in the chemical composition compared to the diblock copolymer series (Section 3.2) allow for a more detailed investigation of the correlations between properties and chemical composition. Similar to the diblock series, the total degree of polymerization for the triblock copolymer series was maintained constant at 100 repeat units (33 units per block). The constant degree of polymerization allows comparing the homopolymers, diblock and triblock copolymers, as varying the total number of repeat units would result in extensive variation of the glass transition temperature (and thus, possibly, of the elastic modulus).\textsuperscript{[28,45]}

As the stiffness of materials containing poly(2-nonyloxazoline) differed much from those of the materials without poly(2-nonyloxazoline), see Section 3.2.2 and 3.2.3, triblock copolymers containing one or more Non blocks were investigated first. In Figure 3.7, the elastic moduli obtained by indentation $E_i$ are shown as a function of the Non weight content. These weight contents were calculated using the number of repeat units determined by $^1\text{H}$ NMR spectroscopy\textsuperscript{[3,6]} and the masses of the repeat units (85, 99, 197 and 147 g/mol for 2-methyl, 2-ethyl, 2-nonyl, and 2-phenyl-2-oxazoline, respectively).

An increase in Non content resulted in a decrease in stiffness (Figure 3.7). This change in stiffness results from the decreasing volume fraction of the glassy phase and the increasing volume fraction of the more compliant, nonyloxazoline-rich semi-crystalline phase. Moreover, as will be discussed in more detail in Section 3.4, the stiffness of the phases is influenced by their exact chemical composition. Figure 3.7a shows the homopolymers, diblock copolymers and triblock copolymer for the combination of Non with poly(2-methyl-2-oxazoline). The $E_i$ of the MeNonMe triblock copolymer is found between that of the Me homopolymer (\textit{i.e.}, the MeMe sample in Section 3.2) and the MeNon diblock copolymer. Likewise, the $E_i$ of EtNonEt is between that of Et and EtNon (Figure 3.7b). For the combinations containing poly(2-phenyl-2-oxazoline), the $E_i$ of PheNonPhe is between that of Phe and PheNon (and NonPhe), while the $E_i$ of NonPheNon is between that of NonPhe and Non.\textsuperscript{[46]}

For the Me/Non and Phe/Non combinations, the stiffness of the AB and BA materials differ to some extent. The higher stiffness of NonMe compared to MeNon is partly attributable to the higher overall Me content. Furthermore, for the copolymers containing Non as the first block, side-reactions (chain-transfer and subsequent chain coupling) occurred.\textsuperscript{[3]} Due to these side-reactions, apart from the desired AB block architecture, some ABA triblock copolymers with Non blocks at the extremities were also formed. The presence of these impurities and the slightly different chemical composition resulted in somewhat different phase-segregation and
crystallization behavior during sample preparation for this material compared to its BA counterpart, causing the differences in stiffness. This is in line with the differences in surface morphology (AFM) between the NonMe and MeNon diblocks\textsuperscript{[12]} and in phase behavior, as evidenced by differential scanning calorimetry, which exhibited slightly different $T_m$ for the AB and BA combinations.

The relation between Non weight content and $E_i$ deviates from linearity for the Me/Non and Phe/Non combinations (Figure 3.7a and 3.7c), but is nearly linear for the Et/Non combinations (Figure 3.7b). The exact variation of $E_i$ with composition for each of these series depends on various factors such as the volume fraction and the stiffness of the amorphous and the crystalline phase. Moreover, especially for the amorphous phase, the stiffness may vary with the chemical composition of the phase and with the amount of absorbed moisture. It is noted that the length of the various blocks in the di- or triblock copolymers, and the difference in chemical structure between the blocks, influence the driving force for the phase-segregation.\textsuperscript{[22]}

Both indenter geometries yielded the same trends in material stiffness as a function of chemical composition (Figure 3.7). The material stiffness of Me and Et, and to a lesser extent the stiffness of Non and Phe, decreases with increasing humidity (see Section 3.2.4), as also observed here by the significant difference between the $E_i$ of Et at 9% and 5.4% relative humidity. However, the differences in magnitude of $E_i$ cannot be attributed solely to the differences in humidity. Thus, part of the discrepancy between the stiffness obtained from Berkovich and spherical indentation is attributed to the different loading times and strain magnitudes/gradients specific to each probe geometry. (The so-called representative strain can be estimated for the spherical probe, given the maximum indentation depth and probe radius,\textsuperscript{[47]} and ranged 6 - 13% for the stiffest and most compliant polymers, respectively; the representative strain for the Berkovich probe is estimated as 8%,\textsuperscript{[47]} but this probe also induced a much sharper strain gradient within the polymer). Potential geometric imperfections or inaccuracies of the empirically obtained indenter area function contribute additional sources of error to the calculated values of $E_i$ for each probe type.
Figure 3.7: Stiffness of the homopolymers, diblock and triblock copolymers with, in total, 100 repeat units, for the (a) Me/Non, (b) Et/Non and (c) Phe/Non combinations measured using a spherical or a Berkovich indenter at reduced relative humidity, RH. Standard deviations may be smaller than the symbols.

The Et/Phe combinations (Figure 3.8) span a smaller $E_i$-range than the Non-containing combinations, as the difference between the stiffness of the homopolymers is smaller. Again the $E_i$ of EtPheEt falls between the diblock copolymer and the homopolymer. The PheEtPhe as measured with the spherical indenter is less stiff than both the PheEt and the EtPhe, which may be attributed to some variation in the humidity during testing (see Experimental section);
an increase in humidity would result in a decrease of the $E_i$ of the humidity-sensitive Et block, see Section 3.2.4. With increasing amount of Phe, the $T_g$ of the copolymer material increases. The material also turns less hygroscopic and thus, the humidity-induced softening is less pronounced, as well. These two factors cause an increase of the material stiffness with increasing Phe content (Figure 3.8).

**Figure 3.8:** (a) Stiffness of the homopolymers, diblock and triblock copolymers for the Et/Phe combinations,[48] measured using a spherical or a Berkovich indenter at reduced relative humidity, RH, and (b) their glass transitions as obtained with DSC (DSC according to ref. 3 and 6).
### 3.3.2 ABC triblock copolymers

Apart from the combinations of two different monomers, the triblock copolymer library contained combinations of three different poly(2-oxazoline) blocks. The material stiffness for the Me/Et/Non and Me/Et/Phe combinations are shown in Figure 3.9 and 3.10, respectively. Also the appropriate weight-averages of the stiffness of the homopolymers are shown (dashed bars in Figure 3.9 and 3.10) for the series measured at 5.4% RH with a Berkovich probe. These weight-averages are based on the degrees of polymerization determined by $^1$H NMR spectroscopy. The $E_i$ of the Me/Et/Non triblock copolymers is lower than the applicable weight-averaged stiffness, which is related to the observed concave trend in Figure 3.7a (where the MeNonMe copolymer also exhibited a lower $E_i$ than expected from the applicable weight average of the $E_i$ of the Me and Non). It is noted that the observed differences between the stiffness of MeNonEt, EtMeNon and EtNonMe are larger than those between their respective weight-averaged stiffness (dashed bars). The higher $E_i$ of MeNonEt compared to EtMeNon and EtNonMe (Figure 3.9) is at least partly attributable to its Non content, as a lower Non content results in a higher $E_i$ (Figure 3.7). This higher $E_i$ is best observable for the measurement with the Berkovich indenter (results obtained on both duplicate sample slides are shown in Figure 3.9), as the humidity was controlled more precisely in these experiments. The Non and Me contents are annotated in Figure 3.9, for clarity with one more decimal than actually justified based on the accuracy of the NMR results. Some difference between the $E_i$ of EtNonMe compared to EtMeNon was observed. This difference, which is not explained by their Non content, may be related to their Me content. It can be expected that a higher Me content increases $E_i$ as the stiffness of MeNonMe (Figure 3.7a) is larger than that of EtNonEt (Figure 3.7b) or any of the Me/Non/Et triblock combinations (Figure 3.9). Indeed, EtNonMe, which has a higher Me content, exhibited a higher $E_i$ than EtMeNon. Moreover, the tendency to phase-separate and to form a nonyl-rich crystalline phase may be influenced by this change in Me content, as the Et/Non combination exhibits less tendency to phase-separate than the Me/Non combination.\textsuperscript{[49]} (Supporting evidence for the difference in phase segregation behavior for the Et/Non combination compared to the Me/Non combination was obtained from surface energy measurements on the triblock copolymer library discussed in the current section.\textsuperscript{[50]}) Finally, the location of the Non block within the chain and/or the occurrence of some chain-transfer and chain-coupling side-reactions may have influenced the crystallization kinetics and thus the resulting phase morphology (domain size, degree of crystallinity, exact composition of the phases, macromolecules connecting different amorphous domains and thereby increasing the resistance to deformation, etc.) and may have contributed to the higher stiffness observed for MeNonEt and EtNonMe compared to EtMeNon. In conclusion, the relation between chemical composition and block order on one hand and phase-separation behavior as well as stiffness on the other hand, is much more complicated than can be covered by a simple weight-averaging of the stiffness of the constituent homopolymers.
Figure 3.9: $E_i$ obtained for the Me/Et/Non triblock combinations with two different indenter geometries. The corresponding weight-averaged $E_i$ of the homopolymers (Berkovich, 5.4% RH) is indicated by a dashed bar.

The $E_i$ of the Me/Et/Phe combinations (Figure 3.10) is, in particular for the Berkovich series, relatively close to the appropriate weight averages of the $E_i$ of the corresponding homopolymers. This straightforward relation may be related to the simple phase-behavior of the system: only one $T_g$ is observed for these triblocks,[6] indicating that no phase-separation occurs. Moreover, only small variation in $E_i$ between the different Me/Et/Phe triblock combinations were observed, in particular for the Berkovich series. The difference between the highest $E_i$ obtained on one of the duplicate samples with a Berkovich on MePheEt and the lowest obtained on EtPheMe is 0.4 GPa, which is only 6% difference. The slightly larger variation in the data obtained with the spherical indenter is attributable to some variation in drying conditions before and relative humidity during these indentation measurements, as the $E_i$ of Me and of Et is sensitive to humidity (Section 3.2.4).
3.4 Influence of the polymer architecture

The distribution of the monomer units over the polymer chain can have a significant influence on the properties of the polymers.\cite{51,52} In this section, the properties of copolymers of 2-ethyl-2-oxazoline and 2-nonyl-2-oxazoline with a random (Et-\textit{r}-Non) architecture are compared to those of corresponding copolymers with a block (Et-\textit{b}-Non) architecture, using a library where the composition is systematically varied in steps of 10 mol\% (Figure 3.11). The polymers were synthesized by living cationic ring opening polymerization in acetonitrile (statistical copolymerization) or butyronitrile (block copolymerization), where the reactivity ratio’s during statistical copolymerization resulted in random copolymers.\cite{7} Chemical characterization by GPC and $^1$H NMR showed that the copolymers exhibited the desired composition and low polydispersity indices.\cite{7} This allowed the elucidation of structure-property relationships.

Figure 3.10: $E_i$ for the Me/Et/Phe triblock combinations. The dashed bars indicate the applicable weight-averaged $E_i$ of the homopolymers for indentations using a Berkovich indenter at 5.4\% RH.

Figure 3.11: Schematic representation of block and random monomer distribution over the polymer chain, for two overall chemical compositions.
3.4.1 Thermal transitions and phase-separation behavior

The thermal transitions of the block and random copolymers were investigated by differential scanning calorimetry; a melting peak in the DSC reveals the presence of crystalline regions at temperatures below the melting transition, while a glass transition reveals the presence of amorphous regions. The determined melting temperature ($T_m$) and glass transition temperature ($T_g$) of the synthesized copolymers are depicted in Figure 3.12.

The $T_g$ of the Non homopolymer is lower than the $T_g$ of Et.\[25\] Therefore, for the Et:Non random copolymers the $T_g$ is reduced with increasing amount of Non. In contrast, the $T_g$’s of the block copolymers containing 33 to 82 wt.% Non is close to the $T_g$ of the Et homopolymer: as a large fraction, or all, of the Non segregates into a Non-rich (semi-)crystalline phase, the glassy phase does not contain as much Non as for the random series.

At higher amounts ($\geq$ 82 wt.%) of Non, the random copolymers also comprise a crystalline phase, with a melting temperature that is considerably lower than for the pure Non homopolymer. With increasing Non content, both $T_m$ and the melting enthalpy (not shown) increase, as less ethyl side chains disturb the crystallization.\[28\] For the block copolymer series, the melting enthalpy increased with increasing Non content, as the volume fraction of the crystalline phase increases with increasing Non content, while the $T_m$ remained almost constant, which indicates, in this case, constant chemical composition of the crystalline phase.

For the Et$_{60}$-r-Non$_{40}$, Et$_{50}$-r-Non$_{50}$ and Et$_{40}$-r-Non$_{60}$ (where the subscripts denote the number of ethyloxazoline and nonyloxazoline units), with Non contents of 57, 67 and 75 wt.%, respectively, DSC measurements were repeated with an annealing period before the last heating step in the DSC measurement program. As the annealing temperature (40 °C) is above the $T_g$ of these materials, appreciable polymer chain segmental motion is possible and can facilitate crystallization. No melting peak was observed for Et$_{60}$-r-Non$_{40}$ after 24 hours annealing at 40 °C, indicating that this material remains amorphous. After annealing Et$_{50}$-r-Non$_{50}$ and Et$_{40}$-r-Non$_{60}$, a melting peak was observed that was not measured without annealing, indicating that a crystalline phase was nucleated upon annealing.

The phases expected to be present at room temperature, based on the DSC results, are summarized in Table 3.3. The crystalline phases will be richer in Non than the amorphous phase, but may contain some Et as well. Similarly, the depression of the $T_g$ compared to the $T_g$ of the Et homopolymer indicates that the amorphous phase of the random copolymers contains Non. For reason of clarity, in Table 3.3 the Non homopolymer is described as ‘crystalline’, though this polymer is most probably semi-crystalline: it may contain amorphous regions that comprise a too small volume fraction to be detected via the DSC heat flow.

In view of the mechanical properties that will be discussed later, Table 3.3 distinguishes between amorphous material that is, when probed at room temperature, below $T_g$ (i.e., glassy), and amorphous material that is at room temperature above $T_g$. Although these two phases are
thermodynamically similar,[28] their mechanical behavior is very different as described in the next section.

![Graph showing glass transition and melting temperatures](image)

**Figure 3.12:** Glass transition temperatures and melting temperatures for the random and block Et:Non copolymers.

**Table 3.3:** Phases expected to be present at 25 °C for the studied compositions based on the DSC data shown in Figure 3.12.

<table>
<thead>
<tr>
<th>Composition, wt.% (mol%)</th>
<th>0  (0)</th>
<th>18  (10)</th>
<th>33-57  (20-40)</th>
<th>66-82  (50-70)</th>
<th>88-100  (80-100)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Block-series</td>
<td>Glassy</td>
<td>Dis-regarded b</td>
<td>Crystalline+glassy</td>
<td>Crystalline+glassy</td>
<td>Crystalline</td>
</tr>
<tr>
<td>Random-series</td>
<td>Glassy (amorphous with $T_g &gt; 25$ °C)</td>
<td>Amorphous above or below $T_g$</td>
<td>Crystalline+amorphous above or below $T_g$</td>
<td>Crystalline</td>
<td></td>
</tr>
</tbody>
</table>

*Materials are listed as containing a crystalline phase if their DSC trace exhibited a melting peak after annealing at 40 °C for durations up to 24 hours or already without annealing.

b One sample is not included in the table as the GPC and $^1$H NMR data showed that it did not possess the chemical characteristics aimed for.

From the DSC experiments it is concluded that the phase-segregation is more pronounced, and the resulting phases are chemically more pure for the block copolymer architecture than for the random architecture. This conclusion was supported by the surface energies obtained by contact angle measurements on spin-cast films of the same materials (Figure 3.13). The surface energy is sensitive to segregation of a component to the surface. At 67, 75 and 82 wt.% Non, the surface energies obtained for the block copolymer architecture were lower (and closer to the surface energy of the Non homopolymer) than those observed for the random
An HTE study of the elastic properties of poly(2-oxazoline)s copolymer architecture (Figure 3.15). This reflects that the block copolymer architecture facilitates the energetically favorable\cite{7-9} segregation of nonyl side chains to the surface, while for random copolymers of corresponding compositions, the Non concentration at the surface is limited due to the close proximity of Et in the copolymer chain. At these compositions, the surface energies of the random copolymers are therefore closer to the surface energy of the Et homopolymer.

![Surface Energy vs Composition](image)

**Figure 3.13:** Surface energies calculated from the contact angles of diiodomethane and ethylene glycol for the random and block Et:Non copolymers. A sigmoidal fit is used to fit the data.

### 3.4.2 Elastic properties

Although all polymers are viscoelastic and thus exhibit mechanical properties that depend on time and temperature\cite{28,53}, glassy polymers (i.e., amorphous polymers characterized below $T_g$) generally exhibit an effective Young’s elastic modulus $E$ (*via* uniaxial tension) or storage modulus $E’$ (*via* dynamic mechanical analysis) of approximately 2.5 to 4.5 GPa.\cite{28,29} As testing temperature approaches $T_g$, $E$ and $E’$ gradually decrease; above $T_g$, the thermal energy of the polymeric chains is large enough that segments of the polymer chain can overcome the secondary bonding among chains, resulting in appreciable segmental mobility and in an elastic modulus below 100 MPa for amorphous materials. The exact temperature range over which the mechanical behavior changes from the glassy to rubbery response depends on the method and timescale of mechanical testing.\cite{28,53} For semicrystalline materials, the elastic modulus drops at $T_g$ to approximately 0.5 to 1.0 GPa, the exact value depending on the degree of crystallinity.\cite{28}

Typical load-displacement responses as measured *via* depth-sensing indentation at 5.4% relative humidity (RH) are shown in Figure 3.14a. The Et homopolymer was more resistant to contact loading than the Non homopolymer, in that the first exhibited a smaller depth of penetration when loaded up to the same maximum applied load. Additionally, the creep
compliance of random copolymers with intermediate Non content (e.g., 57 wt.% Non in Figure 3.14a), was considerable, as indicated by large displacement of the indenter at constant, maximum applied load; this appreciable creep complicated the inference of elastic properties from DSI, but qualitatively indicated lower resistance to deformation over the timescale of the DSI experiment (loading in 10 s and 10 s hold time at maximum load) compared to the Et or Non homopolymers.

The indentation moduli $E_i$ obtained from the analysis of these load-displacement responses are shown in Figure 3.14b. $E_i = 4.3$ GPa was found for Et, a typical value for the $E_i$ of a glassy polymer. $E_i$ of Non was approximately 0.8 GPa. This higher stiffness than typically measured for a polymer probed at a temperature above its $T_g$ is due to the crystallinity of this material (Section 3.2.2). At intermediate compositions, the Et:Non copolymer materials with a block architecture exhibited a higher stiffness than the random copolymers of corresponding compositions (Figure 3.14b). This is caused by the higher degree of crystallinity and the larger difference between their $T_g$‘s and the testing temperature (room temperature) of the block copolymers compared to the random copolymers (Table 3.3 and Figure 3.12), as discussed in more detail throughout this section.

Apart from the indentation experiments performed with a TriboIndenter equipped with a Berkovich indenter at 5.4% RH that are discussed in the remainder of this section, indentation experiments were also performed at 9% RH with a NanoTest600 indentation instrument equipped with a spherical indenter, showing a similar dependence of $E_i$ on composition for the different architectures as shown in Figure 3.14b. For the same reasons as discussed in Section 3.2 and 3.3, all obtained $E_i$ values were somewhat lower than those obtained at 5.4% RH with the Berkovich indenter geometry. Also the indentations performed with a spherical indenter on the random copolymers of 46 and 57 wt.% Non, could not be analyzed, due to the same reasons as discussed below for the indentations on the same materials made with the Berkovich.
The elastic moduli obtained via DSI for the homopolymers and the block copolymer with 50 mol% Non, agree well with the data reported in Section 3.2.3 of this chapter (Table 3.4). Variation in $E_i$, that may be due to differences in synthesis conditions (e.g., polymerization was conducted in another solvent for the random series compared to the block-series) and batch-to-batch and operator variability, was only small. (Presented data are the average from two series of indentations on two duplicate dropcast samples. Standard deviations, omitted in Table 3.4, can be found in the graphics and are typically 0.05 GPa.)
Table 3.4: Comparison of the indentation moduli $E_i$ for all materials that had a corresponding counterpart presented in Figure 3.4a.

<table>
<thead>
<tr>
<th></th>
<th>$E_i$ (GPa) Random copolymers</th>
<th>$E_i$ (GPa) Block copolymers</th>
<th>$E_i$ (GPa) Figure 3.4a</th>
</tr>
</thead>
<tbody>
<tr>
<td>Et homopolymer</td>
<td>4.3</td>
<td>4.3</td>
<td>4.3</td>
</tr>
<tr>
<td>Non homopolymer</td>
<td>0.72</td>
<td>0.80</td>
<td>0.87</td>
</tr>
<tr>
<td>Et$<em>{50}$-b-Non$</em>{50}$</td>
<td>-</td>
<td>1.7</td>
<td>1.7</td>
</tr>
</tbody>
</table>

The random copolymers with 18 and 33 wt.% Non, exhibited a lower $E_i$ than Et homopolymer. At room temperature, these materials are still below their $T_g$ but the difference between their glass transition temperatures and room temperature is smaller than for Et. Due to the hygroscopic nature of Et, this difference will be even smaller than the ~25 °C and ~15 °C, respectively, indicated in Figure 3.12. Traditional mechanical testing of bulk amorphous polymers shows that the change in the elastic modulus at the glass transition occurs gradually.\cite{28,53,54} Thus, the decreased $E_i$ of these random copolymers with respect to the Et homopolymer is not unexpected.

For the random copolymers with 46 and 57 wt.% Non, $E_i$ could not be determined using quasistatic DSI. The quasistatic analysis assumes predominantly elastic material behavior upon initial decrease of the load on the indenter.\cite{23,47} For those two random copolymers, this was clearly not the case: upon unloading, the probe initially continued to displace into the material (46 wt.% Non) or remained at the same depth (57 wt.% Non) due to the appreciable creep. The creep compliance of these two materials was large compared to glassy or semi-crystalline polymeric materials.\cite{55} In addition, all measurements on these materials (46 wt.% Non) or all but one (57 wt.% Non) were outside the depth range of the calibrated probe area function that was employed to determine $E_i$ from DSI experiments. The large time-dependent deformation for materials that are close to $T_g$ when probed at room temperature is partly attributable to their chain length: the poly(oxazoline)s discussed here are only 100 monomer units long (see Scheme 3.1 for the schematic representation of the chemical structure of the units). Therefore, considering that typical numbers of repeat units between entanglements range from ~40 for ethylene-propylene copolymers\cite{56} to ~180 for polystyrene,\cite{29} only few entanglements per polymer chain are expected. Therefore, the entanglements do not provide much resistance to deformation. The moduli displayed in Figure 3.14b for the random copolymers with 33, 67 and 75 wt.% Non should be treated with some circumspection, as creep somewhat affected the analysis accuracy.\cite{57}

Prior to the DSI experiments, all samples were dried for three weeks at 40 °C to remove the solvent used during deposition of the polymer spots. During this drying, crystallization could occur. This crystallization reduced the time-dependent deformation of the random Et:Non copolymers with 75 and 67 wt.% Non, so that the material behavior upon unloading was
predominantly elastic and $E_i$ could be obtained. However, only little or no crystallization occurred for the random copolymers with 57 and 46 wt.% Non. The hypothesized low degree, or even absence, of crystallinity for these materials is supported by the absence of any observable melting peak in the DSC trace after 24 hours annealing for the random copolymer containing 57 wt.% Non (Figure 3.12). As their $T_g$ was close to room temperature and only little or no crystallization had taken place, the time-dependent deformation of the random copolymers with 57 and 46 wt.% Non was too large to determine $E_i$ robustly.

For block copolymers with a composition between the pure-glassy phase and the pure-crystalline phase, $E_i$ is expected to be a volume-weighted average of the modulus of the glassy phase and the crystalline phase.\[54\] With increasing Non content, the volume fraction of the crystalline phase will be increased, and thus the block copolymer elastic properties will increasingly reflect those of the crystalline phase. Indeed, $E_i$ gradually (and almost linearly) decreased from that typical for the glassy phase (4.3 GPa) to that typical for the crystalline phase (0.8 GPa). In conclusion, at intermediate composition the copolymer material with block architecture exhibited stiffer material response than the random architecture, as the block copolymer material has a higher degree of crystallinity and a higher $T_g$ than the random copolymer material. (N.B.: For systems based on other monomer units, the degree of crystallinity may have the opposite effect on the stiffness compared to the current study.\[28\])

Application of a small force oscillation to the indenter allows for investigation of the storage modulus $E'$ and the loss tangent $\tan \delta$. These properties are presented for the random copolymers in Figure 3.15. For two random copolymer materials in Figure 3.14b, the time-dependent plastic or very slow viscoelastic response to the load impeded the determination of $E_i$ from the quasistatic DSI experiments, but dynamic indentation, which probes the reversible (viscoelastic) response to a small contact load oscillation (here, at a frequency of 20 Hz), was performed successfully. $E'$ exhibited a gradual decrease with increasing Non content. For the random copolymers with up to 57 wt.% Non, $\tan \delta$ increased with increasing Non content; at 57 wt.% Non, the majority of the energy produced by the probe oscillation was dissipated, presumably as heat. Large heat dissipation relative to the elastically stored energy is typical for a material that is close to its $T_g$.\[28,53\] When the Non content increased even further, $\tan \delta$ decreased. The difference between the storage modulus $E'$ at 20 Hz and the quasistatic modulus $E_i$ decreased as well (Figure 3.15). It is concluded that the decrease in $\tan \delta$, which indicates a smaller viscous component in the visco-elastic material response, was caused by the increase in the degree of crystallinity upon increasing Non content.

The $E'$ of the block copolymers (not shown) exhibited the same decrease with increasing Non content as did the quasistatic moduli $E_i$. At intermediate compositions, the block copolymer materials were probed at a temperature well below their $T_g$ and contained a larger crystalline volume fraction than their random copolymer counterparts. Therefore, $\tan \delta$ at intermediate compositions...
Non contents is lower for the block architecture than for the random architecture (Figure 3.15).

![Graph](image)

**Figure 3.15:** The storage modulus $E'$ (random series only) and loss tangent $\tan \delta$ (random and block series) obtained by dynamic indentation (5.6 ± 0.4 %RH); quasistatic $E_i$ results are included for comparison.

### 3.5 Structure development with time

It was noted that during storage at ambient humidity, several diblock and triblock copoly(oxazoline)s started to crystallize. As an example, polarized optical microscopy images of the EtEtMe copolymer$^{[44]}$ after two years storage at ambient humidity are shown (Figure 3.16). The so-called ‘Maltezer crosses’ prove crystallinity. The crystallites are present throughout the thickness of the polymer film, as evidenced by the different heights where the crystallites are in focus (Figure 3.16).

![Micrograph](image)

**Figure 3.16:** Polarized optical micrograph of the EtEtMe triblock copoly(oxazoline), after two years of storage at ambient humidity.
The crystallinity was also observed on the Me homopolymer (Figure 3.17). No Maltezer crosses were observed for the Et and Phe homopolymer. The Me homopolymer (behaving as a tough, sticky material) was scraped off the glass slides. DSC analysis after drying the material for 3 days at 45 °C in vacuum, showed a small, broad endotherm (onset at 141 °C, peak at 176 °C), superimposed on a very broad endotherm exhibiting a peak at 105 °C. These endotherms form supporting evidence for the crystallinity of Me, although part of the broad endotherm is attributable to the heat necessary to evaporate the moisture still present in the material after drying.

No Maltezer crosses were observed on the droppcast poly(2-nonyl-2-oxazoline), although this material is semi-crystalline. That absence of Maltezer crosses is due to the small crystallite-size. During storage, no growth of the crystals had occurred for the droppcast Non sample, at least not to the extent that the crystallites would show up as loss of transparency or as Maltezer crosses in the optical microscope. In this context, it should be recalled that the transparent droppcast Non sample had nearly the same elastic modulus as the whitish melt-processed reference sample of identical composition (Section 3.2.1), indicating a comparable degree of crystallinity; however, the difference in transparency between both Non samples apparently indicates differences in their respective crystallite size. Crystallization of poly(2-nonyl-2-oxazoline) is governed by side-chain alignment,[58] while crystallization of poly(2-methyl-2-oxazoline) involves aligning of main-chains with respect to each other. Interestingly, also for poly(2-isopropyl-2-oxazoline), another poly(oxazoline) without a long linear alkyl side-chain, crystallization was reported.[33]

Seemingly, the side-chain alignment for the Non homopolymer is much faster than the alignment for the Me homopolymer, as the Non homopolymers already forms crystals during the cooling steps (40 K/min) in standard DSC measurements, as evidenced by the melting peak in the DSC trace for the poly(2-nonyl-2-oxazoline).[3] The mobility required for the alignment of poly(2-methyl-2-oxazoline) chains was presumably supplied by water taken up from the surrounding atmosphere. This water acts as a plasticizer as it reduces the $T_g$ of poly(2-methyl-2-oxazoline). This phenomenon of humidity-dependent crystallization is also observed for biomolecules (e.g., lactose)[59] and polar polymers, while crystallizable apolar polymers exhibit this behavior in organic solvents.[60]

A second role that is fulfilled by water molecules is evidenced upon drying the poly(2-methyl-2-oxazoline) films. On the stored film, crystallites were observed up to the edge of the droppcast spot (Figure 3.17). However, after drying the sample for two days in vacuum at 45 °C, which is below the $T_g$ of dry Me, and therefore also below a possible melting temperature $T_m$ of Me,[28] a transparent rim was observed, where no Maltezer crosses were observed anymore. In other words: at the rim, where the sample is thin, the crystallites disappeared, while in the thicker center some crystallites still remained. Indeed, upon further drying the size of the transparent rim increased. This suggests that water is built into the crystals, also explaining the relatively low melting temperature compared to the glass.
transition temperature of dry Me: using the onset of the endotherm reported above, $T_g/T_m$ (in Kelvin) was 0.85, while usually this ratio is between 0.4 and 0.7.\textsuperscript{[28]} The observation that after the DSC experiment, the weight of the crucible with Me homopolymer had decreased by 0.175 mg, which was 9% of the mass of the dried DSC sample-material, supports this suggestion. It is hypothesized that the attractive hydrogen-bonding interaction between water and poly(2-methyl-2-oxazoline), which is the driving force for crystallization, is related to the intermolecular interaction additional to the Van der Waals forces that resulted in the high stiffness of poly(2-methyl-2-oxazoline) discussed in Section 3.2.2.

![Figure 3.17](image_url)

**Figure 3.17:** Polarized optical micrograph of the rim of the Me homopolymer after two years of storage at ambient humidity. Before drying, the crystallites were present up till the rim, as verified upon removing the polarization of the light.

### 3.6 Conclusions

The elastic moduli of a diblock and a triblock copoly(2-oxazoline) library were screened in a HTE approach using depth-sensing indentation. Furthermore, libraries were investigated where the random monomer distribution over the polymer chain was compared to the diblock architecture. Depth-sensing indentation was successful, while sample preparation for standard macroscopic tensile or compression testing often fails for such brittle materials. At low RH, the homopolymers that were below their glass transition temperature (2-methyl, 2-ethyl, and 2-phenyl-2-oxazoline) exhibited an elastic modulus $E_i$ of 4.3 to 7.0 GPa. The $E_i$ of the 2-nonyl-2-oxazoline homopolymer (0.8 GPa) was lower, as the material was tested above its $T_g$. Crystallization of the nonyloxazoline prevented the modulus from decreasing into the range typical for amorphous polymers above $T_g$. The $E_i$ of poly(2-ethyl-2-oxazoline) at low RH was low compared to poly(2-methyl-2-oxazoline) and poly(2-phenyl-2-oxazoline) as the $T_g$ of poly(2-ethyl-2-oxazoline) is only 34 °C above the testing temperature. Due to water uptake
from the surrounding atmosphere, even at low RH, \( T_g \) is decreased and, as \( T_g \) approaches the temperature at which the measurements were performed, \( E_i \) is decreased as well. The \( E_i \) of poly(2-methyl-2-oxazoline) was higher than that expected for glassy polymers. This high \( E_i \) is attributed to hydrogen bonding or polar interactions between polymer chains. The \( E_i \) of AB diblock copolymers were between those of the A and B homopolymers. The \( E_i \) of copolymers with one poly(2-nonyl-2-oxazoline) block (~1.4 to 2.0 GPa at low RH) were closest to the \( E_i \) of poly(2-nonyl-2-oxazoline), which is consistent with the glassy phase being the minority volume fraction of such a copolymer. At higher humidities, the \( E_i \) of the poly(2-methyl-2-oxazoline) and poly(2-ethyl-2-oxazoline) decreased dramatically, which is caused by water uptake from the surrounding.

The small increments in chemical composition for the triblock copolymer library allowed for a more detailed study into the parameters governing these material properties. The stiffness of ABA triblock copolymers was in between that of the A homopolymer and of the AB diblock copolymer. Part of the variation in \( E_i \) between corresponding ABC triblock copolymers containing Me, Et and Non could be related to variation in the chemical composition. The differences in composition resulted in slightly different phase segregation and crystallization behavior, which, subsequently, caused the variation in stiffness. The location of the Non block (middle or end block) may have influenced the resulting phase morphology as well. The simpler phase behavior of the Me/Et/Phe system resulted in smaller variation between the stiffness of triblock copolymers with comparable composition than for the Me/Et/Non system. The monomer distribution along the copolymer chains (random vs. block) significantly affected both the nature of the phases present and their transition temperatures. The volume fractions of the amorphous and the crystalline phases, as well as the location of the glass transition temperature with respect to room temperature, governed the mechanical properties.

For random copolymers with intermediate Et:Non composition, the ethyl side chains disturb the crystallization of the nonyl side chains. At the other side of the composition range, the long nonyl side-chains increase the flexibility in the Et-rich amorphous phase, thereby decreasing the \( T_g \). This results in a lower degree of crystallinity and a lower \( T_g \) (i.e., closer to room temperature) for these random copolymers compared to their block copolymer counterparts (the Non in the block copolymers can segregate more easily into Non-rich crystalline regions). Therefore, random copolymers at intermediate Et:Non compositions exhibited greater mechanical energy dissipation (higher \( \tan \delta \)), greater creep compliance and lower elastic moduli \( E_i \) than the block copolymers of corresponding composition.

Consideration of the thermal history of the mechanically interrogated samples improved the understanding of the relation between the phases present in the material and the resulting viscoelastic properties. Main-chain crystallization of poly(2-methyl-2-oxazoline) occurs. In this slow process, water plays a crucial role: it promotes segmental mobility necessary for the crystallization, and it is incorporated in the crystals formed.
In conclusion, poly(2-oxazoline) side groups and the distribution of the monomer units over the copolymer chain have a significant effect on the surface energies, thermal transitions and mechanical properties of the material, as well as on their response to humidity conditions. This demonstrates that structural control is an excellent way to tune and optimize polyoxazoline-based materials for high performance applications which require, alongside other functionalities that copoly(2-oxazoline)s can offer, specific mechanical properties.

3.7 Experimental

Preparation of the polymer spots for indentation measurements. Homopolymers and diblock, triblock and random copoly(2-oxazoline)s have been prepared via sequential living cationic ring opening polymerization.\textsuperscript{[3,6,7]} Twenty (20) mg of each copolymer were dissolved in 50 μL chloroform (Biosolve LTD), except for the chain-extended poly(2-methyl-2-oxazoline), MeMe, which did not dissolve in chloroform at this concentration and was dissolved in demineralized water. After complete dissolution, approximately 5 μL from each solution was pipetted onto a glass slide (Marienfield, Lauda-Königshofen, Germany), with a nominal center-to-center spacing of 4 mm between polymer spots. Four such glass slides were prepared. The diameter and the height (after 2 days drying under ambient conditions) of the spots ranged from approximately 2 to 3.5 mm, and from 100 to 400 μm, respectively, as measured with an optical profilometer (Fogale Zoomsurf) and a mechanical profilometer (Tencor P10). Only the MeMe sample had a significantly lower thickness (50 μm) due to the alternative solvent used.

Accurate determination of the elastic modulus from the indentation load-displacement responses requires flat sample surfaces. Profilometry showed that this condition was met for indentations near the middle of the polymer spots. Some of the polymer spots of the triblock copolymer library exhibited an irregular shape, e.g. a non-circular circumference, cracks or a ridge within the spot. Such morphological irregularities make it more difficult to find a suitable region on the sample surface that is perpendicular to the indentation axis, as consistent with the normal contact loading assumed in data analysis used to extract the elastic moduli from the load-depth responses. In order to improve the data quality, for the Berkovich series on the triblock copolymers, only results are reported if the difference in moduli obtained on duplicate sample-slides was <10%.

One glass slide containing the polymer libraries was dried at ambient conditions for four days, dried for four hours at 40 °C, and subsequently dried at 45 °C under vacuum overnight prior to the indentation measurements using a Nanotest600 indentation instrument (Micro Materials LLC, Wrexham, UK). Two additional glass slides with the libraries were dried for three weeks at ambient conditions and another three weeks at 40 °C in vacuum, and then transferred to a different TriboIndenter indentation instrument (Hysitron, Inc., MN, USA). These samples resided at low humidity (<7%) for one week before testing at 5.4% relative humidity. After the experiments at low RH, the relative humidity was raised to 40% RH and two weeks later the measurements were repeated.

Reference (co)polymer materials. Two solvent-free reference samples were prepared: the PheEt copolymer was dropcast on a separate glass slide and then annealed above the corresponding \( T_g \), and the NonNon homopolymer was compression molded and then heated above the corresponding melting
An HTE study of the elastic properties of poly(2-oxazoline)s
temperature on a separate glass slide. The surface roughness of these reference samples that were processed at relatively high temperature was expected to be greater than that of the library samples. Tapping mode atomic force microscopy (AFM) indicated that even the reference samples possessed relatively smooth surfaces, although the PheEt reference sample surface exhibited some randomly dispersed protrusions (spaced ~1.5 µm apart, surface to peak height <29 nm and $R_a$ of 0.85 nm) and the NonNon reference sample surface exhibited randomly dispersed pits (spaced ~1 µm apart with a surface-to-pit amplitude of <40 nm and $R_a$ of 3.8 nm). These surface conditions may cause minor errors (<5%, in the worst case of indenting precisely on top of a protrusion or in a pit <10%) for the shallowest indents resulting from the lowest maximum loads.\(^{[47]}\) For the indents employing higher loads these errors quickly diminish. A fortunate detail is that NonNon, the sample with the greatest surface roughness, has a low $E$ and therefore relatively deep indents (>400 nm) even at the lowest maximum load.

**Depth-sensing indentation (DSI).** Indentation experiments were conducted on two instruments: a NanoTest600 (Micro Materials LLC, Wrexham, UK; maximum force of 35 mN at NT1 gain settings) and a TriboIndenter (Hysitron, Inc Minnesota, MN, USA; maximum force of 10 mN). The humidity in the NanoTest600 indenter case was regulated by flushing with nitrogen gas and by pumping the air-nitrogen mixture from the indenter case through a tube of desiccant. During the measurements, the relative humidity (RH) was maintained at 9.0 ± 0.8% via the nitrogen flow only, to avoid noise due to the circulation pump, while the temperature was maintained at 25 ºC. The indentations were executed in load control mode, with a loading time, hold time at maximum load, and an unloading time of 2 s, 10 s and 1 s, respectively. For visco-elastic materials, such a combination of a hold time and a quick unloading is necessary for determining $E_i$.\(^{[36,37]}\) No thermal drift correction was applied as the thermal drift is typically very small (~0.01 nm/s) for this instrument. Three indentations (spaced 30 µm apart) to 2 mN maximum load were made per sample at an optically inspected position on every polymer spot where the surface appeared smooth and perpendicular to the loading direction. Measurements were performed using a rounded conical, diamond indenter with an effective radius of 4.1 µm. For several samples, indentations with a Berkovich (trigonal pyramid) indenter were made as well. On the MeMe sample, profile scans of the residual indentations were made using the NanoTest600: the indenter tip scanned the surface with 50 µN topography load and 0.25 µm/s scanning velocity. The indentation experiments with the TriboIndenter were performed at 5.4 ± 0.4% and 40 ± 1% RH with a diamond Berkovich indenter. The relative humidity was measured using a Hygrometer testo 608-H2. Before every indent, the indenter was held in contact with the surface, to allow for piezoactuator stabilization (35 s) and drift correction (40 s), at a contact load of only 0.5 µN to prevent any deformation prior to the indentation experiment. The drift rate (typically 0.1 nm/s) was automatically determined over the last 20 s of the 40 s period. After lifting the tip 30 nm and reapproaching the surface (surface detection at a load of 0.5 µN), the tip was loaded to maximum load in 10 s, held at maximum load for 10 s and unloaded in 2 s. The maximum load was reduced in steps of 300 µN from 3 mN to 300 µN. From the 10 measurements (spaced 50 µm apart) per sample, the first two were left out from the analysis to even further reduce the influence of drift. On the MeMe and MeEt samples, residual indents were imaged using the TriboIndenter Berkovich diamond indenter as a contact profilometer with a preload of 0.5 µN.
The contact depth and area of the indents were, even for the lowest loads, at least 150 nm and 0.9 µm² respectively. Furthermore, the strained material volume extended much deeper than the indent itself. As the indentation length scales were much larger than the lengths of the polymer chains studied (smaller than 40 nm in completely stretched conformation), the ‘composite’ stiffness of the phases present in the material is obtained.

**Depth-sensing indentation analysis.** Load-displacement responses were analyzed using the method of Oliver and Pharr [23] by fitting the unloading response from $0.95P_{\text{max}}$ to $0.20P_{\text{max}}$ with the conventional power law form to obtain the slope at the start of the unloading $S$. The projected contact area as a function of contact depth (the ‘area function’) was determined by prior indents on quartz, the standard reference material. For the TriboIndenter, this area function was extended to larger distances from the tip apex than could be reached on quartz by indentations on polycarbonate. From the area function and the contact depth $h_c$ the projected contact area $A$ can be calculated. Using $\beta = 1$, the reduced modulus $E_r$ is then calculated and subsequently, with $E_{\text{diamond}} = 1140$ GPa, $v_{\text{diamond}} = 0.07$ and $v_{\text{sample}} = 0.4$, $E_i$ is obtained. $E_i$ of polymers slightly exceeds the value of $E$ obtained by uniaxial tension due to several factors including high strains relative to the elastic limit, superposed hydrostatic stress, and assumptions of contact at the indent perimeter [24,61]. Occasionally, an indentation response was neglected from analysis due to local surface imperfection-induced deviation from the other responses measured on the same sample. The error bars present one standard deviation out of eight or seven (TriboIndenter) and three (NanoTest600) measurements, unless otherwise stated.

**Dynamic depth-sensing indentation.** Storage moduli $E'$ and loss tangent $\tan \delta$ were determined using the TriboIndenter nanoDMA (nano dynamic mechanical analysis) module, whereby an oscillating load (nominally 10 µN, frequency 20 Hz) was superimposed over the quasistatic load (nominally 300 µN). The storage modulus $E'$ and $\tan \delta$ are calculated from the ratio and the phase lag between the applied load oscillation and the resulting displacement oscillation [47,62,63]. The latter was between 0.9 and 4.5 nm in amplitude. The presented storage moduli $E'$ have been converted from ‘reduced’ to ‘indentation’ storage moduli, using the same $E_{\text{diamond}}$, $v_{\text{diamond}}$ and $v_{\text{sample}}$ as listed above. Five experiments were conducted on both duplicate samples of one copolymer material; the first two were disregarded to minimize effects of thermal drift and the average and standard deviation out of the six remaining measurements are reported. It is noted that the contact area used to calculate the storage modulus is somewhat flawed (see Chapter 2).

**Differential scanning calorimetry (DSC).** Thermal transitions were determined by differential scanning calorimetry on a Netzsch DSC 204 F1 Phoenix under a nitrogen atmosphere from −100 °C to 170 °C with a heating rate of 40 K/min for the glass transition temperature and a heating rate of 10 K/min for the melting temperature (the first heating run to 170 °C, which was followed by a cooling run at 40 K/min, was not considered for the subsequent calculations). For Et$_{60}$-r-Non$_{40}$, Et$_{50}$-r-Non$_{50}$ and Et$_{40}$-r-Non$_{60}$, DSC measurements were repeated with an annealing period before the last heating step in the DSC measurement program to provoke crystallization. The annealing was performed at 40 °C for 24 hours for Et$_{60}$-r-Non$_{40}$ and Et$_{50}$-r-Non$_{50}$ and for 10 minutes (preceded by slow unassisted cooling from 200 °C to 40 °C) for Et$_{40}$-r-Non$_{60}$.

**Thermal gravimetric analysis (TGA).** Thermal gravimetric analysis was conducted (Netzsch TG209 F1) at a heating rate of 20 K/min on 5 to 10 mg of selected diblock copolymer materials to probe the hygroscopicity of these materials. These samples, which were taken from storage vials that were not
hermetically sealed, were not dried before the TGA experiments. These materials are assumed to be equilibrated with ambient humidity.

**Infrared spectroscopy (FT-IR).** FT-IR was performed using a Perkin Elmer SpectrumOne single bounce ATR instrument. Spectra were taken after storing the materials for two weeks in a desiccator (1.7% RH), transporting the desiccator to the FTIR, quickly transferring with tweezers a grain of each material onto the ATR crystal, crushing the grain and measuring immediately afterwards.

**Surface energy determination.** Contact angle measurements were performed on polymer films prepared by spin coating of chloroform solutions (20 mg/mL) of the polymer on pre-cleaned microscopy slides at 1000 rpm during 90 seconds using a WS-400/500 series spin-coater from Laurell Technologies Corporation. An automated OCA30 optical contact angle measuring instrument from Dataphysics was used to determine the contact angles of both diiodomethane and ethylene glycol as apolar and polar test liquids, respectively. The surface energy (SE) was calculated using the equation of state theory.[8,64]

**Polarized optical microscopy.** (Polarized) optical microscopy was conducted using an Axioplan imaging 2, (Zeiss, Jena, Germany) at various magnifications.

### 3.8 Appendix

Apart from the modulus, also a hardness $H$ can be determined by the Oliver and Pharr method.$^{[23]}$ This is usually defined as the mean contact pressure, *i.e.*, the load just prior to unloading, $P_{\text{max}}$, divided by the projected contact area $A(h_c)$:

$$H = \frac{P_{\text{max}}}{A(h_c)} \quad (3.5)$$

As the contact area depends on both the plastic and the elastic response of the material, the obtained hardness values do not reflect solely the material’s resistance to plastic deformation, and are lower than a hardness value that would reflect the plastic deformation only.$^{[65]}$

Interestingly, the hardness and moduli obtained by indentation using a self-similar indenter probe (Berkovich) for the materials discussed in Section 3.2 exhibit a linear relation (Figure 3.A). The relatively small Y-axis offset of the obtained fit (0.0097 GPa) shows that the relation is nearly proportional (with 0.071 as the slope). As discussed elsewhere,$^{[61,63]}$ the hardness obtained for materials exhibiting time-dependent deformation depends on the experimental parameters. Therefore, the exact relation between $H$ and $E_i$ depends on the applied loading rate, hold time and unloading rate. The here observed linearity is an indication that the resistance to plastic deformation scales approximately with the resistance to elastic deformation, as mathematically derived elsewhere.$^{[65]}$

However, correlations between $H$ and $E_i$, such as shown in Figure 3.A are not very sensitive to deviations from linearity in the relation between the resistance to elastic and plastic deformation.$^{[65]}$

Therefore, not more than an indication on the linearity between elastic and plastic deformation can be obtained from Figure 3.A.
Figure 3.A: The correlation between elastic modulus $E_i$ and the mean contact pressure $H$ for diblock copolymers at two relative humidities, together with a fit for the data obtained at 5.4% relative humidity.

3.9 References and notes


During this work, we observed for MeEtPhe an $E_i$ that was 0.4 GPa lower than for the triblocks with comparable composition but different block order. This triggered us to assess its
DSC data, which demonstrated a ~8 °C lower $T_g$ than for its counterparts and, finally, also its $^1$H NMR data. Those data showed that for the MeEtPhe and also for MeEtMe and MeEtNon, the wrong stock solution was used, so EtEtMe, EtEtPhe and EtEtNon copolymers were synthesized instead. Therefore, no results are shown for MeEtMe, MeEtPhe and MeEtNon. The ability to point out this error actually underlines the accuracy of the physical characterization.

[46] The PheNonPhe and the NonPheNon stiffness for the Berkovich series are based on eight measurements on one dot only, as the spot on the duplicate slide was not measured.
[48] The indentation experiments with the Berkovich on PheEtPhe resulted in an $E_i$ higher than expected combined with a large standard deviation, and the duplicate spot was not measured. Therefore, that $E_i$ is not presented.
[57] Some quasistatic indentation moduli displayed in Figure 3.14b should be treated with circumspection: for the random copolymers of 33 and 67 wt.% Non, the displacement during unloading is clearly not only governed by elastic material response: the ratio of the displacement rate at the start of the unloading to the displacement rate at the end of the hold period is only 1.8:1 and 4.6:1 for these samples, respectively. Furthermore, for the random copolymers with 67, 75 and 82 wt.% Non the result is based on only two, four or five load-displacement responses, respectively, as the other responses (with higher maximum loads) were outside the depth range of the probe area function calibration.
Chapter 4

Elastic properties of supramolecular materials

Abstract
The small volume probed during DSI testing render the technique suitable for mechanical characterization of compounds of which, in the early research stage, only small amounts are synthesized, as is the case for the materials described in this chapter. Using non-covalent interactions, block copolymers can be assembled. In addition, the supramolecular moiety allows for the incorporation of optical, responsive, or self-repairing properties.

The mechanical properties of terpyridine-functionalized polystyrene/poly(butylacrylate) AB-[diblock copolymers, and the corresponding AB-[M]-BA architectures obtained through metal-ligand coordination were investigated. Depending on the phase-separation behavior and, therefore, on the degrees of polymerization of both blocks, the supramolecular linking increased the material stiffness significantly.

Alternating 1,1-diphenylethylene/styrene copolymers exhibit a high material stiffness. Connecting, using metal-ligand interactions, alternating 1,1-diphenylethylene/styrene copolymers of various degrees of polymerization with poly(ethylene glycol) resulted in supramolecular A-[M]-B block copolymers. The stiffness of these block copolymers spanned a relatively large range.

Part of this chapter has been accepted for publication: C. Ott, J. M. Kranenburg, C. Guerrero-Sanchez, S. Hoeppener, D. Wouters, U. S. Schubert, Macromolecules 2009.
4.1 Introduction

In supramolecular chemistry, non-covalent interactions, such as metal coordination, hydrogen bonding, van der Waals forces, \(\pi-\pi\) interactions and electrostatic effects are used to obtain new materials and/or highly ordered structures via spontaneous self-assembly.\[^{[1]}\] This research area is inspired by biological systems where weak non-covalent interactions are present abundantly. Supramolecular bonds between molecules can be used to engineer new materials where functionalities such as conductivity,\[^{[2]}\] luminescence,\[^{[3,4]}\] and self-healing properties\[^{[5]}\] are incorporated and mechanical properties\[^{[3,6]}\] and processability\[^{[6]}\] are improved. The extraordinary versatility of this approach relies on the easy tuning of bond strength, lifetime and directionality by applying external stimuli such as temperature, pH value and redox state.\[^{[7]}\]

Self-healing properties can be incorporated by careful tuning of the binding strength and the molecular architecture, resulting in systems where supramolecular bonds break above a critical level of deformation, but can heal when the fracture surfaces are brought into contact again.\[^{[5,8,9]}\] For elastomers it was shown that the different types and binding strengths of non-covalent interactions result in a different trade-off between re-processability and mechanical properties.\[^{[10]}\]

![Increasing Strength of Interactions](image)

**Figure 4.1:** Several different supramolecular interactions exist; their binding strength is weaker than that of covalent bonds.\[^{[7]}\]

Tethering chelating ligands\[^{[11-14]}\] (e.g. bipyridines or terpyridines) to macromolecules allows the formation of materials, in the presence of suitable transition metal ions, that combine the characteristic features of polymers and metal-ligand complexes. Most commonly used metal ions for terpyridine systems are Fe, Ru, Os, Co, Ni, Pt, Cu, Mn, Ag, Zn, Cd, and Hg in low oxidation states which form pseudo-octahedral complexes with two terpyridine ligands upon complexation.\[^{[15]}\] Os(II) and Ru(II) ions are of special importance since no ligand exchange takes place. Therefore, they are called inert metal-terpyridine complexes. Metallo-supramolecular block copolymers can be synthesized by linking different polymer chains via *bis*-terpyridine complexes.\[^{[16,17]}\]
The powerful strategy of combining controlled/living polymerization techniques with supramolecular chemistry allows the synthesis of hybrid materials using the supramolecular complexation approach, generating complex systems from well-defined polymer blocks in a kind of LEGO© procedure.[18] Block copolymer architectures can be prepared in which chemically different polymer blocks are linked together via metal-ligand complexes. In this way, new block copolymers with specific photochemical, electrochemical and photophysical properties[19-21] can be created in a straightforward fashion. Such systems have been investigated into detail in our group and have been coined ‘metallo-supramolecular block copolymers’.

The combination of two thermodynamically incompatible polymer segments (of various lengths) within the same material gives rise to a wide range of phase morphologies.[22] The supra-molecular link between the different segments reduces the length-scale of the phase separation.[22,23] Depending on the lengths of the block copolymers and the interactions between the blocks, the phase morphology can be tailored,[22] thereby modifying the mechanical properties of the material.

Depth-sensing indentation forms a suitable technique to probe the elastic properties of supramolecular materials that, in the early research stage, are usually synthesized on a sub-gram scale, as this technique requires only small amounts of material for testing.

### 4.2 Polystyrene-poly(butyl acrylate) block copolymers

Functionalized block copolymers can be synthesized via nitroxide-mediated polymerization (NMP) with sequential monomer addition using a terpyridine-functionalized alkoxyamine based on 2,2,5-trimethyl-4-phenyl-3-azahexane nitroxide (TIPNO) as the initiator. By first adding the \( n \)-butyl acrylate monomer, and subsequently the styrene monomer, polystyrene-block-polybutylacrylate-terpyridine (PS\(_{x}\)-b-PBA\(_{y}\)-Tpy) diblock copolymers were synthesized in an approach comparable to the synthesis described in ref. 14. The degree of polymerization of the PS and the PBA blocks were determined by integrating the relevant \(^1\)H NMR spectroscopy peaks. Table 4.1 also lists the molar masses and the polydispersity indices (PDI) as determined by gel permeation chromatography (GPC). The molar masses determined by both methods are in good agreement.[24]
Table 4.1: Functionalized polystyrene-\textit{b}-poly(butyl acrylate) diblock copolymers.

<table>
<thead>
<tr>
<th></th>
<th>$^1$H NMR</th>
<th>GPC*</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>$M_n,\text{NMR}$ (g/mol)</td>
<td>$M_n$ (g/mol)</td>
</tr>
<tr>
<td>PS$<em>{140}$-\textit{b}-PBA$</em>{90}$-Tpy</td>
<td>26700</td>
<td>23500</td>
</tr>
<tr>
<td>PS$<em>{330}$-\textit{b}-PBA$</em>{260}$-Tpy</td>
<td>68300</td>
<td>57200</td>
</tr>
</tbody>
</table>

* GPC was performed on a Waters Styragel HT4-column with a RI detector (Waters 1414) using a mixture of chloroform, triethylamine and isopropanol (94:4:2) as the eluent; calibration: PMMA standards.

These \textit{mono}functionalized terpyridine diblocks were complexed with Fe(II) acetate in a solvent mixture (8:2) of chloroform (CHCl$_3$) and methanol (MeOH), which was refluxed overnight. The counter ion was exchanged from acetate ($\text{AcO}^-$) to hexafluorophosphate ($\text{PF}_6^-$) using NH$_4$PF$_6$. A similar approach is described in ref. 25. The materials were purified by BioBead columns (BB-SX1, CH$_2$Cl$_2$) followed by two times precipitation from CHCl$_3$ into cold MeOH. The $^1$H NMR spectra of the final purified AB-[Fe]-BA block copolymers showed that no uncomplexed terpyridine was present. The representative structure of the resulting PS-\textit{b}-PBA-[Fe]-PBA-\textit{b}-PS diblock copolymers is shown in Scheme 4.1.

Scheme 4.1: Schematic representation of polystyrene-poly($n$-butyl acrylate) block copolymer materials complexed with iron ions.

The uncomplexed and complexed compounds were characterized by differential scanning calorimetry (DSC). For PS$_{140}$-\textit{b}-PBA$_{90}$-Tpy, a single, very broad, glass transition was observed (Figure 4.2a) indicating incomplete phase-separation. Due to the small block length, the driving force for phase-separation is reduced.$^{[22]}$ The DSC trace of its complexed counterpart exhibited (reproducibly) a glass transition with a large excess enthalpy at $-47 \, ^\circ\text{C}$, while the change in slope in its DSC trace at $82 \, ^\circ\text{C}$ indicates another $T_g$ with a limited visibility due to the broadness of the transition, which may indicate a large variation in the size of the PS-rich phase. The exact location of the $T_g$ is difficult to determine, and therefore not shown in Figure 4.2a. It is noted that the complexation, the concomitant presence of the Fe$^{2+}$ and PF$_6^-$ ions and/or the higher effective degree of polymerization changed the phase segregation behavior for this material. Also for other systems, it has been reported that the presence of ions influences the phase-segregation behavior.$^{[26,27]}$
Elastic properties of supramolecular materials

For PS$_{330}$-b-PBA$_{260}$-Tpy, two glass transitions were observed. The $T_g$ of the PBA-rich phase was located at approx. $-35$ °C (Figure 4.2), which is somewhat above the $T_g$ of $-49$ to $-54$ °C reported for PBA in literature.$^{[28]}$ The difference with the literature value indicates that either some polystyrene or terpyridine is present in the PBA-rich phase. The presence of the latter can be easily understood from Scheme 4.1. A smaller glass transition was observed at 99 °C, which is attributable to the PS phase. The DSC trace of its complexed counterpart was nearly identical, only the $T_g$ of the PBA-rich phase was located at slightly lower temperature, and the associated excess enthalpy was slightly higher.

![DSC traces obtained for the complexed and uncomplexed (a) PS$_{140}$-b-PBA$_{90}$-Tpy and (b) PS$_{330}$-b-PBA$_{260}$-Tpy materials.](image)

**Figure 4.2:** DSC traces obtained for the complexed and uncomplexed (a) PS$_{140}$-b-PBA$_{90}$-Tpy and (b) PS$_{330}$-b-PBA$_{260}$-Tpy materials.

On the uncomplexed and complexed compounds, indentation experiments were performed. The material stiffnesses, obtained by analyzing the unloading branch of the obtained load-displacement responses,$^{[29]}$ are shown in Table 4.2. The complexed and uncomplexed PS$_{140}$-b-PBA$_{90}$-Tpy exhibited a higher stiffness than the corresponding PS$_{330}$-b-PBA$_{260}$-Tpy material, which is attributable to their higher PS content (the PS:PBA mass ratios are given in Table 4.2). The DSC results showed that the complexed and uncomplexed PS$_{330}$-b-PBA$_{260}$-Tpy material consists of two phases. The PS-rich phase is at room temperature below its glass transition, and therefore glassy. The PBA-rich phase is above its glass transition, and thus
much softer than the PS-rich phase. The resulting material stiffnesses are therefore lower than the typical material stiffness of polystyrene (usually, indentation experiments yield \( E_i = 4.2 \) GPa for polystyrene).

Table 4.2: Material stiffness \((E_i)\) of the PS-\(b\)-PBA-Tpy materials.

<table>
<thead>
<tr>
<th>PS:PBA mass ratio</th>
<th>Uncomplexed</th>
<th>Complexed</th>
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<tbody>
<tr>
<td>(PS_{140\text{-}b\text{-}PBA_{90}\text{-}Tpy})</td>
<td>1.26:1</td>
<td>0.63 ± 0.02 GPa</td>
</tr>
<tr>
<td>(PS_{330\text{-}b\text{-}PBA_{260}\text{-}Tpy})</td>
<td>1.03:1</td>
<td>0.32 ± 0.03 GPa</td>
</tr>
</tbody>
</table>

For the \(PS_{140\text{-}b\text{-}PBA_{90}\text{-}Tpy}\) material, the stiffness is increased upon complexation. The hard A-domains can act as cross-links by connecting several chains. Upon complexation, effectively AB-[M]-BA copolymers are formed. When the hard A-blocks at the extremities of the supramolecular ‘chain’ phase-segregate into different hard-block domains, the resulting mechanical interaction between different hard block domains impedes the material deformation, resulting in a higher resistance to elastic deformation, i.e., a higher \( E_i \).

On the other hand, for the \(PS_{330\text{-}b\text{-}PBA_{260}\text{-}Tpy}\) material the modulus remained approximately constant upon complexation, which can be understood from the nearly identical DSC traces for the complexed and uncomplexed material, and the fact that the density of supramolecular bonds is lower than for the \(PS_{140\text{-}b\text{-}PBA_{90}\text{-}Tpy}\) material, due to its higher degree of polymerization compared to \(PS_{140\text{-}b\text{-}PBA_{90}\text{-}Tpy}\). It is therefore not too surprising that the effect of the complexation is at least smaller. Furthermore, PS extremities from the same AB-[Fe]-BA supramolecular chain may reside in the same lamella, which is probably less effective in raising the modulus than both chain ends segregating into different domains. (Based on the PS and PBA volume fractions obtained for the \(PS_{330\text{-}b\text{-}PBA_{260}\text{-}Tpy}\), phase-segregation is expected to result in a lamellar\(^{[22]}\) morphology.)

In conclusion, it is shown that supramolecular linking by metal-ligand complexation can increase the material stiffness substantially. However, whether the material stiffness increases depends on the density of the supramolecular groups and on the phase-segregation behavior of the material, which, in turn, is influenced by the degrees of polymerization of the different blocks and by the complexation.

### 4.3 Poly(ethylene glycol)-superpolystyrene copolymers

Alternating 1,1-diphenylethylene/styrene copolymers can be used up to higher temperatures than polystyrene due to the stiffening of the polymer main chain by the extra phenyl-ring.\(^{[30]}\) Therefore, they are often referred to as “superpolystyrene” (SPS). A-[M]-B block copolymers were synthesized by linking terpyridine-functionalized SPS to terpyridine-functionalized
poly(ethylene glycol) as shown schematically in Scheme 4.2. The ruthenium(III) ions in the RuCl$_3$ poly(ethylene glycol) monoclinic complex were reduced to ruthenium(II). The Cl$^-$ counterions were exchanged using NH$_4$PF$_6$.\[31\] ABA block copolymers were synthesized by reacting poly(ethylene glycol) with terpyridine groups on both ends with the RuCl$_3$ superpolystyrene monoclinic complex. The synthesis, purification, as well as the evidence (from GPC, GPC with a photo-diode-array detector and $^1$H NMR spectroscopy) for a successful complex formation and purification are described elsewhere.\[31\] Table 4.3 summarizes the number average molar masses and the polydispersity indices (PDI) of the starting materials and the corresponding block copolymers obtained by $^1$H NMR spectroscopy and GPC. The degrees of polymerization of the SPS and the PEG block are obtained by comparing the relevant $^1$H NMR peak intensities of protons belonging to the terpyridine moiety to that of protons characteristic for the SPS and the PEG.\[31\] Also the glass transition temperatures of these materials as observed by DSC (Figure 4.3) are listed in Table 4.3.

Interestingly, the GPC results of the metallo-supramolecular block copolymers show a decrease in $M_n$ with increasing length of the SPS block. This inaccuracy can be attributed to the calibration (PEG standards) and the solvent used for the GPC measurements: DMF is a poor solvent for the SPS block, resulting in a collapse of the SPS, and therefore a small hydrodynamic radius and a long elution time. Furthermore, the interaction of the complex with the column material impedes accurate determination of the molar mass by GPC for the complexed materials. The important observation from the GPC traces (which can be found in ref. 31) is not so much the obtained $M_n$, but the observation that the molar mass distribution is unimodal (as also suggested by the low PDI values), which indicates a successful block copolymer synthesis.

![Scheme 4.2: Schematic representation of the preparation of A-[Ru]-B copolymers via supramolecular metal-ligand interactions.](image-url)
Table 4.3: Number average molar mass ($M_n$), polydispersity indices (PDI) and glass transition temperatures ($T_g$) of the uncomplexed copolymers and the corresponding metallo-supramolecular block copolymers.

<table>
<thead>
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<th>$^{1}H$ NMR</th>
<th>GPC</th>
<th>DSC</th>
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<tr>
<td></td>
<td>$M_n$ (g/mol)</td>
<td>$M_n$ (g/mol)</td>
<td>PDI</td>
</tr>
<tr>
<td>SPS$_{11}$-[</td>
<td>3600</td>
<td>2100 *</td>
<td>1.17 *</td>
</tr>
<tr>
<td>SPS$_{22}$-[</td>
<td>6700</td>
<td>4700 *</td>
<td>1.11 *</td>
</tr>
<tr>
<td>SPS$_{39}$-[</td>
<td>11600</td>
<td>7800 *</td>
<td>1.14 *</td>
</tr>
<tr>
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<td>10800 *</td>
<td>1.21 *</td>
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<tr>
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<td>7200</td>
<td>5700 **</td>
<td>1.05 **</td>
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<tr>
<td>SPS$<em>{22}$-[Ru]-PEG$</em>{70}$</td>
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<td>5200 **</td>
<td>1.11 **</td>
</tr>
<tr>
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<td>4700 **</td>
<td>1.12 **</td>
</tr>
<tr>
<td>SPS$<em>{66}$-[Ru]-PEG$</em>{70}$</td>
<td>22800</td>
<td>4400 **</td>
<td>1.08 **</td>
</tr>
</tbody>
</table>

* GPC in DMA with LiCl (2.1 g/L) as eluent using polystyrene calibration.
** GPC in DMF with NH$_4$PF$_6$ (0.8 g/L) as eluent using poly(ethylene glycol) calibration.

The glass transition $T_g$ observed by DSC of the terpyridine-functionalized SPS increased from 137 °C for $n = 11$ to 165 °C for $n = 66$ (Figure 4.3a, Table 4.3). This is in agreement with the common observation that the $T_g$ is reduced for smaller chain lengths.$^{[32,33]}$ The SPS chains are expected to be more rigid than polystyrene chains because the extra phenyliner restricts its free rotation. Indeed, the glass transition temperature of the SPS was higher than for polystyrene: the $T_g$ of conventional polystyrene of corresponding $M_n$ increases from 55 °C to 89 °C and reaches at higher molar masses a plateau-value of 100 °C.$^{[28,32]}$ For comparison purposes, also SPS$_{11}$-[Ru]-SPS$_{11}$ was prepared. This material exhibited a $T_g$ of 162 °C, which is slightly higher than the $T_g$ observed for SPS$_{22}$-[-. Furthermore, the SPS$_{11}$-[Ru]-SPS$_{11}$ exhibited only negligible excess enthalpy, in contrast to the uncomplexed SPS-[. The SPS$_n$-[Ru]-PEG$_{70}$ block copolymers show a decreased $T_g$ compared to the corresponding SPS$_n$-[ counterparts: due to the softer poly(ethylene glycol), PEG, present in or around the SPS-rich phase, the chains in this phase obtain segmental mobility already at lower temperatures (Table 4.3). Moreover, the melting peak of polyethylene glycol at around 50 °C is clearly visible in the DSC graph (Figure 4.3b). Also the SPS$_{11}$-[Ru]-PEG$_{44}$-[ showed a comparable melting point (at approximately 55 °C, data not shown).$^{[34]}$
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Figure 4.3: Thermal transitions of (a) the alternating terpyridine-functionalized copolymers and (b) the complexed block copolymers, as measured by DSC.

In order to study the elastic behavior of the SPS-[ and the SPS-[Ru]-PEG materials, depth-sensing indentation (DSI) experiments were conducted. In spite of the gentle drying procedure after dropcasting, several supramolecular materials exhibited extensive cracking due to the volume change upon drying. One of the advantages of DSI is that spots where the film adhered to the substrate could be easily identified (from the absence of fringes in the optical image of the film) and indentation experiments could be successfully performed exactly on those spots. Only on the SPS$_{66}$-[Ru]-PEG$_{70}$ samples, no suitable spots were found. Cracks in the films indicate brittleness of the material. For very brittle materials cracking may occur also on the smaller scale during the indentation experiment. In that case, the method employed to analyze the indentation load-displacement responses is not valid. Therefore, for selected materials, the surface was imaged with the indenter tip after performing the indentation experiments. However, no fracture was observed at the corners of the indents or elsewhere around the indents.

The indentation modulus of SPS$_n$-[ was 5.91 GPa with a standard deviation of 0.27 GPa (average and standard deviation obtained by treating all indents on SPS$_n$-[ as one dataset). The
indentation modulus of $\text{SPS}_n$ decreased to a very minor extent with increasing degree of polymerization, from $6.00 \pm 0.27$ GPa for $n = 11$ to $5.74 \pm 0.18$ GPa for $n = 66$. This small decrease, which is less than one standard deviation, might be caused by a tiny amount of solvent that remained trapped for the SPS with higher degree of polymerization $n$, but could be removed from the studied SPS samples with lower $n$. The absence of a clear dependency on the degree of polymerization also indicates that the effect of the terpyridine endgroup on the materials stiffness can be neglected.

An $E_i$ of 4.2 GPa was obtained for the commercial polystyrenes (indentation moduli for Styron 678, Styron 648 and N5000 were very close to each other), which corresponds well with indentation moduli of polystyrene reported in literature for indents to maximum indentation depths of 0.5 to 0.7 µm.\[35\] (For polymers, the indentation modulus $E_i$ exceeds the Young’s elastic modulus $E$ due to some material pile-up at the indent perimeter, non-linear viscoelasticity and some other factors.\[36\]) Gausepohl et al.\[30\] observed a Young’s modulus of 4.2 GPa for SPS compared to 3.2 GPa for polystyrene. A good agreement is observed between the ratio of the stiffnesses reported by Gausepohl, $E_{PS}/E_{SPS} = 0.76$, and the ratio obtained in the current work, $E_{i,PS}/E_{i,SPS} = 0.71 \pm 0.03$.

The elastic behavior of the obtained supramolecular A-[Ru]-B block copolymers was investigated as well. Figure 4.4 shows that upon loading to the same load, the displacement of the indenter probe into the surface of SPS$_{22}$-[Ru]-PEG$_{70}$ is larger than into SPS$_{39}$-[Ru]-PEG$_{70}$ reflecting its softer character. In Figure 4.5, the obtained indentation moduli are presented as a function of SPS content. This measure for the SPS content is calculated by dividing the mass of the SPS by the sum of the masses of the SPS, terpyridine moieties, (counter)ions, and PEG. The modulus of the terpyridine-functionalized superpolystyrene is shown in Figure 4.5 as well, at a SPS content set to 1. It is noted that the stiffness is usually modeled as a function of the volume fraction of the constituting phases and not of the weight fractions of the components.\[37\] Considering that the density of SPS, which is necessary to calculate the SPS volume fraction, is unknown and that at least for some of the materials the phases consist of a mixture of PEG and SPS, weight fractions are plotted in Figure 4.5. With increasing weight fraction of the hard-domain forming block, i.e., with increasing length of the SPS blocks, the stiffness of the A-[Ru]-B block copolymer increases (filled circles in Figure 4.5). We note that with increasing length of the SPS block, the weight fraction of the metal-ligand complex (MLC) and the PF$_6^-$ counterions decreases (annotated numbers in Figure 4.5), which may influence the stiffness of the material, for instance by increasing the electrostatic interactions or by influencing the phase behavior of the material.\[38-40\]

Polyethylene glycol is semicrystalline (as reflected by the melting peak in Figure 4.3b) and, depending on the crystallinity, hygroscopic. This implies that the elastic properties of the PEG-containing materials may be affected by their processing history as well as by the humidity. To check the humidity influence on the stiffness of the supramolecular copolymers, the indentation measurements were repeated at 45% relative humidity. For apolar polymers
such as polystyrene and SPS, the humidity did not have any effect on the load displacement responses, and thus also not on the modulus. Also the A-[Ru]-B materials containing PEG did not show any significant decrease in modulus upon repeating the experiments at ambient humidity. It is therefore concluded that at the investigated SPS-contents the influence of the humidity can be neglected.

**Figure 4.4:** Indentation load-displacement responses for selected supramolecular AB and ABA block copolymers.

Figures 4.4 and 4.5 show also load-displacement responses and indentation moduli, respectively, for SPS$_{11}$-[Ru]-PEG$_{44}$-[Ru]-SPS$_{11}$ and SPS$_{11}$-[Ru]-PEG$_{44}$-[Ru]-SPS$_{11}$. These materials exhibited a higher stiffness than the A-[Ru]-B block copolymers of comparable SPS content synthesized with monofunctionalized PEG$_{70}$ (filled circles in Figure 4.5). The higher stiffness for the materials containing the shorter PEG is attributed to their higher Ru$^{2+}$ and PF$_6^-$ ion contents. Small-angle X-ray scattering above the melting point of the PEG showed for PS$_{20}$-[Ru]-PEO$_{70}$ that the MLC and the counterions form randomly located domains surrounded by a mixed PEG/PS phase. For the PEG$_{44}$ materials, the domains containing the MLC and counterions are located closer to each other and the MLC and counterion weight fraction is higher than for the PEG$_{70}$ materials. Therefore their effect on the deformation behavior increases. These domains are expected to increase the materials stiffness through electrostatic interaction and/or by impeding the motion of the attached SPS and PEG chain. Furthermore, the presence of the MLC and the counterions may induce changes in the phase-separation behavior of the PEG and SPS as well. Also the smaller size of the PEG may cause differences in phase-separation (and crystallization) behavior compared to the PEG$_{70}$ materials, resulting in changes in the relative amounts of the phases present and their thermal transition temperatures, thereby also influencing the materials stiffness.
Chapter 4

Figure 4.5: The stiffness of the SPS and the supramolecular block copolymers as a function of the SPS weight fraction. The counterion + metal-ligand complex weight fraction is annotated to the data. For the SPS-[Ru]-PEG$_{70}$ the degree of polymerization of the SPS is added in brackets.

4.4 Conclusions

New AB-[M]-BA, A-[M]-B diblock copolymers and A-[M]-B-[M]-A triblock copolymers were characterized in which the polymer blocks are linked together by an iron(II) or ruthenium(II) complex. It was demonstrated that the elastic modulus of supramolecular materials can be altered by changing the chain architecture from AB-[ to supramolecular AB-[M]-BA block copolymers. Furthermore, the stiffness can be controlled varied by varying the chemical composition. The overall chemical composition and the mechanical stiffness can be tuned by varying the length of one or both of the blocks, as shown for supramolecular A-[M]-B copolymers. The high modulus of SPS, which is approximately 35% higher than for PS, provides a wide range for tuning the stiffness of such block copolymers.

The elastic properties of supramolecular materials could be probed using only minimum amounts of material. In order to fully understand the complex interplay of the various phenomena influencing this material stiffness, such as the extent of phase-segregation, the phase morphology and, for the PEG, the degree of crystallization, the help of other characterization techniques (for instance, small angle X-ray spectroscopy) is required.
4.5 Experimental

**Differential scanning calorimetry.** Thermal transitions were determined on a NETSCH 204 F1 Phoenix DSC in a nitrogen atmosphere. The crucible lids were pierced so that any present solvent could evaporate during the first run. The first heating run was disregarded. The analyzed DSC trace for the PS-PBA-[ in Section 4.2 and the SPS-[Ru]-PEG in Section 4.3 were obtained upon heating from −100 to 150 °C at 40 K/min and −50 °C to 225 °C at a rate of 20 K/min, respectively.

**Preparation of PS-PBA-Tpy films for indentation.** ~5 mg of the (un)complexed PS-PBA-Tpy compounds was dissolved in ~40 µL chloroform. From each solution, several droplets were cast onto a glass slide (Marienfeld, Lauda-Köningshofen, Germany). After slow evaporation of the solvent and thorough drying, indentation experiments were performed on the remaining circular films (~40 µm thick).

**Preparation of superpolystyrene-PEG films for indentation.** Polymer films were prepared for depth-sensing indentation by dropcasting the materials onto glass slides. The solutions contained 5 mg polymer in 50 µL chloroform (Biosolve). Several commercial polystyrenes, Styron 678 and Styron 648 (DOW Chemical) as well as N5000 (Shell), were dropcast from toluene and dried thoroughly, also employing temperatures above their glass transition.

**Indentation experiments.** Indentation on the PS-PBA materials was performed using a Hysitron TriboIndenter (Minneapolis, Mn) equipped with a Berkovich (trigonal pyramid) indenter. Load levels ranging from 600 to 100 µN were used, resulting in shallow indents to avoid the substrate effect. Measurements were repeated on at least two films of the same compound, showing good reproducibility. Loading took place in 10 s loading. After a 10 s hold time, unloading took place in 0.5 s. Indentation experiments were repeated after longer drying periods and drying at temperatures above the $T_g$ of polystyrene, resulting in nearly identical data.

The elastic properties of the PS-PEG samples were studied at 11% relative humidity by depth-sensing indentation (DSI) using a Hysitron TriboIndenter equipped with a Berkovich probe. During the indentation experiments, the tip was loaded to maximum load in 10 s, held at maximum load for 10 s, and unloaded in 0.5 s. For each material, the experiments were repeated on at least two different dropcasted samples, and at least five maximum loads (1500, 1200, 900, 600 and 300 µN). For SPS$_{11}$-[Ru]-PEG$_{70}$, lower loads were chosen: 300, 250, 200, 150, 100, 50 µN. Multiple indentation experiments were performed on SPS$_{n}$-[ employing maximum loads of 400, 1000 and 1600 µN. The polystyrenes were measured employing maximum loads of 2700, 2400, 2100, 1800, 1500, 1200 µN, and indentation experiments were repeated on SPS$_{n}$-[ at these loads as well. The first two indentation responses were left out to minimize the effect of thermal drift.

**Analysis of the indentation load-displacement responses.** The load displacement responses obtained from DSI were analyzed using the method proposed by Oliver and Pharr. Reduced moduli $E_r$ were converted to modulus of elasticity $E_i$ (where the subscript denotes ‘indentation’) using 0.35 as the Poisson’s ratio.
4.6 References and notes


The determination of the number average molar mass by GPC relies on measuring the retention time of the dissolved polymer, which is governed by the hydrodynamic radius of the polymer in the GPC solvent. The relation between retention time and the molar mass is established using polymer calibration standards. If the sample material swells to a different extent than the calibration polymer, which is usually the case, the same molar mass results in a different hydrodynamic radius and thus a different retention time. The degrees of
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Polymerization determined by $^1$H NMR spectroscopy are established from the ratio of peak areas caused by protons in various chemical environments. The peak area caused by the protons of the terpyridine moiety are compared to the peak areas caused by protons characteristic to the poly(n-butyl acrylate) and the polystyrene. Various factors, such as the setting of the baseline, cause some inaccuracy in the determined degrees of polymerization and, thus, of the determined molar mass.


[34] It is noted that apart from the crystalline fraction, part of the PEG is expected to be amorphous and above its glass transition. Furthermore, the crystallinity observed with DSC is higher then the crystallinity of the samples subjected to indentation discussed later in the contribution, as during the DSC experiment but prior to the analyzed traces, the samples were dried at high temperature and subsequently cooled to lower temperatures than the indentation samples; crystallization of PEG proceeds at a lower temperature than melting (ref. 42) and is enhanced by thorough drying.


[41] When plotting the moduli as a function of SPS + MLC + counterion weight fraction, all datapoints are right-shifted by the value annotated in Figure 4.5. Then, the SPS$_{11}$-[Ru]-PEG$_{44}$-[Ru]-SPS$_{11}$ material is on the trendline constituted by the SPS-[Ru]-PEG$_{70}$ materials, but the SPS$_{11}$-[Ru]-PEG$_{44}$-[Ru]-PEG$_{44}$-[Ru]-PEG$_{44}$-[Ru]-PEG$_{44}$-[Ru] still is located above this trendline. Also after shifting the SPS$_{11}$-[Ru]-PEG$_{44}$-[Ru]-PEG$_{44}$-[Ru]-PEG$_{44}$-[Ru]-PEG$_{44}$-[Ru]-PEG$_{44}$-[Ru]-PEG$_{44}$-[Ru] data to account for the uncomplexed terpyridine on the other side of its PEG-chain, this material remains stiffer than the trendline.

[43] For the SPS$_{11}$-[Ru]-PEG$_{44}$-[Ru]-SPS$_{11}$ material, an additional reason for the higher stiffness compared to the SPS-[Ru]-PEG may be its different architecture (ABA vs. AB). However, this represents probably only a small effect as the hard phase is the continuous phase at these SPS contents (ref. 22); then additional interactions between the hard phase regions are not as effective in raising the stiffness as for thermoplastic elastomers, where the soft phase is the continuous phase.

Chapter 5

An HTE approach to cross-linking of EPDM

Abstract
The applicability of depth-sensing indentation (DSI) as a characterization tool for high-throughput experimentation (HTE) in the field of rubber cross-linking was investigated. DSI results obtained on peroxide-cured ethylene-propylene-diene rubbers (EPDMs) were correlated with the state of cure and the mechanical properties of the vulcanizates. A good correlation was found between the indentation depth at fixed loading conditions and the rheometer torque, the Shore A hardness, the modulus and the compression set. Also the possibilities of high-throughput sample preparation via solution routes were investigated. A moderate-throughput solution route for mixing of the curative and the rubber could be established. A higher-throughput mixing route, however, gave unsatisfactory results. The indentation depth measured on peroxide-cured vulcanizates mixed via the (moderate-throughput) solution-route agreed well with the indentation depth obtained on corresponding vulcanizates compounded via conventional mill mixing. By indentation on vulcanizates cured for various curing times, a rheometer curve could be constructed. The conversion of the EPDM unsaturation and, thus, the extent of addition reactions were quantified by Raman spectroscopy. Using both the indentation and the Raman data, the cross-link density due to combination was estimated. This estimate was close to the cross-link density due to combination calculated from the amount of radicals available upon decomposition of the peroxide.

Part of this chapter has been or will be published:
Chapter 5

5.1 Introduction

5.1.1 Cross-linking of EP(D)M polymers

The polymerization of ethylene, propylene and a non-conjugated diene yields statistical terpolymers with a low glass transition temperature (approximately \(-55 \, {^\circ}{C}\)) and no or little crystallinity. This material is called EPDM, where the ‘M’ in EPDM indicates that the carbon atoms in the polymer main chain are fully saturated, in contrast to polydiene rubbers such as natural rubber (NR) and butadiene rubber (BR).\(^{[1]}\) This saturation results in a good thermal, oxidative and ozone stability. Because of this stability, EPDM rubber is used in many outdoor applications such as sealings for cars, window gaskets and roof sheeting.\(^{[2,3]}\)

EPDM can be cross-linked using either sulfur or peroxide. During curing, cross-links are formed that connect the EPDM chains and, thereby, cause the typical elastomeric resilience of rubbers. Cross-linking with a peroxide yields a network with superior thermal stability in comparison to vulcanization with sulfur, allowing applications at relatively high temperatures.

A simplified scheme for peroxide curing of EPDM in the absence of coagentia is shown in Scheme 5.1. Upon heating, the peroxide decomposes into two radicals. Reaction of these radicals with EPDM yields EPDM macro-radicals. Cross-links are formed via combination of two macro-radicals or via addition of a macro-radical to the unsaturation of an EPDM macromolecule.\(^{[4,5]}\) In the simplified scheme, the EPDM macroradical depicted is an alkyl radical. Recently, it was reported that also allyl radicals derived from the EPDM unsaturation are formed, which gives rise to the corresponding allyl combination and addition cross-links.\(^{[6]}\)

\[ \begin{align*}
\frac{\Delta T}{\gamma} \begin{array}{c}
R\sim\overset{-}{\overset{\sim}{O}}\sim\overset{-}{\overset{\sim}{O}}\sim R \\
\end{array}
\end{align*} \]

\[ \begin{align*}
&\text{combination} \\
&\text{addition} \\
&\text{H-transfer}
\end{align*} \]

\[ \begin{align*}
\text{EPDM}^* + \text{EPDM} \\
\text{EPDM} + \text{EPDM}^*
\end{align*} \]

Scheme 5.1: Simplified reaction scheme for the peroxide cross-linking of EPDM without coagentia present.\(^{[4,5]}\)
Peroxide curing is often carried out in the presence of multi-unsaturated chemicals, named coagentia, to enhance the vulcanization rate, the state of cure and the vulcanize properties.\[7\] Typical coagentia are triallyl cyanurate, triallyl iso-cyanurate, trimethylolpropane trimethacrylate and more polar coagentia such as zinc dimethacrylate and $N,N'$-m-phenylene dimaleimide.\[7\] Other chemicals, the so-called ‘scorch retarders’, decrease the macro-radical concentration during the initial stages of the curing, and thereby allow more time for processing the rubber compounds and for shaping of the products.\[8\]

The common approach to investigate the cross-linking kinetics and the final state of cure of rubbers is rheometry. Rheometry is based on the measurement of the torque necessary to maintain a fixed rotation amplitude at a specified frequency during cross-linking of the compounds. The change in the torque during curing, $M_h - M_l$, is a quantitative measure for the state of cure of EP(D)Ms.\[9\] The highest torque after cross-linking $M_h$ and the lowest torque $M_l$ are indicated in Figure 5.1.

<table>
<thead>
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<th>Increasing amount of cross-linker</th>
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<td>Torque (Nm)</td>
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<td>Time (minutes)</td>
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<tr>
<td>$M_h$</td>
</tr>
<tr>
<td>$M_h - M_l$</td>
</tr>
<tr>
<td>$M_l$</td>
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*Figure 5.1:* A rheometer (photograph from ref. 10) probes the change of the torque required to impose an oscillating material deformation as a function of the curing time. The change in the torque during curing $M_h - M_l$ is indicated.

Common tests to probe the mechanical properties of rubbers include Shore hardness measurements, tensile testing and compression set measurements. The Shore hardness is calculated from the deflection of a spring with a calibrated stiffness characteristic, which is attached to a stylus that is pressed onto the rubber. Various standardized stylus geometries and spring stiffness characteristics are used, resulting in several Shore hardness scales. For the Shore A scale, a truncated cone is used.\[1,2\] The Shore A hardness is 100 for a very hard material that pushes the indenter entirely into the housing of the instrument, resulting in a maximum deflection of the spring and zero indentation depth into the material. The Shore A hardness is zero for a very soft material that does not cause any deflection of the spring, resulting in an indentation depth of 2.5 mm (in unstressed state the cone extends 2.5 mm out of the housing). Intermediate indentation depths result in intermediate Shore A hardness values. The elastic modulus and the viscoelastic behavior of the material govern the Shore A hardness.\[2\]
A uniaxial tensile test allows the determination of the ‘modulus 100%’, ‘modulus 200%’, ‘modulus 500%’ and the stress and strain at break. These moduli are the engineering stress levels at 100%, 200% or 500% elongation, thus they are defined differently than the Young’s modulus. The compression set describes the deformation that remains after imposing a specified compression and subsequently relaxing the sample. The remaining deformation as percentage of the imposed deformation is the reported compression set: a low value indicates good resilience.

**Figure 5.2:** A Shore A hardness measurement device (photograph from ref. 11).

### 5.1.2 HTE investigation of EPDM elastomers

Various grades of EPDMs are available, with different ethylene/propylene ratios, diene structures and contents, molar masses, molar mass distributions and degrees of branching. Furthermore, a variety of peroxides and additional chemicals such as coagents can be used for curing. The curing speed, the cross-link density and the final properties depend on the type and the amounts of rubber, peroxide and coagent used, as well as on the curing temperature. Finally, practical EPDM compounds contain very large amounts of (reinforcing) fillers (mainly carbon black), oil and other additives such as antioxidants, waxes, etc.\[^3\] The multitude of these variations in EPDM types, curing systems, other compound ingredients and curing conditions results in a large parameter space for process and product optimization. Preparation and characterization of large sets of samples at minimal effort per sample *via* a high-throughput experimentation (HTE) approach is therefore likely to provide a cost-effective way to optimize EPDM curing formulations and procedures. Furthermore, if the starting polymers are synthesized using a HTE approach,\[^12\] the situation may arise that only small amounts of various new EPDMs are available for investigation of their curing behavior (at various cross-linker and coagent levels). In such situations, HTE techniques, that commonly use only small amounts for sample preparation and characterization, may provide a means to nevertheless obtain the desired information on curing behavior and vulcanizate properties.
5.1.3 **Aim of this chapter**

This chapter aims to develop HTE sample preparation, curing and characterization methods for EP(D)M vulcanization. In order to investigate structure-property relationships, both mechanical and spectroscopic characterization were conducted. This chapter starts with investigating the applicability of DSI as a means to characterize the state of cure of elastomers. After establishing the usefulness of DSI for vulcanize characterization, also the other HTE steps are included in the investigation (Table 5.1). As industrial equipment for rubber compound mixing involves large amounts for efficient economical mixing, mixing *via* solution routes has been investigated. The first solution route (Section 5.3) is ‘HTE-like’ in the sense that only small amounts of material are necessary, but remains relatively labor-intensive. The second route allows more automation, and is investigated in Section 5.4.

Practical rubber compounds contain large amounts of fillers, notably carbon black and oil. These ingredients are omitted in the current work to reduce the complexity of the structure-property relationships. However, the presented methods (or modified versions thereof) may be usable for characterization of these systems as well.

**Table 5.1:** The chemical aspects, the sample preparation and the characterization techniques applied in this chapter.

<table>
<thead>
<tr>
<th>Section</th>
<th>Topic</th>
<th>Sample preparation</th>
<th>Characterization</th>
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<tbody>
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<td>5.2</td>
<td>Several EP(D)Ms at different peroxide levels</td>
<td>HTE milligram scale</td>
<td>Spectroscopy</td>
</tr>
<tr>
<td>5.3</td>
<td>Curing as a function of time</td>
<td>HTE-like' sub-gram scale</td>
<td>Indentation</td>
</tr>
<tr>
<td>5.4</td>
<td>Solubility and HTE sample preparation</td>
<td>Mill-mixed</td>
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5.2 Investigating the state of cure by depth-sensing indentation

Under the condition that the type of rubber and the type of curing agent within a set of vulcanizates are comparable, the state of cure and various mechanical properties are directly correlated, independent of how that state of cure is obtained.\[1\] This is shown schematically in Figure 5.3. This section investigates the applicability of DSI as a HTE characterization method for EPDM curing. Results from such a characterization method need to correlate with the state of cure and with macroscopic properties (dashed arrows in Figure 5.3). In order to investigate such correlations, several EP(D)Ms, mixed with various amounts of peroxide, were cured and characterized by conventional testing techniques, as well as by DSI.

The vulcanizates discussed in this Section were prepared using EPDMs containing 5-ethylidene-2-norbornene (ENB) as the diene, at ENB contents of 9\%, 4.3\% and 1.9\% (by weight), EPDM containing 4.5 wt.\% dicyclopentadiene (DCPD) as the diene, and one EPM which did not contain any diene. These EP(D)Ms were mixed with a peroxide cross-linker, \textit{bis(t-butylperoxy-\textit{i}-propyl)benzene} (BPPB, see Scheme 5.2) used as a 40\% master batch (BPPB MB). Subsequently, these compounds were cured in a rheometer to obtain the rheometric data, or in a hot press to obtain films for macroscopic testing and indentation testing.

\[1\]
Scheme 5.2: The chemical structure of \textit{bis}(t\text{-}butylperoxy\text{-}i\text{-}propyl)benzene (BPPB).

5.2.1 Conventional testing

Increasing the peroxide level resulted in an increase of rheometer torque differences for all EP(D)Ms (Figure 5.4a). The EPDM rubbers with 9\% and 4.3\% ENB showed a larger torque difference than the 1.9\% ENB-EPDM, and a much larger torque difference than the EPM, which does not contain any diene, at the same peroxide level. The increase in torque was nearly equal for the 4.3\% ENB and the 9.0\% ENB series, which is somewhat unexpected. 4.5\% DCPD-EPDM yielded more or less similar results as 4.3\% ENB-EPDM, in agreement with previously established similar peroxide curing efficiencies of these dienes.\cite{5}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure5.4.png}
\caption{(a) Rheometer torque and (b) Shore A hardness as a function of the amount of peroxide for five types of EP(D)Ms; 1 phr BPPB MB = 1 gram BPPB master batch per hundred grams of EP(D)M rubber; lines are added to guide the eye.}
\end{figure}
The compounds were cured as 2 and 6 mm plaques in a hot press, as well. The Shore A hardness of the resulting vulcanizates was measured. The Shore A hardness (Figure 5.4b) showed the same trends with peroxide content and EPDM type as the torque difference (Figure 5.4a). However, the difference between the Shore A hardnesses of the 1.9% ENB-EPDM on the one hand and those of the 4.3% and 9.0% ENB-EPDMs on the other hand was only 1 to 4 units (depending on the peroxide content), so the Shore A hardness provided less discrimination between the different ENB-EPDM series than the torque difference. Clearly, the peroxide-cured EPM exhibited very low Shore A hardness, due to the lower molar mass of the EPM starting material. The results from the other conventional tests (tensile test and compression set) are presented in Section 5.2.3.

5.2.2 Characterization by depth-sensing indentation

Indentation experiments were performed on pieces cut from the 2 mm thick vulcanize plaques. A ~4.7 µm radius tip was pressed onto the films with a load of 20 µN. The resulting maximum indentation depths ranged from 1 to 3 µm. The indentation depths for the Shore A measurements presented in Figure 5.4b ranged from ca. 1 mm for the harder rubbers to ~2 mm for the less densely cross-linked rubbers. As a result, the difference between the length-scale of the depth-sensing indentation and the Shore A hardness measurement is three orders of magnitude. Therefore, the sample dimensions for the depth-sensing indentation experiments can be much smaller than for the Shore A measurements, where a sample thickness of at least 6 mm and a width and length of at least 30 mm is required. As with Shore hardness, the displacement measured by DSI depends on the elastic modulus and on the viscoelastic behavior of the material. Therefore, test conditions such as the loading time, the maximum load and the dwell time at this load (see Experimental section) were kept constant. Load-displacement responses, showing the deformation during loading, hold at maximum load and unloading are displayed in Figure 5.5. In particular, the less densely cross-linked rubbers exhibited a large displacement during the hold period (creep). The slightly cross-linked EPM sample (without diene), indicated with closed symbols in Figure 5.5, showed a high displacement rate even at the end of the hold period, and a large hysteresis in the load-displacement response. Usually the final displacement after unloading deviated from zero. This residual deformation indicates that the samples did not behave as ideal rubbers. Mareanukroh, Li, Tsou and Lim have presented Young’s moduli derived from indentation experiments on elastomers. They either used Hertz’s law, which allows calculation of the Young’s elastic modulus from the loading response of the material, or applied the Oliver and Pharr’s analysis, which determines the elastic modulus from the initial slope of the unloading curve. A qualitative observation based on the Hertz analysis is easily visible in Figure 5.5. For indentations with a spherical indenter on a linear elastic material with elastic modulus $E$, the load $P$ is related to the displacement $h$ as

$$P = rac{4}{3} E h^3 / R$$

where $R$ is the radius of the indenter.
\[ P = c \cdot E \cdot h^{3/2} \]  

(5.1)

where the constant \( c \) is related to the radius \( R \) of the indenter.\textsuperscript{[14,18]} This relation is valid for \( h << R \). However, at \( h = 800 \) nm this relation may be used without introducing large errors. At constant depth, for instance 800 nm, the load \( P \) was higher for the densely cross-linked material than for the slightly cross-linked material, indicating a higher modulus for the former. Similar qualitative observations can be made on the moduli obtained using the Oliver and Pharr method, which is based on the slope at the start of the unloading curve: the E-moduli obtained for the various samples increased with increasing torque difference and modulus 100%. Although these E-moduli revealed the expected trend, the quantitative values are not reliable due to the non-Hookean elastic behavior of the material\textsuperscript{[20]} and/or due to the formation of a pre-indent in the material (deformation during the approach before the actual measurement starts) and are therefore not presented here. The Oliver and Pharr analysis and the Hertz analysis assume a linear relation between stress and elastic deformation of the material and an initially flat material surface. Furthermore, the zero displacement (the displacement when the indenter touches the surface at the start of the loading) needs to be determined accurately. The steep initial slope of the loading curve of the slightly cross-linked sample, followed by a decrease of the slope around 500 nm (Figure 5.5) indicates non-Hookean behavior and/or pre-indent formation (the slope of the loading response for spherical indenters on ideal elastic materials should increase up to contact depths of approx. \( \frac{1}{4} R \), thus the observed change in slope around 500 nm indicates that the material is not ideal linear elastic and/or the surface is initially not flat). Changing the indentation experiment conditions did not solve these problems.\textsuperscript{[21]} As the obtained moduli are skewed, the maximum indentation depth is chosen as a practical measure to be compared with the Shore A hardness, although this measure has the drawback that it depends on the applied load and the indenter shape, and is, therefore, only a relative characterization measure.

Figure 5.5: Load-displacement graphs on the 2 mm vulcanize films show more creep (horizontal arrow) and a higher maximum indentation depth (vertical arrow) for a slightly cross-linked EPM rubber (closed symbols) than for the more densely cross-linked EPDM rubber (open symbols); for both rubbers, the load-displacement response is shown in duplo.
The effect of sample thickness on the DSI results was studied (Figure 5.6). Three to four maximum indentation depth measurements are presented per micro-tome film thickness; the average and the standard deviation from five or more measurements are presented for measurements on the surfaces of the as-received samples. The thickness of the micro-tomed sections from the EPM vulcanizate with 1.25 phr BPPB MB, \textit{i.e.} with the lowest cross-link density and hardness, varied from section to section. As the indentation depths on the thin sections were $1/10$ of the total film thickness ($20 \ \mu$m), some substrate effect can be expected.\cite{18} On the micro-tome sections of $50 \ \mu$m thickness, where effects from the hard glass substrate should be negligible, the indent was indeed deeper. All indentation results discussed in the remainder of this chapter were obtained by indentation on the vulcanizate surface, \textit{i.e.}, not affected by any substrate effect.

![Figure 5.6: Comparison between depth-sensing indentation measurements on micro-tomed sections (thickness below 100 \mu m), and on the surface of the as-received samples (approximately 2000 \mu m thick) for two peroxide-cured EP(D)Ms.](image)

5.2.3 \textit{Indentation and macroscopic tests on the vulcanizates}

As expected, vulcanizates with a higher peroxide content showed a smaller maximum indentation depth (Figure 5.7a). With the exception of the 9\% ENB-EPDM series, an increase in ENB content resulted in smaller indentation depths. The indentation depths of the DCPD-EPDM series were close to the indentation depths on the 4.3\% and 1.9\% ENB-EPDM series. The unexpected proximity of the data for the 4.3\% and the 9\% ENB series was observed in the Shore A hardness as well (Figure 5.4b). Obviously, the state of cure governed the indentation depth. Therefore, a correlation curve was constructed that related the maximum indentation depth to the torque difference (Figure 5.7b). The standard deviation in the maximum indentation depth ranged from 0.02 to 0.11 $\mu$m and was always smaller than 6\%.

The Shore A hardness is, by its definition, linearly related to a millimeter-sized indentation depth,\cite{2} where a low indentation depth corresponds to a high Shore A hardness. Figure 5.8 shows that also the small scale indentation depth decreases with increasing Shore A hardness. The five EP(D)Ms follow the same correlation curve (Figure 5.8). In the Shore A hardness
range from 35 to 60, this correlation was linear: deviations from linearity, that could occur as the applied load, the measurement time, the indenter shape and, therefore, the representative strain[22] were different for both techniques, turned out to be small. The observed linearity is discussed in more detail in Appendix 1.

Figure 5.7: Depth-sensing indentation results of the EP(D)M vulcanizates (a) as a function of the peroxide masterbatch content, and (b) as function of the cross-link density as indicated by the rheometer torque difference, for five types of EP(D)M; lines are guides to the eye only.[23]

Figure 5.8: Correlation between Shore A hardness (truncated cone indenter, load depends on indentation depth, reading 3 s after application of the load) and maximum indentation depth (~4.7 µm radius indenter, load = 20 µN, reading after 10 s hold time) for five EP(D)M rubbers cured with various amounts of peroxide.

Under the condition that the type of rubber, the types and amounts of oil and filler and the type of curing agent within a set of vulcanizates are comparable, direct correlations can be made between various mechanical properties.[1] The current set of vulcanizates consists of peroxide-cured, amorphous EP(D)M rubbers without filler and oil and, therefore, most of their macroscopic properties were mutually related. As the DSI results correlate with the Shore A hardness, these indentation results may be used as a predictor for other macroscopic properties as well. The relation between the modulus 100% and the maximum indentation
depth exhibited indeed one correlation for all of the EP(D)Ms studied (Figure 5.9a). Materials with a low maximum indentation depth exhibited a higher modulus 100%. In general, vulcanizates with a low maximum indentation depth had a low elongation at break (Figure 5.9c), and in the range probed here, a low tensile strength (Figure 5.9b). The tensile strength and, to a lesser extent, the elongation at break did not show a single shared correlation for all the EP(D)M types; the EPM series was in particular distinct from the other series. The poorer correlation of tensile strength and the elongation at break with maximum indentation depth was not very surprising, as the correlation between these ultimate properties and the Shore A hardness is not always that good, either.

![Graphs a, b, c, d, e showing correlations between maximum indentation depth and various properties](image)

**Figure 5.9:** Maximum indentation depth as a predictor for macroscopic properties; lines are guides to the eye, (a, b, c) or linear fits (d, e).
The compression sets both at 23 °C and 70 °C showed a reasonable correlation curve (Figures 5.9d and 5.9e). The approximate linearity in the correlation of maximum indentation depth with the compression set is discussed in more detail in Appendix 2. The compression sets seemed to be slightly offset for the different EPDM types. The 9.0% ENB-EPDM with 2.5 phr BPPB masterbatch vulcanizate, with a maximum indentation depth of 1.57 µm, deviated somewhat from the correlation curves in Figure 5.9 (a, d and e). This is most probably due to experimental scatter in the maximum indentation depth on this sample (see also Figure 5.7b and Figure 5.8). The modulus 100% for the highest cross-linked DCPD-EPDM sample (2 MPa) was a bit off as well. This may be due to experimental factors such as scatter or the fact that this sample failed near 100% elongation. Alternatively, it may indicate that DCPD-EPDM exhibits a different correlation between modulus 100% and indentation depth than ENB-EPDM, for instance due to its higher ethylene content which may promote strain-induced crystallization. The tensile strength and elongation at break of the least cross-linked sample (EPM, 1.25 phr BPPB masterbatch) could not be determined reliably.

As depicted schematically in Figure 5.3, the rubber compound formulation governs the cross-link density (Figure 5.4a), which in its turn governs the mechanical properties. Correlations between the state of cure and the DSI results, as well as between various mechanical properties and the DSI results (dashed arrows in Figure 5.3) were explored. The presented results show that, for vulcanizates that are expected to obey the same correlations, the indentation depth obtained on a vulcanizate can be used to estimate the state of cure, as well as some of its mechanical properties (Shore A hardness, modulus 100% and compression sets at 23 and 70 °C).

5.3 EPDM curing kinetics

For successful HTE experimentation, the sample preparation needs to be high-throughput compatible as well. In order to investigate a HTE-compatible sample preparation via a solution approach, vulcanizates compounded by mill mixing were compared to corresponding vulcanizates mixed via a solution route. The curing time was varied in order to introduce an additional variable (namely: time) to the discussion, i.e., to investigate the curing kinetics.

5.3.1 Compound formulation and sample preparation

The cross-linker was mixed into the EPDM using a solution route described as solution route A in the Experimental section. Aliquots of mill-mixed and solution route compounds of comparable BPPB content were placed on aluminum sample slides. A slide, 0.5 mm thick, with holes (6.5 mm diameter) served as a ‘spacer’ plate and a glass slide finalized the ‘sandwich’ set-up. Several of these slides were made, and cured for various time steps in a hot
press. The lower transparency of the mill-mixed vulcanizates compared to the solution processed vulcanizates (Figure 5.10) is caused by additional components (whiting, silica) in the master batch that was used to mill mix the BPPB into the EPDM.

Figure 5.10: Sample slide (76 × 26 mm) after vulcanization and removal of the glass slide.

5.3.2 Peroxide reaction products on the vulcanizate surface

Initially, Raman spectroscopy of peroxide-cured EPDMs showed unexpected results; in some cases even higher C=C intensities (at 1688 cm\(^{-1}\)) were found after curing than before. This was attributable to undesired extra Raman signals close to 1688 cm\(^{-1}\) originating from BPPB reaction products, which were present as small crystals on the vulcanizate surface and in the vulcanizate (Figure 5.11). This was proven by Raman spectroscopy on heated BPPB, confocal Raman spectroscopy on particles on the vulcanizate surface and GC-MS of the THF that was used to rinse a vulcanizate, as briefly discussed below.

Figure 5.11: Optical microscopy showed that crystals were present on the vulcanizate surface.

Raman spectra of BPPB and the BPPB masterbatch are shown in Figure 5.12. Furthermore, BPPB was placed in a vial and heated to 160 °C. Upon heating, the white BPPB flakes turned into a yellow/brown sticky substance. The spectrum obtained for this substance contained several peaks that were also present in the BPPB spectrum, namely 2927 cm\(^{-1}\), 1601 and 1585 cm\(^{-1}\) (aromatic CCH quadrant stretch),\(^{[24]}\) 1085 cm\(^{-1}\) and 1001 cm\(^{-1}\) (aromatic C-C stretch).\(^{[24]}\) In addition, a strong peak was present at 1684 cm\(^{-1}\), which is attributable to an aromatic ketone (see below). The latter overlaps with the peak at 1688 cm\(^{-1}\) that is needed to quantify the ENB conversion (see the 9% ENB-EPDM spectrum).
Figure 5.12: Raman spectra of pure BPPB, BPPB-masterbatch, heated BPPB and 9% ENB-EPDM, showing that upon heating the BPPB, a peak at 1684 cm\(^{-1}\) is formed that overlaps with the ENB peak at 1688 cm\(^{-1}\) (for the spectrum of the heated BPPB, extensive baseline correction was needed because of fluorescence).

Confocal Raman spectroscopy on the particles observed on the vulcanizate surface yielded spectra with a strong peak at 1000 cm\(^{-1}\). This peak, which indicates the presence of an aromatic ring, is also present in the BPPB spectra both before and after heating (Figure 5.12). Other peaks observed by confocal Raman spectroscopy that were also present in the spectrum of BPPB but not in the spectrum of the EP(D)Ms, were located at 1600, 1588 and 1086 cm\(^{-1}\). For some particles also a broad peak overlapping the 1688 cm\(^{-1}\) position was observed.

Gas chromatography with mass spectrometry identification (GC-MS) was conducted at DSM-Resolve on the THF that was used to rinse the EPM vulcanizate containing 10 phr BPPB-MB. For comparison, heat-treated BPPB was measured as well. The following chemicals were identified both in the THF and in the heated BPPB (in order of increasing GC retention time):

a. 1,1'-((1,3-phenylene)\textit{bis}-ethanone;

b. 1,1'-((1,4-phenylene)\textit{bis}-ethanone;

c. dihydroxy-\textit{m}-diisopropylbenzene;

d. 1-(3-[1-hydroxy-1-methylethyl]phenyl)-ethanone;

e. dihydroxy-\textit{p}-diisopropylbenzene;

f. 1-(4-[1-hydroxy-1-methylethyl]phenyl)-ethanone.

The (mixed) alcohol and ketone species are the expected decomposition products of the BPPB. Because of the appreciable polarity arising from their carbonyl or hydroxyl groups, they are probably not miscible with the EPDM matrix and, consequently, phase separate. Chemicals resembling a, b, d and f, for instance 4'-methylacetophenone, indeed have a strong Raman peak at 1680 cm\(^{-1}\) that is attributable to the carbonyl vibration of the aromatic ketone.\[^{25}\]
The BPPB decomposition products could be removed by immersion of the vulcanizates in acetone. This was verified by optical microscopy before and after immersion, as well as by a significant improvement in the Raman spectra of EPM vulcanizates. Alternatively, the crystals could be removed by heating; above 90 °C the particles melted and subsequently evaporated, as observed by optical microscopy employing a heating stage. The higher melting temperature compared to that of BPPB (44 to 48 °C) is most probably also attributable to their higher polarity.

5.3.3 Reproducibility and choice of curing times

Mill-mixed compounds of 9% ENB-EPDM with 1.25, 2.5 and 5.0 phr BPPB MB were compression molded in triplicate for 20 and 30 minutes. As expected, the obtained indentation depth decreases with increasing peroxide content (Figure 5.13a). The indentation depths obtained after 20 minutes curing were, within experimental accuracy, equal to those obtained after 30 minutes. This is in agreement with the rheometer torque measurements for these vulcanizates: The torque difference after 30 minutes curing is less than 3% higher than after 20 minutes curing. The observed variation in indentation depth between replicate experiments is approximately 0.07 µm. The reported indentation depths are the average of at least 10 measurements, allowing to report standard deviations for the indentation data.

Because of the addition reactions taking place during peroxide cross-linking of EPDM (Scheme 5.1), a decrease of the ENB unsaturation peak intensity can be expected. The intensity of the \( \text{C} = \text{C} \) vibration normalized to the \( \text{CH}_2 \) scissoring vibration, obtained by Raman spectroscopy, is shown in Figure 5.13b. With increasing amount of BPPB, the remaining \( \text{C} = \text{C} \) peak intensity decreased, i.e., the ENB conversion increased. (The normalized peak height of the 9% ENB-EPDM starting material was 0.146). The variation between replicate experiments is ~0.003, which translates into a variation of approximately 2% in the ENB conversion.

Based on the full cure after 20 minutes, vulcanization times of 1, 2, 4, 6, 8, 10 and 20 minutes measurements were chosen for a kinetic study. The 10 minutes curing experiment was performed in duplicate.
Figure 5.13: Reproducibility study on (a) the indentation depth and (b) the C=C peak intensity obtained on 9% ENB-EPDM vulcanizates cured for 20 or 30 minutes at three peroxide levels; averages for corresponding samples cured for the same time are indicated by horizontal lines.

5.3.4 Spectroscopy, indentation and comparison with rheometry

Figure 5.14a shows the indentation depth as a function of curing time for 9% ENB-EPDM at three BPPB levels. In order to facilitate the comparison between the mill mix and the solution route, the cross-linker concentration for the mill-mixed compounds is also denoted as the pure BPPB content. With increasing cure times, the material gets stiffer and the indentation depth decreases. Figure 5.14b shows the conversion of the ENB unsaturation for these vulcanizates. The conversion increases with time and peroxide content. The C=C conversion and the mechanical response show the largest change within the first 10 minutes of curing at 175 °C. This is in agreement with the half-life time of the BPPB at 175 °C, which is 57 s.[26]

The observed results for the samples prepared by the solution route are compared to those on the mill-mixed compounds in Figure 5.15. A good agreement was obtained, as shown by the linear fits. The conversions obtained by Raman spectroscopy (Figures 5.14b and 5.15b) exhibited some scatter, even though the acquisition times were rather long. This is related to the modest Raman peak height of the ENB C=C vibration and the concomitant sub-optimal signal-to-noise ratio of the Raman signal.
Figure 5.14: (a) Indentation depths under defined loading conditions as a function of curing time, for three peroxide contents, employing two mixing routes; (b) conversion of the ENB C=C of 9% ENB-EPDM for the same samples.

Figure 5.15: A fairly good agreement was observed between the (a) indentation and (b) Raman results on the peroxide-cured 9% ENB-EPDM vulcanizates prepared via the solution route and via mill mixing.
The conventional macroscopic approach to investigate curing behavior is a rheometer experiment. In such experiments, the torque increase during vulcanization is measured continuously. In Figure 5.16, the indentation depths measured on samples cured for different durations (Figure 5.14) are compared with the torque differences at the corresponding curing times. The compounds with different amounts of BPPB share the same correlation curve. This indicates that differences in the heating rate and the exact curing temperature, that may be present between the rheometer and the compression mold samples, are so small that they do not impede estimating the rheometer torque from the indentation results as will be shown below.

**Figure 5.16:** Comparison between indentation and rheometer results for 9% ENB-EPDM cured with 0.5, 1 or 2 phr peroxide (torque-differences are only measured for the mill-mixed compounds).

In case of HTE synthesis of the rubber starting materials, resulting in limited material availability, it can be worthwhile to use indentation to reconstruct a rheometer curve. Then, a relation between indentation results and rheometer data that is obtained on comparable materials is necessary. The procedure is illustrated using the data of the mill-mixed compounds with 0.5 and 2.0 phr BPPB to construct the relation between indentation depth and torque difference. This relation (Figure 5.17a) is then used to construct a rheometer curve for the ‘new’ materials (here: mill-mixed and solution-processed compounds with 1.0 phr BPPB). Figure 5.17b shows the constructed ‘rheometer’ curve, with the actual rheometer curve included for comparison (it is noted that the rheometer curve for 0.5 and 2.0 phr peroxide reached plateau values of 1.1 and 2.1 N m). The agreement observed in Figure 5.17b between the experimental torque values and those estimated by indentation is fairly good.

An advantage of using indentation to reconstruct a rheometer curve is that 20 mg (per time step and curative level) suffices, compared to ~5 gram (per curative level) for a rheometer experiment. However, this method can be relatively laborious as a separate sample slide has to be vulcanized and measured for every time step.
5.3.5 Combination and addition reactions

As shown in Scheme 5.1, the main chemical reactions involved in the vulcanization are the combination of two EPDM macro-radicals, and the addition of an EPDM macro-radical to an EPDM unsaturation. Here, the combination and addition reactions are estimated using the indentation results and Raman conversions presented in Figure 5.14. The adopted analysis is outlined in Figure 5.18.

**Figure 5.17:** (a) Fitted correlation between indentation depth and rheometer torque difference for the mill-mixed 9% ENB-EPDM compounds with 1.25 and 2.5 phr BPPB MB; (b) actual rheometer curve for mill-mixed compound, and constructed rheometer curve for mill-mixed and solution route compounds with 1 phr BPPB (N.B.: Torque = Torque difference + 0.15 Nm, the minimum torque observed during the rheometer experiment).

**Figure 5.18:** The analysis employed to study the cross-link density development using the indentation and Raman results.
The total network density in mmol/kg EPDM of the set of vulcanizates discussed in Section 5.2 has been obtained by solid-state $^1$H NMR relaxation measurements. From this total network density, the chemical cross-link density is obtained by subtraction of the entanglement density (which is obtained by extrapolating the total network density as a function of peroxide content to 0 phr peroxide). An empirical correlation between the indentation depth upon loading to 20 µN and the chemical cross-link density has been constructed (solid line in Figure 5.19). Obviously, higher chemical crosslink densities correspond to smaller indentation depths. Using this correlation, the indentation depths for the kinetic experiments shown in Figure 5.14a have been converted into the total chemical cross-link density.

Every cross-link formed via an addition reaction corresponds to the conversion of one residual diene unsaturation. Based on the original amount of ENB (9% by weight) and the mass of an ENB moiety (120 g/mol), the initial C=C concentration in the EPDM was calculated to be 749 mmol/kg EPDM. Then, the number of addition cross-links in mol/kg EPDM can be determined from the C=C conversion shown in Figure 5.14b. In the absence of chain-transfer and other side-reactions and assuming the simplified reaction scheme presented in Scheme 5.1, the difference between the total chemical cross-link density and the cross-link density due to the addition reactions can be attributed to the combination reactions (Figure 5.18).

As discussed, the total network density is the sum of the chemical cross-link density due to addition and combination reactions, and the network density due to entanglements. Some entanglements are trapped, while others can disentangle on the time-scale of DSI or rheometer testing. Because of the variation in molar mass, degree of branching, etc., the relation between the total chemical cross-link density and the effective network density at the time-scale of mechanical testing that determines the experimentally observed indentation depth, may differ for the different types of EP(D)Ms. Consequently, it is expected that the indentation depth relates better with the total network density than with the total chemical cross-link density. Indeed, the total network density obtained in the $^1$H NMR relaxation study correlated fairly good with the indentation depth (dotted line in Figure 5.19, $R^2 = 0.95$), while the correlation between total chemical cross-link density and indentation depth was only moderate (solid line in Figure 5.19, $R^2 = 0.91$; adding an extra parameter $c = 5.6$ to the fitting equation $Y = (a / X^b) + c$ also resulted in $R^2 = 0.91$).
Figure 5.19: Correlation between the total chemical cross-link density (data from ref. 28) and the indentation depth for a set of peroxide-cured EP(D)Ms. For the same samples, also the relation between the total network density and the indentation depth is shown.

Figure 5.20 shows that the total cross-link density and the cross-link density due to addition increase with curing time. The curves reach a plateau after slightly more than 20 minutes, indicating completion of the free radical reaction. A larger cross-link density is obtained at higher BPPB content. The difference between the total cross-link density and the cross-link density due to addition is attributed to combination reactions, as shown schematically by the arrows in Figure 5.20. After 20 minutes curing, the cross-link densities due to combination are 24, 50 and 81 mmol/kg for the mill-mixed compounds containing 0.5, 1 and 2 phr BPPB, respectively. By solid-state NMR investigation of comparable vulcanizates, cross-link densities due to combination of 15, 29 and 59 mmol/kg were obtained for the 0.5, 1 and 2 phr BPPB compounds, respectively.\[28\] Macro-radicals involved in the addition reactions are not consumed, and are still available for combination reactions afterwards (Scheme 5.1). Therefore, the number of cross-links due to combination reactions can be compared to the number of radicals formed upon decomposition of the BPPB. Each BPPB molecule (molar mass of 338.5 g/mol) can form four radicals. With one combination per two (macro)radicals, the cross-link density due to combination would be 30, 59 and 118 mmol/kg EPDM for the 0.5, 1 and 2 phr BPPB compounds, respectively. The cross-link density attributable to combination reactions shown in Figure 5.20a is in-between the maximum dictated by the number of available peroxide molecules and the cross-link density due to combination reactions found by solid-state NMR.

The indentation and the Raman data exhibit some scatter. Furthermore, some inaccuracy is introduced by converting the indentation depths to total chemical cross-link density using a correlation of moderate quality (solid line in Figure 5.19) and by obtaining the combination cross-link density via a subtraction. For these reasons, a discussion of the relative
contributions of the addition and combination reactions and the development of these contributions with curing time is considered to be beyond the accuracy of the current approach.

![Graph](image)

**Figure 5.20**: The development of the total chemical cross-link density (closed symbols) and the addition cross-link density (open symbols) with time, for 9% ENB-EPDM with various amounts of BPPB for (a) mill-mixed and (b) solution-processed compounds. Vertical arrows indicate the cross-link density due to combination reactions (lines are guide to the eye only). [30]

### 5.4 Limitations to solution route mixing

#### 5.4.1 A higher-throughput sample preparation

In order to reduce the preparation time required per sample, another sample preparation route was investigated. In this preparation route (named solution route B in the Experimental section), small disks were punched out of EP(D)M films that were pressed at low temperature. A solution containing the curative was prepared and the amount required to obtain the desired composition was dispensed onto the EPDM disks using an automated pipetting system. After allowing time for diffusion, the EPDM disks were dried.
Solution route B with toluene as solvent resulted in a more homogeneous mixing of the curative with the EPDM than with cyclohexane as solvent. This was observed by polarized optical microscopy: upon dispensing triallyl cyanurate, a coagent for peroxide-curing, onto the EPDM disks using a toluene-based stock solution no crystallization was observed, whereas dispensing identical amounts using a cyclohexane-based stock solution of similar concentration resulted in crystallization. This is attributable to the different evaporation rates of both solvents. Toluene evaporates slower than cyclohexane and therefore allows more time for diffusion, i.e., mixing, of the curative into the EPDM.

The accuracy of the concentration obtained via solution route B depends on the accuracies of the mass of the punched disks and of the dispensed amount of solution. The fixed punch diameter and thickness of the spacer platelets allowed control over the mass of the punched rubber disks. The deviation from the average mass for disks prepared from the same film was always better than 11% and the relative standard deviation was 8% (measured by weighing 17 and 6 disks taken from two different films, average mass was typically 22 mg). The pipetting robot is designed for dispensing aqueous solutions. Therefore, its accuracy for dispensing toluene-based solutions had to be verified. A balance was placed in the pipetting robot, an EPDM disk was placed on the balance and toluene was dispensed, imitating the solution route B procedure. Accurate reading of the balance was only possible after the pipetting robot finished the dispensing procedure and came to a full stop (so some evaporation of the toluene has taken place before reading of the mass). After dispensing 10 µL, a weight change of 8.7 mg was observed, which is the mass expected based on the dispensed volume and the density of toluene (0.87 g/mL). A relative standard deviation < 2% and a maximum deviation from the average < 3% were observed (8 measurements). In a second approach, multiple aliquots of a BPPB solution were dispensed on each of the 12 disks on two slides. After thorough drying to remove the toluene, the mass increases resulting from the remaining peroxide (typically 8 mg) were measured. The observed mass changes for the two slides were 4% higher and 2% lower than the expected values, respectively, which indicates that the systematic error is rather small. In summary, the largest source for inaccuracy for solution route B is the variation in the mass of the punched disks. The overall inaccuracy may be as large as ~9%, so it is advisable to perform experiments in triplicate to obtain results that are not too much influenced by this random variation.

Compounds with 0.8, 1.0 and 1.7 phr BPPB were prepared via solution route B. After drying, some of the disks were turned upside-down. The films were cured, immersed in acetone to remove the peroxide decomposition products, dried and characterized, where it was investigated whether the indentation experiments on the disks that were turned and the disks that were not turned gave the same results. Indentation on surfaces where the BPPB solution was deposited resulted in stiffer responses than indentation on surfaces opposite to the side where the BPPB was dispensed, i.e., indentation on the turned samples (Figure 5.21).
Moreover, the indentation depths obtained on the surfaces where 1.0 phr BPPB was deposited and on the opposite surfaces are smaller and slightly larger, respectively, than those obtained for compounds containing similar BPPB contents prepared via solution route A (Figures 5.13 and 5.14a). This shows that the cross-link density varied through the vulcanizate volume. The diffusion of the BPPB in the EPDM, which could take place in the presence of toluene after dispensing as well as at elevated temperature during the curing, was not sufficient to obtain a homogeneous distribution of the BPPB in the EPDM.

![Indentation depth graph](image)

**Figure 5.21:** Indentation depths obtained on surfaces pipetted onto and opposite surfaces, of 9% ENB-EPDM cured with various BPPB levels. BPPB contents are nominal values, i.e., the deposited amounts of BPPB solution were not adjusted for deviation of the EPDM disk masses from the average mass obtained of the disks from the same film.

Repeated deposition of additional toluene onto the EPDM disks after depositing the curative via solution route B, and subsequently storing the sample slides in a saturated toluene atmosphere may enhance the migration of the curative in the EPDM. If the homogeneity is then considerably enhanced, the presented method still constitutes a viable sample preparation method, at least for curatives with a sufficiently good solubility in EPDM (Section 5.4.2).

### 5.4.2 Solubility of the curative in the EP(D)M

To increase the ease of handling as well as for health, safety and environmental reasons, industrial rubber compounding is commonly performed using masterbatches, which are commercially available.\[^{[2,26]}\] The cross-linking chemicals (peroxide, coagents) are pre-mixed with, for instance, mineral fillers and/or polymers. During compounding, the masterbatch pellets are broken into smaller particles and dispersed through the EPDM by the mechanical work of the mixing equipment. In addition, the curative will partly dissolve and diffuse into the EPDM. During solution route mixing, however, the curative is molecularly dissolved in a solvent and migrates together with the solvent into the EPDM. Upon drying, the curative remains in the rubber while the solvent evaporates. For both mixing routes, the solubility of
the curative in the EPDM (and in the solvent) is important, as poor solubility results in compositional inhomogeneity throughout the rubber. An example of a compound formulation where solution processing (solution route A, see Experimental section) resulted in severe heterogeneity is shown in Figure 5.22. Upon evaporation of the solvent mixture, the poorly soluble coagent phase separated, resulting in heterogeneity at the mm-scale. As discussed in Section 5.4.1, the homogenization at curing temperature resulting from the increased solubility and mobility of the curative is limited (in particular for the coagent in Figure 5.22, which only melts at 195 °C\[31\]). For poorly soluble curatives, a different dispersion of the curative in the rubber sample and, thus, a different cross-link density and cross-link distribution will be obtained for both mixing routes. Consequently, the indentation and Raman results will differ. Therefore, the solution route is not a suitable HTE sample preparation method for curatives with a poor solubility in EPDM, as the results can not be translated into the desired information on industrial-scale curing.

The solubility of BPPB and two coagentia in EPDM have been investigated by polarized optical microscopy (POM) and differential scanning calorimetry (DSC). Compounds of the curative in EP(D)M were prepared and subsequently cooled below the crystallization temperature to ensure that any curative not dissolved in the EP(D)M crystallized. From the presence or absence of crystals (POM) or of a melting peak (DSC), solubility limits were determined.\[32\] The solubility limit of BPPB in EPDM was >10 phr. The solubility limit of triallyl cyanurate (TAC) was ~2.5 phr, which is high enough to investigate practically relevant compound formulations via the solution route. As shown in Figure 5.22, the solubility limit of \(N,N'-m\)-phenylene dimaleimide (PDM) is much lower than 2.5 phr: upon evaporation of the solvents, the PDM phase separated. The lower solubility limit of PDM compared to that of TAC and BPPB is related to its higher polarity; EPDM is apolar and therefore mixes better with less polar curatives.\[7\]

**Figure 5.22:** The poor solubility of \(N,N'-m\)-phenylene dimaleimide (PDM) in EPDM resulted in compositional inhomogeneity throughout the sample volume; the coagent phase-separates as elongated yellow crystals. The PDM content is 2.5 phr, a solvent mixture of acetone and cyclohexane was used.
5.5 Conclusions and outlook

Because of the good correlation with the rheometer torque, the indentation depth measured by DSI under defined loading conditions can be used as a tool to characterize the state of cure of EPDM vulcanizates. The obtained indentation depth decreases when more peroxide is added or when the EPDM contains more diene, i.e., with increasing cross-link density. Moreover, the maximum indentation depth can serve as a small-scale analog for the Shore A hardness. A good agreement was found, both for the indentation depths and for the diene unsaturation conversions, between BPPB-cured compounds prepared via a solution route and via mill-mixing. By varying the curing time in a hot press the curing kinetics of EP(D)M can be studied on a small scale, providing similar results as rheometer studies on normal lab-scale.

The total chemical cross-link density in mol/kg could be determined by correlating the indentation results with solid-state NMR relaxation results, and the cross-link density due to addition reactions could be obtained from Raman spectroscopy data. The cross-link densities due to combination obtained from the difference between both were, at completion of the free radical reaction, close to the values expected from the amount of radicals available upon decomposition of the BPPB.

The described moderate-throughput solution route is successful for mixing of curatives with a good solubility into the EP(D)M. A higher-throughput solution route, which consisted of automated pipetting of curative solutions onto rubber disks, was not yet successful.

The sample handling and curing procedure resulted in sample plates (Figure 5.10) that were compatible with the requirements for HTE-characterization posed by the DSI-instrument and the Raman spectrometer. Considering the ease and speed of a rheometer experiment, the described sample handling and curing procedure was relatively laborious for studying the curing kinetics. However, this procedure offers a promising approach to obtain large series of fully cured vulcanizates in a time-efficient way. Moreover, it is a promising procedure when only a limited amount of the starting rubber material is available.

The current study was performed on amorphous rubber without fillers or oil. In order to obtain representative indentation results when a filler is distributed in the rubber material, the indentation depth should be increased; In order to obtain a fair volume average of the rubber stiffness, the strain field of the indent has to be large compared to the filler particle size or particle agglomerate size. A possible additional reason requiring adjustment of the applied load is the increased vulcanizate stiffness caused by the presence of the filler (on the other hand, the oil will reduce the stiffness). If higher loads are applied, sensitivity issues and measurement difficulties related to the relatively low loads (the employed load was only 0.2% of its full load range) will decrease.
Characterization by Raman spectroscopy will probably become more difficult for compounds containing oil or fillers; Raman spectroscopy on carbon black filled vulcanizates, for instance, is virtually impossible due to absorption of the incident (laser) light and subsequent heating of the sample.[33]

5.6 Experimental

Starting materials. Compounds were prepared by DSM Elastomers using amorphous EPM rubber and EPDM rubbers with 5-ethylidene-2-norbornene (ENB) and dicyclopentadiene (DCPD) as the dienes (Table 5.2). The molar masses $M_w$ of these EP(D)Ms ranged from 140 to 330 kg/mol. The cross-linking agent, bis(t-butylperoxy-i-propyl)benzene (BPPB), was added as a 40% masterbatch, which is commercially available as Perkadox 14-40MB-gr (AKZO Nobel). The BPPB masterbatch (BPPB MB) was mixed with the rubber in amounts of 1.25, 2.5, 5 phr (parts per hundred parts rubber, i.e. g masterbatch per 100 g EPM or EPDM) on an open mill. For the EPM, also a compound with 10 phr BPPB MB was prepared. No oil or fillers were added.

Table 5.2: Composition, rubber grade and curing times of the EPM copolymer and EPDM terpolymers.

<table>
<thead>
<tr>
<th></th>
<th>EPM</th>
<th>1.9% ENB-EPDM</th>
<th>4.3% ENB-EPDM</th>
<th>9.0% ENB-EPDM</th>
<th>4.5% DCPD-EPDM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene (wt.%)</td>
<td>49</td>
<td>54</td>
<td>52</td>
<td>48</td>
<td>55</td>
</tr>
<tr>
<td>Propylene (wt.%)</td>
<td>51</td>
<td>44</td>
<td>44</td>
<td>43</td>
<td>40</td>
</tr>
<tr>
<td>ENB (wt.%)</td>
<td>-</td>
<td>1.9</td>
<td>4.3</td>
<td>9.0</td>
<td>-</td>
</tr>
<tr>
<td>DCPD (wt.%)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>4.5</td>
</tr>
<tr>
<td>Manufacturer</td>
<td>DSM</td>
<td>Exxon Mobil</td>
<td>DSM</td>
<td>DSM</td>
<td>DSM</td>
</tr>
</tbody>
</table>

Industrial vulcanization, rheometry and mechanical testing. The compounds were fully cured in an MDR 2000 E rheometer from Dynisco (formerly Alpha Technologies) at 175 °C to measure the increase in torque necessary to maintain a specified rotation amplitude during curing.[34] The cure time required for a 90% torque increase, t90, was determined. The compounds were also cured (at DSM Elastomers) as 2 mm and 6 mm plaques in a hot press at 175 °C; cure times were t90 + 10% for 2 mm vulcanizates and t90 + 25% for 6 mm vulcanizates, to account for the influence of film thickness on the time necessary to heat the material to the cure temperature. These vulcanized samples were characterized by tensile testing, compression set at 23 °C and 70 °C and Shore A measurements according to ISO or DIN methods.[13] For the modulus 100%, the tensile strength and the elongation at break, the median out of 5 experiments per sample is presented, as prescribed by the applicable ISO standard.[13]

Sample preparation and indentation experiments for Section 5.2. Two slices were cut from the 2 mm vulcanized plaques using a razor blade. These slices were rinsed with acetone to remove surface contamination, placed on a microscopy glass slide and heated to 90 °C in vacuum. After this drying step, the vulcanizate slices adhered to a certain extent to the glass slide, preventing any error from compliance of an air gap between the sample and the glass slide. In addition, for selected vulcanizates,
indentation experiments were performed on sections that were cryogenically micro-tomed perpendicular to the surface of the vulcanizates. The micro-tomed sections were 20 to 50 μm thick (measured with an optical profilometer, Fogale Zoomsurf) and had an area of approximately 2 × 3 mm. Not cross-linked 4.3% and 9.0% ENB-EPDMs were molded to 0.5 mm films in a hot press at 160 °C and measured by indentation, as well.

**Indentation experiments for Section 5.2.** The indentation experiments were performed with a TriboIndenter (Hysitron, Minneapolis, MN) equipped with a nanoDMA 1D transducer. Before every measurement, the piezo element was stabilized for 35 s while keeping the indenter tip in contact with 0.3 μN load, and the thermal drift was measured during 40 s at a contact load of 0.4 μN (0.2 μN for the non cross-linked rubbers). The indenter was lifted 100 nm to let the material recover from the small pre-load; upon reapproach the measurement was started. The diamond tip was pressed onto the surface at a loading rate of 10 μN/s and unloaded at 10 μN/s after a 10 s hold time at maximum load (20 μN). The conical indenter (nominal half opening angle of 30°) had a spherical apex of approx. 4.7 μm radius (assuming an ideal sphere with radius R and an ideal cone with 30° half opening angle, the sphere to cone transition occurs at R/2, i.e. ~2.4 μm). The indenter shape was determined by indenting on fused quartz for which the modulus was known and subsequently the indenter shape calibration was extended to 2.0 μm contact depth by indenting on polycarbonate. Measurements were performed in an automated run. Two sets of three indents with 40 μm spacing were made on each slice from each vulcanizate. Indentation load-displacement responses obtained on the two different slices from the same vulcanizate usually matched very well and were, therefore, analyzed as one data-set. The surface of the samples was not perfectly flat due to crystals of peroxide decomposition products and pits or grooves present locally. Furthermore, for some indentations, improper surface detection upon reapproach resulted in a sudden step in the first μN of the loading response (usually the maximum indentation depth for these curves was nearly equal to the maximum indentation depth of responses without such a step). DSI measurements showing a load-displacement response deviating from the majority of the measurements on that sample (for instance a step in the load-displacement response, a sudden change in slope of the loading response, a highly deviating slope or a highly different maximum indentation depth) were not included in the calculation of the maximum indentation depth (average and standard deviation). The error bars in the Figures present one standard deviation.

**Solution route A.** A stock solution of the curative in cyclohexane was prepared. ~0.5 gram of EPDM was weighed. The desired amount of stock solution was pipetted into a bottle. After adding extra cyclohexane so that the total cyclohexane volume was ~0.8 mL, the EPDM was inserted into the bottle. Overnight vortexing was applied. After that, the bottle was opened and the compound was dried. The obtained BPPB contents in Section 4.3 were 0.52, 0.99 and 2.0 phr in 9.0% ENB-EPDM, respectively.

**Solution route B.** At a temperature below 80 °C, a film of EPDM was pressed, out of which afterwards a ~6 mm diameter disk was punched. By manual or automated pipetting, the desired amount of toluene-based stock solution was added to the film. For some of the samples, additional toluene was added to improve the migration of the curative into the EPDM disk. After allowing some time (overnight) for the curative to migrate into the EPDM, the material was dried in vacuum. A typical EPDM ‘disk’ weighed 17 mg and a typical dispensed amount of stock solution is 2 times 7 μL,
depending on the desired curative level. Automated pipetting was performed using an AnalytikJena FasTrans pipetting system equipped with 20 µL tips.

**Compression molding and sample preparation, Section 5.3 to 5.4.** The compounds were cured in a preheated compression mold (Fontijne) at 175 °C. The compounds were ‘sandwiched’ between an aluminum slide and a glass slide (the latter was chosen because of its low roughness) whereby a spacer plate, 0.5 mm thickness, with 6.5 mm diameter holes was used. The exact amount of compounds deposited in the holes in the spacer slide proved to be not very critical, though a too large amount (> 28 mg) sometimes caused cracking of the glass slide (filling of the wells required nominally 14 mg). During pressing, some surplus compound material was pressed out of the holes and ended up in-between the spacer and the aluminum sample plate, or even in an adjacent empty hole. Afterwards, the glass slide was removed and the aluminum slides with the vulcanizated samples were immersed in acetone for several days to remove the BPPB decomposition products, as those decomposition products have a Raman-active vibration that interferes with the C=C signal of the ENB. Furthermore, these particles cause surface roughness which should be avoided for the indentation experiments.

**Indentation experiments, Section 5.3 to 5.4.** The indentation experiments were performed using a Hysitron TriboIndenter equipped with a 2D transducer and a conospherical indenter (loading to 20 µN in 2 s, 10 s hold time at 20 µN and subsequently unloading in 2 s). A 2D transducer was chosen because of the lower stiffness of the spring inside the transducer, and its lower electronic drift compared to the 1D transducer. No thermal drift correction was applied, as some samples were so soft that actually not the creep but the visco-elastic deformation at the preload is probed, and typical real drift rates cause only minor changes (<10 nm) in the indentation depth.

**Raman spectroscopy.** The Raman spectroscopy experiments were performed using an Avalon Instruments Raman Station equipped with a 785 nm laser and a high-throughput experimentation stage. The intensity of the C=C ENB peak at 1688 cm\(^{-1}\) was determined as the base-line corrected peak maximum on integration from 1717 to 1660 cm\(^{-1}\). This peak height was normalized by the peak height of the CH\(_2\) scissoring vibration (1439 cm\(^{-1}\))\(^{[35]}\) obtained by integration from 1504 to 1395 cm\(^{-1}\). A calibration line determined using EPDMs with 9.0 and 4.3 % ENB showed that the peak height correlated well to the C=C content (R\(^2\) = 0.993).

**Confocal Raman spectroscopy.** To investigate particles on vulcanizate surfaces, confocal Raman spectroscopy was conducted using a Jobin Yvon Horiba LABRAM spectrometer with a 515 nm laser and a 100x long distance objective.

### 5.7 Appendices

1. **Correlation between maximum indentation depth and Shore A hardness**

For elastic materials, the load \(P\) relates, for the first part of a spherical indentation, to the total displacement \(h\) as:\(^{[14,18]}\)

\[
P_1 = c_1 \cdot h_{sphere}^{3/2} \tag{5.2}
\]

For a cone, the relation between load and displacement is:\(^{[14,18]}\)

\[
P_2 = c_2 \cdot h_{cone}^2 \tag{5.3}
\]

The Shore A hardness, \(ShoreA\), is related to the displacement of a cone into the material:
\[ \text{Shore} A = 100 - c_3 \cdot h_{\text{cone}} \]  
(5.4)

Combining Equations (5.2) and (5.3) gives

\[ h_{\text{cone}} = \sqrt[3/4]{\frac{P_2 \cdot c_1}{P_1 \cdot c_2}} h_{\text{sphere}}^{3/4} \]  
(5.5)

Substituting Equation (5.5) into Equation (5.4) gives

\[ h_{\text{sphere}} = \frac{1}{c_3^{4/3}} \left( \frac{P_1 \cdot c_2}{P_2 \cdot c_1} \right)^{2/3} \cdot (100 - \text{Shore} A)^{4/3} \]  
(5.6)

The power (4/3) is not equal to 1, so in a first approximation a linear relation between the indentation depth during spherical indentation and the Shore A hardness should not be expected. However, dependent on the probed range, a formula of the general shape

\[ y = (100 - x)^{4/3} \]  
(5.7)

may be approximated by a line. Here \( y \) relates to \( h_{\text{sphere}} \) i.e., the maximum indentation depth in Figure 5.8, and \( x \) is the Shore A hardness. The linear approximation (linear fit in the range 30 < \( x \) < 60) is shown in Figure 5.A.

![Figure 5.A](image)

**Figure 5.A:** Approximation for the general shape that may be expected for Figure 5.8 (maximum indentation depth vs. Shore A hardness), together with a linear fit over 30 < \( x \) < 60 to this shape.

To be more precise, during the depth-sensing indentation experiment, the load was independent of the depth (\( P_1 \) constant), while for Shore A hardness measurements, the load \( P_2 \) significantly changes with the displacement due to the spring loading. Then, Equation (5.3) can be replaced by:

\[ P_2 = P_{\text{const}} - c_4 \cdot h_{\text{cone}} = c_2 \cdot h_{\text{cone}}^2 \]  
(5.8)

Solving the second order polynomial

\[ c_2 \cdot h_{\text{cone}}^2 + c_4 \cdot h_{\text{cone}} - P_{\text{const}} = 0 \]  
(5.9)

gives

\[ h_{\text{cone}} = \frac{-c_4 \pm \sqrt{c_4^2 + 4 \cdot c_2 \cdot P_{\text{const}}}}{2 \cdot c_2} \]  
(5.10)
The correlation between $h_{sphere}$ and Shore A hardness can then be obtained more precisely by combining Equations (5.2), (5.4) and (5.10). Actual values for the constants $c_1$, $c_2$, $c_3$, $c_4$, $P_1$ and $P_{const}$ are necessary to sketch this correlation more precisely (some of these constants were derived elsewhere,[36] in the framework of estimating the compressive elastic modulus from the Shore A hardness). This is, in principle, possible but not pursued here. Due to the dependence of the Shore A load on the displacement $P_1/P_2$ in Equation (5.6) increases if $h_{cone}$ (or, alternatively, $h_{sphere}$) increases. This will increase the deviation from linearity.

Furthermore, for deeper indents during depth-sensing indentation, the parabolic indenter shape approximation is no longer valid for the sphere. This will increase the deviation from linearity for the deeper indents. On the other hand, the Shore A cone is truncated and mounted on a cylindrical shaft, so a load- displacement response closer to the typical sphere response is expected than for an ideal cone, thereby decreasing the deviation from linearity.

Non-Hookean elastic deformation and possibly, in particular for the less densely cross-linked materials, plastic deformation occur. These deformations will possibly result in a change of the elastic strain field that makes the strain fields of the cone more similar to the strain field of the sphere, analogous to the effective indenter shape concept discussed by G. M. Pharr and A. Boshakov.[37] This will decrease the deviation from linearity.

In summary, a linear relationship between maximum indentation depth and Shore A hardness was not expected a priori. However, linearity over a certain range of the Shore A hardness is supported by the theoretical assumptions discussed here.

2. Correlation between compression set and maximum indentation depth

Figures 5.9d and 5.9e suggest a linear relation between the maximum indentation depth and the compression sets at 23 and 70 °C, respectively. An ideal linear elastic material will have zero compression set. The loading during the DSI test of this ideal elastic material results in a non-zero maximum indentation depth. This depth determines the crossing of the correlation curve with the horizontal axis in Figures 5.9d and 5.9e. The less densely cross-linked vulcanizates deviate more from ideal linear elastic behavior than the more densely cross-linked vulcanizates. Therefore, the compression set increases with increasing maximum indentation depth. It turns out that the increase in maximum indentation depth due to the lower E-modulus, and increased time-dependent deformation, and the increase in compression set relate approximately linearly. This linearity was not a priori expected as the time-scales during testing are different, although it was expected that they would correlate.

5.8 References and notes

An HTE approach to cross-linking of EPDM


[21] Reducing the time the indenter tip rests at the surface before the actual test is performed did not diminish the pre-indent sufficiently to obtain reliable results using Hertz’s theory or the Oliver and Pharr analysis. Increasing the maximum load results in a deeper indent and, therefore, in a smaller error in the Oliver and Pharr analysis due to any pre-indent. However, the depth range of the indenter shape calibration (calibrated up to a maximum contact depth of 2.0 µm) limits the load range suitable for Oliver and Pharr’s analysis. Furthermore, non-Hookean (non-linear elastic) deformation would then still skew the calculated moduli.

[22] The differences in the shape of both indenters results in different representative strains, which is an important consideration for non-Hookean materials; ignoring the truncation, the Shore A indenter gives a representative strain of ~60% while the representative strain during spherical indentation is smaller, with the exact value depending on the indentation depth, see ref. 18.

[23] No indentation depth is reported for the EPM containing no BPPB, as this uncross-linked, low molar mass material was expected to be too soft and sticky for accurate characterization.

As both the mill-mixed compounds with 1.25 and 5.0 phr BPPB-MB and the compounds with 2.5 phr BPPB-MB contain the same peroxide and do not contain coagentia, establishing a rheometer curve by such indentation experiments would in practice not be a very worthwhile study: the reaction kinetics are governed by the peroxide half life time at the cure temperature, so one only needs to obtain, via indentation or otherwise, the maximum torque \( M_h \) to establish the full rheometer curve. Nevertheless, under other circumstances, for instance when coagentia are used, this approach may be useful.

Selected members of the set of vulcanizates were measured again by indentation to secure identical indentation testing conditions, i.e., the same transducer, drift correction settings, etc., as used for the data reported in Figure 5.14a.

The total cross-link density obtained for the 2 phr BPPB solution-route compound cured for 20 minutes is not accurate, as the indentation depth from which it was calculated was outside the correlation curve range (Figure 5.19).

It is noted that phase-separation at the (sub) \( \mu \)m-scales, such as reported for EPDM/coagent systems by H. G. Dikland, S. S. Sheiko, L. van der Does, M. Möller, A. Bantjes, *Polymer* 1993, 34, 1773-1775, will not be identified by polarized optical microscopy or differential scanning calorimetry. However, such small-scale phase separation does not lead to macroscopic spatial composition inhomogeneities, either.

Chapter 6

Correlations between chemical and physical changes of polyester coatings under UV irradiation

Abstract
In order to investigate the degradation of aromatic polyester coating materials, the surface hardness of irradiated aromatic polyester coatings was measured by depth-sensing indentation. The observed changes in the hardness were correlated with the chemical changes due to the photodegradation. Upon exposure to ultraviolet (UV) irradiation, an increase in the hardness was observed. The increase in the hardness was more pronounced when the exposure to UV was performed in air than when performed in nitrogen atmosphere. Characterization by infrared spectroscopy showed that exposure in air results in extensive carbonyl and hydroxyl group formation (photooxidation). On the other hand, when the ageing was performed in nitrogen atmosphere, such groups are only formed to a minor extent. Gel permeation chromatography proved that chain scission and cross-linking take place simultaneously during the UV irradiation. The extent of both chain scission and cross-linking is higher when aging is performed in air than in nitrogen. However, the hardness increase for the coating material was predominantly attributed to the formation of the polar groups. Also the hardness of the polyester coating materials aged in a set-up with a closer resemblance to natural weathering conditions was measured. Differences in the ageing behavior between two polyester materials and between two ageing conditions could be correlated, among other factors, to the absorption spectrum of the polymers.

Part of this chapter has been submitted for publication: P. Malanowski, J. M. Kranenburg, F. Scaltro, R. A. T. M. van Benthem, L. G. J. van der Ven, J. Laven, G. de With, Correlation between chemical and physical changes of poly(neopentyl isophthalate) coatings under short wavelength UV irradiation.
6.1 Introduction

Organic coatings are widely used in, for instance, buildings, bridges and automobiles\cite{1} to protect the substrate (metal, wood, etc.) against corrosion or other degradation. Also aesthetic considerations are a major motive to apply coatings and paints. Organic coatings contain, apart from pigments, extenders and additives, a polymeric binder. For a dry coating, the binder content is typically $\sim$50\% (by weight).\cite{2} Unfortunately, during outdoor use, numerous factors like UV irradiation, water and temperature can cause changes in the chemical structure of the binder. These changes can influence the physical properties, ultimately leading to cracking, gloss loss, blistering and/or delamination, thereby reducing the service life of the coating.\cite{3} The correlation of chemical reactions taking place during ageing with the resulting changes in physical properties is essential for the understanding of the coating lifetime. A common approach to improve the understanding of the correlation between chemical and physical changes, that will be followed in this chapter as well, is to simplify the coating system of study by omitting the pigments, extenders and additives.\cite{1,3-5}

Ultraviolet (UV) light, which is present in the spectrum of the sun, is one of the dominant factors affecting the durability of polymeric materials outdoors. In order to speed up the investigation of the degradation and to improve the reproducibility of the exposure conditions, weathering is often carried out using dedicated equipment. In such equipment, the light exposure and the temperature are increased. Alternatively, the coating materials can be exposed to shorter wavelength irradiation, thereby aggravating the exposure condition, as well.\cite{2,3,5}

One of the main chemical reactions taking place under the influence of UV radiation is chain scission (photolysis). Radicals formed from this reaction can abstract hydrogen or react with oxygen (photooxidation). Additionally, radicals can recombine and form networks (photocross-linking).\cite{3,6} All these chemical reactions can change the chemical nature of the polymer (decrease or increase the molar mass, increase the polarity) and thereby influence its mechanical properties.\cite{7-9} As depth-sensing indentation is able to probe the mechanical behavior of small material volumes, this technique can be applied to probe the changes in mechanical properties of coatings that have only a limited thickness. It has been reported that in some cases UV irradiation of polymers leads to a hardness increase,\cite{1,4,5,10-13} in other to a decrease.\cite{5,14} However, in most cases an increase of hardness is reported. The impact of chemical degradation on the physical properties may depend on which reaction (chain scission, cross-linking) is dominant, the relative ratio of these reactions and possible synergistic effects. During ageing usually a number of mechanisms are involved, simultaneously. Therefore, determining the contribution of each specific reaction to the change of the physical properties is almost impossible.

In the first part of this investigation, poly(neopentyl isophthalate) and poly(neopentyl terephthalate) coatings, abbreviated as PNI and PNT, respectively, were aged under UV
irradiation in a UVACUBE ($\lambda > \sim 254$ nm). The schematic representations of their chemical structures are shown in Scheme 6.1. To allow detailed chemical investigations, the coating materials were not cross-linked prior to ageing, while for real-life use, the binders are cross-linked.\(^2\)\(^,\)\(^3\) Ageing was carried out in different atmospheres (air and nitrogen) in order to distinguish oxygen-dependent chemical reactions and their influence on the mechanical properties. Since the temperature can influence the mechanism of photodegradation and consequently the physical properties, PNI coatings were aged at two different temperatures. The hardness values obtained on these coatings are discussed in conjunction with the results obtained by attenuated total reflectance Fourier-transform infrared spectroscopy (ATR-FTIR), gel permeation chromatography (GPC) and gel content measurements. Indentation experiments were also performed on PNI and PNT coatings exposed in a Suntest XXL+ ($\lambda > \sim 300$ nm) at conditions closer to natural conditions.

\begin{center}
\includegraphics[width=\textwidth]{Scheme6.1.png}
\end{center}

**Scheme 6.1:** Schematic representation of (a) poly(neopentyl isophthalate), PNI, and (b) poly(neopentyl terephthalate), PNT.

### 6.2 Exposure in the UVACUBE

PNI and PNT were dissolved in N-methyl-2-pyrrolidone (NMP), applied onto an aluminum substrate and dried, resulting in 12 $\mu$m thick coatings. The coatings were dry and amorphous as verified by FT-IR and DSC, respectively (see Experimental section). Subsequently, the coating materials were subjected to accelerated weathering in a UVACUBE apparatus, where the coating materials were subjected to irradiation of 254 to 600 nm wavelength. The weathering was performed at 15 $^\circ$C below and at 10 $^\circ$C above the glass transition temperature of the polyesters, i.e., at 68 and 43 $^\circ$C for PNI, and 62 and 37 $^\circ$C for PNT, respectively.

### 6.2.1 Hardness measurements

After exposure in the UVACUBE, the hardness, defined as the mean contact pressure at the start of the unloading, was measured. Although the hardness is not a true material constant (see Chapter 2), it is a suitable measure to compare materials, and it is particularly often used in the field of coating technology, possibly because the hardness is less sensitive to the substrate effect than the elastic modulus obtained by indentation $E_i$.\(^{\text{[15]}}\)

In Figure 6.1, load-displacements responses are shown for PNI after ageing in nitrogen and air at 43 and 68 $^\circ$C, respectively. The most compliant response is found for the starting material. Upon ageing, the material gets stiffer, in particular when the ageing is performed in air. From
these load-displacement responses, the hardness was evaluated using the method proposed by Oliver and Pharr.\textsuperscript{[16]} The obtained hardness results are summarized in Figure 6.2. The hardness increases as a function of exposure time (10 and 20 h) and temperature of ageing (43 and 68 °C). However, the atmosphere of ageing (air vs. nitrogen) was found to be the most important factor influencing the surface hardness of coatings. UV exposure of PNI coatings for 20 hours at 68 °C under air leads to an increase of the hardness of approximately 30% and under nitrogen of only ~7%.

![Figure 6.1](image1.png)

**Figure 6.1:** Load-displacement responses of PNI coatings, UV exposed in air and nitrogen conditions (a) at 43 °C and (b) at 68 °C. Multiple indentation loads were employed; here, load-displacement responses obtained upon loading to 1800 µN are shown.

![Figure 6.2](image2.png)

**Figure 6.2:** Development of the hardness of PNI coatings, UV exposed in air and nitrogen atmosphere, at 43 and 68 °C.

Also for the second polyester coating material investigated, PNT, the increase in the hardness is higher upon ageing in air compared to nitrogen atmosphere (Figure 6.3). Interestingly, for the PNT coatings aged in air, the largest change took place in the first 10 hours, while for the PNI coatings, the hardness increase after 20 hours irradiation is approximately double the hardness change after the first 10 hours. Possibly, the material hardness increases towards an
equilibrium due to competition between two effects of the photodegradation: hardness increase and volatilization. The hardness of the coating surface may be higher than that of the material closer to the substrate, as more photodegradation takes place at the surface. If the top layer is removed due to ongoing chain-scission (see below), resulting in small moieties that volatilize, the hardness increase is mitigated, resulting in a decrease of the slope in Figure 6.3 for the PNT aged in air. (The slightly lower hardness of the PNT aged in nitrogen compared to the starting material may be attributable to variability in the hardness of the starting material. The starting PNT was from a different batch than the aged coatings reported in Figure 6.3, and may have slightly higher hardness due to tiny crystallites.)

![Graph showing hardness over ageing time](image)

**Figure 6.3:** Development of the hardness of PNT coatings, UV exposed in air and nitrogen, at 37 and 62 °C.

Both polyester coating materials exhibited in general an increase in the hardness, in particular when the ageing is performed in air. This hardness increase is caused by one or more of the main mechanisms involved in the photodegradation of polyester:

1. **Photooxidation** leads to the formation of polar groups (mainly carbonyl and hydroxyl moieties). These groups can interact with each other *via* hydrogen bonding and/or dipolar interaction. New carbonyl and hydroxyl groups may also interact with virgin polyester. PNI contains two ester carbonyl groups in each repeating unit, which may well serve as hydrogen bond acceptors.

2. **Photolysis** leads to chain scission. Related to the phenomenon of “physical ageing” of glassy polymers it has been suggested that due to faster relaxation of smaller molecules in the glassy state, an increase of hardness can take place.\[^{10}\] On the other hand it has also been proposed that fragmentation can lead to a decrease of the hardness.\[^{5,14}\]

3. **Photocross-linking** leads to the formation of a 3-dimensional network, which is a possible explanation for the significant hardness increase.

In order to investigate which of these mechanisms is most pronounced, the hardness increases are correlated with chemical changes in the coating material (Section 6.2.3). These chemical
changes have been investigated for PNI by ATR-FTIR, GPC and by measurement of the gel content.[17] For PNT irradiated in air, ATR-FTIR investigations have been performed as well.

### 6.2.2 Chemical changes upon ageing of PNI

The formation of functional groups at the surface of the polyester coating during photodegradation was examined with attenuated total reflectance Fourier-transform infrared spectroscopy (ATR-FTIR). Figure 6.4 shows changes in the carbonyl region of the PNI exposed to UV irradiation in nitrogen and in air atmosphere at 68 °C. The corresponding changes in the hydroxyl region are presented in Figure 6.5. Ageing of polyester coatings in nitrogen leads only to little changes in the ATR-FTIR spectra as compared to ageing in air atmosphere. The development of carbonyl groups (1850 to 1600 cm\(^{-1}\)) is probably caused by the formation of anhydrides, carboxylic acids and aldehydes. The increased absorption in the OH region (3600 to 2500 cm\(^{-1}\)) is attributed to hydroxyl groups originating from carboxylic acid (mentioned above), alcohol and/or hydroperoxide. PNI aged in nitrogen and air at 43 °C exhibited qualitatively similar changes in the FTIR spectra as upon ageing in the same atmosphere at 68 °C. However, the extent of the changes at 43 °C was lower (spectra can be found in ref. 17).

The extent of polar group formation (C=O, OH) at the polyester coating surface increases as a function of exposure duration and temperature (43 and 68 °C). However, the most important factor determining the development of polar groups is the atmosphere (air vs. nitrogen). Figure 6.6 shows the development of the ‘carbonyl index’ of the polyester coating when UV irradiated in nitrogen and air at 43 and 68 °C. Here, the carbonyl index is defined as the change in the peak area in the carbonyl region, where the aromatic vibration at 723 cm\(^{-1}\) is used as reference (see Experimental section). Only exposure in air leads to major changes in the ATR-FTIR spectra.

The differences in the formation of functional groups in air and nitrogen can obviously be explained by the accepted mechanism of photolysis and photooxidation.[3] Under influence of UV irradiation, the polyester chains break-down (photolysis) and radicals are formed. Under nitrogen, these radicals can only abstract hydrogen or recombine. As a consequence of the hydrogen abstraction, only a small amount of additional hydroxyl and carbonyl groups can be formed. This explains the relatively small changes observed with ATR-FTIR of coatings aged in nitrogen. In an air atmosphere, the same radicals can, apart from hydrogen abstraction and recombination, react with oxygen (photooxidation) and form numerous new hydroxyl and carbonyl end groups, which leads to the aforementioned larger changes observed with ATR-FTIR.
Correlations between chemical and physical changes of polyester coatings under UV irradiation

Figure 6.4: ATR-FTIR spectra (region of C=O band) of PNI coatings that are exposed to UV in air and nitrogen conditions at 68 °C. Intensity is normalized to the peak at 1716 cm⁻¹.

Figure 6.5: ATR-FTIR spectra (region of OH/OOH band) of PNI coatings that are exposed to UV in air and nitrogen conditions at 68 °C. The intensity is normalized to the peak at 2967 cm⁻¹.

Figure 6.6: Carbonyl index of PNI coatings UV exposed in air and nitrogen at 43 and 68 °C.
The aged coatings were dissolved in THF, and gel permeation chromatography was conducted to investigate changes in molar mass. Figure 6.7 and 6.8 show GPC chromatograms of PNI aged in nitrogen and in air at 68 °C and at 43 °C, respectively. Both molecules with higher and with lower molar mass are formed during UV exposure in nitrogen and air. This indicates that chain scission and cross-linking reactions take place simultaneously. The extent of both the chain scission and the cross-linking increases with increasing ageing duration (10 and 20 hours) and temperature (43 and 68 °C). The rates of both reactions differ between air and nitrogen conditions. However, the influence of the weathering atmosphere on the extent of the chain scission and cross-linking is not as pronounced as on the formation of polar groups at the surface observed with ATR-FTIR.

Extensive cross-linking leads to the formation of a gel (insoluble cross-linked network). The gel content was measured gravimetrically as described in the Experimental section. Figure 6.9 shows the amount of gel collected from PNI aged in nitrogen and air atmosphere at 43 and 68 °C. Also in this case, the extent of gel content increases with increasing time (10 and 20 hours), temperature (43 and 68 °C) and atmosphere (nitrogen and air) of ageing. The difference in the extent of chain fragmentation and cross-linking between air and nitrogen can be explained by the chemistry of the degradation processes. In nitrogen some of the radicals formed during photolysis can recombine and form carbon-to-carbon cross-linked molecules. In air, besides the radicals resulting from direct photolysis, photooxidative decomposition of the polymer chain leads to additional radical formation. The mechanism of photooxidation involves hydroperoxide formation, which, after decomposition, result in a higher total number of radicals present for ageing in air compared to ageing in nitrogen. A higher concentration of radicals implies a higher probability of recombination and higher rate of cross-linking (gel formation). Besides of carbon to carbon recombination, also ether and perether bridges can be formed.

![Figure 6.7: GPC chromatograms of PNI coatings exposed to UV irradiation in air or nitrogen atmosphere at 68 °C.](image-url)
Figure 6.8: GPC chromatograms of PNI coatings exposed to UV irradiation in air or nitrogen atmosphere at 43 °C.

Figure 6.9: Gel content of PNI coatings that are exposed to UV irradiation in air or nitrogen at 43 or 68 °C.
6.2.3 Correlation between chemical changes and hardness

Photodegradation strongly influences the chemical characteristics of the polyester coatings and these changes are reflected in their mechanical properties. The three main mechanisms of the photodegradation of polyester (photolysis, photooxidation and photocrosslinking) are interrelated. However, for sake of clarity their influences on the hardness are discussed separately below.

Photo-oxidation leads to the formation of polar groups (mainly carbonyl and hydroxyl). These groups can interact with each other, or with the virgin polyester, \( \text{via} \) hydrogen bonding and/or dipolar interaction. These interactions can strongly influence the physical properties of polyester coatings. The C=O formation shown by ATR-FTIR (Figure 6.9) clearly correlates with the hardness data (Figure 6.2). The ageing in air leads to a significant development of carbonyl and hydroxyl bands as well as to a large increase of hardness. During ageing under nitrogen, photooxidation can not take place, so only small changes in the ATR-FTIR spectra and a small increase of the hardness are observed.

Photolysis leads to chain scission and may enhance the “physical ageing”. In the current study, the GPC results showed that the extent of chain scission increases with exposure time and temperature, and is higher in air than in nitrogen. However, as can be seen by comparing Figures 6.2, 6.7 and 6.8, there is no clear correlation between the extent of fragmentation of the polymer and its hardness.

Photocrosslinking leads to gel formation. The highest gel content was found for coatings aged for 20 hours at 68 °C under air conditions. Indeed, these coatings show the highest hardness. However, the gel content and hardness data show no clear correlation. For instance, ageing of the polyester coatings for 20 hours at 43 °C in air or for 20 hours at 68 °C in nitrogen resulted in similar gel contents (\(~17\%\)), while their hardness values differ. The hardness of the coating aged in air increases ~18%, compared to only ~7% for the coating aged in nitrogen. This shows that there must be at least one additional factor affecting the hardness of polyester coating. Therefore, it is concluded that the formation of polar groups has a dominant effect on the development of the hardness.

In this respect, it is recalled that most of the hardness increase during ageing of PNT in air occurred in the first 10 hours of ageing (Figure 6.3). An additional 10 hours of ageing resulted only in a modest hardness change. Interestingly, this is also reflected by the extent of the formation of polar groups (C=O, OH). The absorption in the relevant regions of the ATR-FTIR spectrum after 20 hours was only slightly higher than after 10 hours (Figure 6.10). This supports the conclusion presented above that the hardness is strongly determined by the polar groups formed due to photo-oxidation.
Correlations between chemical and physical changes of polyester coatings under UV irradiation

Figure 6.10: ATR-FTIR spectra, (a) region of OH/OOH band, and (b) region of C=O band, of PNT coatings that are exposed to UV in air at 62 °C. Intensity is normalized to the peak at (a) 2967 cm⁻¹ or (b) 1716 cm⁻¹.

6.3 Long-time exposure in the Suntest XXL+

Both coating materials were also subjected to ageing under irradiation with a spectrum that is approximately similar to that of the sun. In contrast to the ageing experiments reported in Section 6.2, where shorter wavelength irradiation was used, the irradiation spectrum in the Suntest XXL+ had a cut-off wavelength at ~300 nm. In order to accelerate the testing, the coatings were irradiated continuously, while in natural ageing conditions the intensity varies gradually from very low intensity irradiation (night) to a maximum intensity that depends on the weather. The hardness of the coatings aged in the Suntest XXL+ was measured, and correlated with the chemical characteristics that have been obtained for these coatings.[18]

6.3.1 Surface hardness

In Figure 6.11, load-displacements responses are shown for PNT coatings aged for up to 5000 hours in the Suntest XXL+. Upon ageing, the PNT coatings get stiffer. Figure 6.12 shows the hardness of PNI and PNT as a function of exposure time. Irradiation of PNT for up to 6000 hours resulted in a large increase of hardness (hardness increased by 100%). In contrast, no
significant increase of the hardness of PNI was observed after up to 10000 hours of irradiation.

The ageing resulted in an increased surface roughness, in particular for PNT, as observed by confocal microscopy (data not shown). Scanning the indenter with a low contact force over the coating surface also showed that the surface roughness of PNT had increased (Figure 6.13). The roughness can impede accurate determination of the hardness as the assumption that the indenter indents a flat surface that is perpendicular to the loading axis, is then not valid. The large standard deviations for PNT coatings aged for more than 4000 hours can be attributed to the increased roughness. Hardness values obtained from deeper indents are less influenced by the surface roughness. A second reason to repeat the indentation experiments at higher loads is related to the coating thickness. Due to photodegradation, small moieties such as CO, CO₂, and CH₂O are formed.⁴⁻¹⁻⁸ These moieties can volatilize, resulting in a decrease of the coating thickness. Indeed, the thickness of PNT coatings aged for up to 6000 hours was reduced from 12 µm to 6 µm. Hardness measurements on thin coatings may be influenced by the substrate (aluminum). In order to examine the influence of the surface roughness and the reduced thickness of the degraded PNT coatings on the obtained hardness, an additional series of indentation experiments was carried out on PNT coatings aged for 4000, 5000 and 6000 hours employing higher loads, resulting in deeper indents. The results (Figure 6.12) were almost identical to those obtained at lower indentation depths, which indicate that the effects from both surface roughness and substrate effect are only small.

![Figure 6.11: Load-displacements responses of PNT coatings, UV exposed in the Suntest XXL+ for up to 5000 hours.](image)
Correlations between chemical and physical changes of polyester coatings under UV irradiation

Figure 6.12: Development of the hardness of PNI and PNT coatings aged in the Suntest XXL+.

Figure 6.13: Scanning the coating surface with the indenter showed that ageing increased the surface roughness. (a) PNT aged for 200 hours; (b) PNI aged for 6000 hours; (c) PNT aged for 6000 hours. Sharp protrusions on the coating surface appear as triangles in image (c) due to the geometry of the indenter tip used for imaging.

6.3.2 Chemical changes upon ageing

The increase in the hardness for PNT on one hand, and the absence of such an increase for PNI, can be related to the difference in their material specific absorption spectra (Figure 6.14). PNT absorbs more of the radiation than PNI, as shown by the larger overlap of the PNT absorption spectrum with the spectral power distribution of the Suntest XXL+ (Figure 6.14). Due to this larger absorption, the extent of the chemical changes is also expected to be larger for PNT than for PNI. Figure 6.15 shows ATR-FTIR spectra (carbonyl region) of the PNI and PNT aged in the Suntest XXL+. Ageing of PNI leads only to minor changes in the ATR-FTIR spectra (Figure 6.15a), while for PNT extensive changes in the ATR-FTIR spectrum are observed (Figure 6.15b). The formation of so many new carbonyl groups (probably anhydride, carboxylic acids and aldehydes) indicates extensive photooxidation.

Also in terms of gel formation, which results from cross-linking during photodegradation, extensive differences were observed between PNI and PNT (Figure 6.16). During the first
2000 hours of ageing, for PNT the gel content increased to about 50%. During an additional 1000 hours of ageing, it only slightly increased. Even longer ageing resulted in decomposition of the gel, and, therefore, a reduction of the gel content to about 40% (for 6000 hours of ageing). In the case of PNI, the first indication of gel formation was found only after 9000 hours of ageing. After 10000 hours of ageing, the gel content reached about 5%.

Figure 6.14: Absorption of PNI and PNT, compared to the irradiation the PNI and PNT were exposed to in the Suntest XXL+.

Figure 6.15: ATR-FTIR spectra (region of C=O band) of (a) PNI and (b) PNT coating surface, aged up to 10000 and 6000 hours, respectively. Spectra are normalized to the peak at 1716 cm\(^{-1}\).
6.3.3 Correlation between chemical changes and hardness

In Section 6.2 it was found that, although cross-linking is a plausible reason for a hardness increase, the presence of polar groups (C=O and OH) have a dominant effect on the mechanical properties of aged PNI coatings. That conclusion was drawn based on PNI and PNT coatings ageing in the UVACUBE ($\lambda > 254$ nm) under air and nitrogen conditions. The results shown in this section are in agreement with that data: Even though further UV-irradiation of PNT coatings aged for up to 3000 hours leads to a slight decrease of the gel content, the hardness still increases, as does the amount of polar groups. Ageing of PNI under these conditions resulted in relatively small changes in the carbonyl region of the ATR-FTIR spectra. This resulted in a rather insignificant hardness increase.

A large increase in the hardness also indicates a rising tendency of the coating to crack.\(^{[19]}\)

This phenomenon was indeed observed for PNT coatings aged for 4000 hours and longer, as shown by scanning electron microscopy (data provided in ref. 18). The cracking occurred for coatings that exhibited a hardness increase of $\sim 100\%$ (Figure 6.12). The extent of cracking was not so extensive that it would result in invalid DSI results (indenting right on a crack does not provide reliable load-displacement responses). In contrast to the PNT coatings, no cracking upon UV exposure was observed for the PNI coatings addressed in Figure 6.12.
6.4 Conclusions

In this chapter, increases in the hardness of coating materials upon ageing were correlated with the chemical changes in the materials. The hardness of both polyester coating materials studied, PNI and PNT, increased with time and temperature of exposure in the UVACUBE ($\lambda > \sim 254$). Larger increases in the hardness were observed when the UV irradiation was performed in air than when performed in nitrogen atmosphere.

It was found that the hardness changes correlated with the development of carbonyl and hydroxyl groups, which is attributed to photooxidation. Carbonyl and hydroxyl groups formed by photooxidation can interact with each other or with the virgin polymer via hydrogen bonding and dipolar interaction, and in this way strongly increase the hardness of the coating material. Formation of cross-links due to the photodegradation may constitute an additional, smaller, cause for the hardness increase.

In the second part, the photodegradation of PNI and PNT coatings upon ageing in a Suntest XXL+ was studied. A large increase in the hardness of PNT was observed, while the hardness of PNI remained approximately constant with ageing time. This was attributed to the absorption spectra of both coating materials: The higher absorption for PNT resulted in larger changes in its chemical characteristics, as observed by ATR-FTIR and gel content measurements, than for PNI. The extensive chemical changes taking place in the PNT coating material resulted in a significant increase of the hardness and in failure of the coating by cracking. Again, the hardness increase correlated to the formation of polar groups. PNI showed a much smaller extent of degradation and, as a consequence, a minor increase of the hardness and no cracking.
6.5 Experimental

**Materials.** Poly(neopentyl isophthalate) (PNI) and poly(neopentyl terephthalate) (PNT), were provided by DSM, and are described in more detail elsewhere.\(^\text{[17,18]}\) The number average molar masses of PNI and PNT as determined using GPC (solvent: THF, PS calibration) were 9650 g/mol and 3850 g/mol, respectively. Their glass transition temperatures were 58 and 53 °C, respectively.

**Coating preparation.** The polyester was dissolved in \( N \)-methyl-2-pyrrolidone (NMP) at a concentration of 30 wt.% and subsequently applied on an aluminium plate (cleaned with ethanol and acetone) using a doctor blade. Coatings were dried in an oven at 120 °C for one hour; all NMP was evaporated as confirmed by FTIR (C=O at 1675 cm\(^{-1}\)). After drying the polyester remained amorphous, as checked with DSC. The film thicknesses were measured with a TWIN-CHECK Instrument (List-Magnetic GmbH). The coating thickness after drying was approximately 12 μm.

**UV exposure in the UVACUBE.** In the first part of this investigation, coatings were exposed to radiation in the 254 to 600 nm range in a UVACUBE apparatus (Dr. Hönle AG, equipped with a high pressure Mercury lamp). The intensity of the light was 40 W/m\(^2\) in the range of 250 to 300 nm and 210 W/m\(^2\) in the range of 300 to 400 nm, as measured with AvaSpec AVS SD2000 Fiber Optic Spectrometer (Avantes) using a FC-UV050-2 fiber. In the UVACUBE, the coatings were placed in a thermostatic box set at 68 °C or at 43 °C covered with quartz glass and continuously purged with either dry air or dry nitrogen. The distance from the samples (5 cm \( \times \) 5 cm) to the lamp was 20 cm. The samples were exposed to UV light for either 10 or 20 hours.

**UV exposure in the Suntest XXL+.** In the second part of this investigation PNI and PNT coatings were aged using a Suntest XXL+ (ATLAS), equipped with xenon lamps. The light emitted by the xenon lamps was filtered with daylight filters (\( \lambda > \sim 300 \) nm). The spectral distribution of the light provided by this system nearly resembles the solar spectral distribution with an intensity of the light in the range of 300 to 400 nm of 60 W/m\(^2\). The relative humidity and temperature in the chamber were 25% and 45 °C and the temperature of the black standard was 70 °C.

**Depth-sensing indentation (DSI).** DSI was conducted with a TribolIndenter (Hysitron), equipped with a 2D-transducer and a Berkovich tip at 25 °C under reduced humidity (13.2 ± 0.3 % RH). A loading scheme of 10 s loading to maximum load (\( P_{\text{max}} \)), 10 s hold at maximum load and 1 s unloading was applied. For each sample, at least one series of 10 experiments was performed in which the maximum load was varied in steps of 300 μN from 3000 μN to 300 μN. For coatings that exhibited a relatively high surface roughness and low thickness (PNT after 4000, 5000 and 6000 hours of ageing in a Suntest XXL+), additionally a series of 8 measurements was performed at higher load levels, namely ranging from 4200 to 2100 μN. The first two measurements of each series were disregarded to exclude the effect of thermal drift. For samples where two or more series of ten indents were made, no significant differences were observed between the series.

**DSI analysis.** The indentation load-displacement responses were analyzed using the procedure proposed by Oliver and Pharr.\(^{[16]}\) The mean contact pressure is taken as a measure of the hardness \( H \) of the material:

\[
H = \frac{P_{\text{max}}}{A} \tag{6.1}
\]
where $P_{\text{max}}$ is the load at the beginning of the unloading and $A$ is the projected contact area, which depends on the contact depth $h_c$ and the tip shape. The tip area function calibration was performed on polystyrene, assuming a constant elastic modulus for polystyrene in the contact depth range from 126 to 954 nm (see Appendix). The unloading responses were fitted from $0.95 \cdot P_{\text{max}}$ to $0.20 \cdot P_{\text{max}}$ with the conventional power law form to obtain the slope at the start of the unloading $S$, that is used in the calculation of the contact depth.$^{[16]}$ The obtained fits match well with the unloading responses even outside of the range used for fitting: $R^2$ was observed to be larger than 0.999. The power law exponents ranged from 1.6 to 2.4. The cause for lower values than the value of 2 expected for the contact of a cone onto an elastic halfspace$^{[20]}$ are discussed by Bolshakov and Pharr.$^{[21]}$ For some of the fits power values higher than 2 were obtained. This is possibly attributable to non-linear elastic and visco-elastic response of the polymer material. It was noted that the hardness decreased with the contact depth. Therefore, in order to achieve a fair comparison, the hardness was evaluated at constant contact depth (400 nm, for the higher load series 550 nm) for the various ageing conditions (evaluation at another contact depth gives the same trends at somewhat shifted hardness values, see Appendix), whereby a linear fit was applied to the hardness data as function of contact depth for the various ageing conditions.

It is admitted that the procedure to calculate the projected contact area is developed for elastic-plastic materials and the actual projected contact area may be somewhat different for visco-elastic-plastic materials such as polymers.$^{[22,23]}$ Moreover, the hardness obtained by indentation depends on experimental settings such as the loading time, hold time and unloading rate.$^{[24-26]}$ We ascertained that the creep rate at the end of the hold period is small compared to the unloading displacement rate. Therefore, the unloading slope is not influenced by creep and can be used to evaluate the contact area. Although depth-sensing indentation does not provide absolute values for the hardness, the obtained hardness can be used as a reliable measure to compare different samples.

**Tip area function calibration.** Crucial to the evaluation of the hardness is the tip area function calibration, which is therefore described here. The tip area function was established on polystyrene ($M_n = 95$ kg/mol, PDI = 1.33) drop cast from a toluene solution and afterwards thoroughly dried under vacuum above its glass transition temperature, as the available load range of the TriboIndenter did not allow to determine the tip shape up to the desired contact depth on fused quartz. Indentation experiments were performed on the polystyrene employing various maximum load levels such that the contact depths ranged from 126 to 954 nm. The indentation modulus $E_i$ of the PS determined for the three deepest indents using the ideal Berkovich area function was 4.58 GPa (employing a Poisson’s ratio $\nu$ of 0.35), which is close to the value of $\sim$4.5 GPa reported by Briscoe et al.$^{[26]}$ for indentations in this indentation depth range. Using $E_i = 4.58$ GPa, the indenter area function for lower depths was constructed based on the shallower indentation responses, resulting in a relation, the so-called area function, between the contact depth $h_c$ and the projected contact area $A$.

$$A = 24.5 h_c^2 - 980.13 h_c + 29506 \sqrt{h_c}$$

(6.2)

This area function results in a projected contact area $A$ which is at 200 nm 23% higher than for a perfect Berkovich. For contact depths between 126 and 954 nm, the modulus of polystyrene was constant by definition, while the hardness was 0.24 GPa for the deepest indents and increased $\sim$13% with decreasing contact depth. The hardness is somewhat lower than the value of $\sim$0.27 GPa observed
Correlations between chemical and physical changes of polyester coatings under UV irradiation

by Briscoe et al.\textsuperscript{[26]} This can probably be attributed to the higher unloading rate used in the current work.

The material hardness increase is also reflected by a decrease in the contact depth to maximum indentation depth ratio ($h_c/h_{max}$ decreased 3%, from 0.86 to 0.84) which may be due to the tip apex rounding (which results in a lower strain and therefore less plastic deformation). Moreover, due to the presence of inherent length-scales, such as the polymer chain length, self-similarity is not completely obeyed.

**Topographic imaging.** Height images of the coating surfaces were made by scanning the Berkovich indenter tip over the surface, using the piezo element of the TriboIndenter, at a setpoint force of 1 µN. The scanning velocity was set low enough (~7 µm/s) that the forward and the backward trace overlap (apart from a small lateral shift due to the piezo hysteresis). As the obtained image constitutes a convolution of the tip shape and the surface topography, and the factory calibration of the piezo element was not verified, the results should be used on a qualitative base.

**Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR).** ATR-FTIR was performed using a BioRad Excalibur FTS3000MX spectrometer equipped with a diamond crystal (Golden Gate). Spectra of the surface of the PNI coatings were recorded in the range of 4000 to 650 cm$^{-1}$ with a resolution of 4 cm$^{-1}$. A small piece was cut from the coated panel and pressed on the ATR crystal. Spectra in the range of 2300 to 3700 cm$^{-1}$ were normalized to the peak at 2967 cm$^{-1}$ (CH$_3$ antisymmetric stretching) and in the range of 1500 to 1900 cm$^{-1}$ to the peak at 1716 cm$^{-1}$ (C=O stretching). The ratio of the carbonyl peak area between 1900 and 1625 cm$^{-1}$ and the peak area at 723 cm$^{-1}$ attributed to the aromatic ring was calculated. The value of that ratio in excess over its starting value is defined as the “carbonyl index” and is used as a measure for the formation of carbonyl groups.

**Gel permeation chromatography (GPC).** GPC was carried out using a WATERS 2695 separation module and a Model 2414 refractive index detector at 40 °C. The column set consisted of a Polymer Laboratories PLgel guard column (5 µm particles, 50 × 7.5 mm), followed by two PLgel mixed-C columns (5 µm particles, 300 × 7.5 mm), calibrated at 40 °C using polystyrene standards (Polymer Laboratories, $M = 580$ up to $M = 7.1 \times 10^6$ g/mol). Tetrahydrofuran (Biosolve, stabilised with BHT) was used as eluent at a flow rate of 1.0 mL/min. Prior to the GPC analysis, the polyester was removed from the substrate and dissolved in THF. In the case of aged polyester, the insoluble (cross-linked gel) part of the polymer was removed by filtration (0.2 µm PTFE filter) and the soluble part (concentration ~5 mg/mL in THF) was analyzed. Data acquisition and processing were performed using WATERS Empower 2 software. Chromatograms were scaled to the maximum peak height.

**Gel content measurements.** Gel contents were measured gravimetrically. The adhesion of the polyester coating to the aluminium substrate was very high and peeling off the coating for gel content measurement was not possible. Instead, the weight of the coating together with the substrate was measured first. Then, the polyester was washed off the substrate with THF and the weight of the bare substrate was measured. The soluble part of polyester was separated from the gel part by filtration (0.2 PTFE filter). After evaporation of THF (vacuum oven, 24 hours at 75 °C) the weight of the soluble fraction was measured. From the weights of the coating with substrate, the bare substrate and the soluble fraction, the weight of the gel content was calculated.
Absorption of PNI and PNT. UV spectroscopy was performed using an UV/VIS/NIR spectrometer Lambda 900 (Perkin Elmer). Spectra were collected in the range of 500 to 200 nm. For this measurement PNI and PNT were dissolved in chloroform (0.177 g/L) and placed in quartz cuvettes (1 cm).

Suntest XXL+ spectrum measurement. The spectral power distribution of the irradiation in the Suntest XXL+ was measured using an ultraviolet radiation spectroradiometer MSS 2040-UV.

6.6 Appendix

Evaluation of the hardness of aged PNI at a contact depth of 250 nm

The presented hardness values after various ageing conditions were evaluated at a contact depth of 400 nm. In that procedure, a linear fit was applied to the hardness data as function of contact depth; typically, the applied loading conditions and maximum load levels resulted in a contact depth range from 160 to 540 nm.

Evaluation at other contact depths than 400 nm resulted in the same trends with ageing conditions, as shown for PNI in Figure 6.A (to be compared with Figure 6.2). However, somewhat higher hardness values are observed. It is noted that, as discussed in the Experimental section, also for polystyrene a hardness increase is observed upon evaluating the hardness at smaller contact depths (at \( h_c = 400 \) nm, the hardness of the polystyrene was 0.265 GPa, compared to \( H = 0.271 \) GPa at \( h_c = 250 \) nm). Below, the hardness for the aged PNI as evaluated at 250 nm is shown.

![Figure 6.A: Hardness of PNI coating material after various ageing conditions evaluated at a contact depth of 250 nm.](image-url)
6.7 References


Chapter 7

Verification of key assumptions to the analysis method

Abstract

Depth-sensing indentation on visco-elastic polymers is discussed in more detail using several amorphous copoly(2-oxazoline)s possessing a random monomer distribution over the polymer chain. Results obtained by both quasistatic and dynamic indentation experiments will be discussed. The copolymers are tested at room temperature, just below their glass transition. The closer to the glass transition, the more the assumptions for the analysis of the quasistatic indentation data are violated, since the analysis procedure is developed for elastic-plastic materials. It is shown that erroneous analysis results due to extensive viscous deformation can easily be identified by comparison of the creep rate at the end of the hold period with the unloading displacement rate. Alternatively, it can be identified from the power of the fit to the unloading response.

As variation to the identification of the glass transition of amorphous polymers by the maximum in the loss tangent as function of temperature, the loss tangent as a function of the composition was investigated. Also here, the loss tangent nicely exhibited the onset of the glass transition, as well as the expected dependency on the testing frequency.

Another assumption for the analysis of quasistatic indentation responses is that no cracking occurs around the indent or at the indent corners. Indents on polystyrene, which is known to be susceptible to stress localization, were imaged by scanning the indenter over the residual impressions. It was shown that the indentation equipment is sensitive enough to visualize cracks by topographic imaging that had resulted in only modest changes in the load-displacement response.
Chapter 7

7.1 Introduction

The analysis procedure used in this thesis to obtain the indentation modulus $E_i$ from the load-displacement responses is based on a couple of assumptions, as summarized in Chapter 2. These include the assumptions that:

1. the unloading is predominantly elastic;
2. the tip-sample adhesion is so small that it does not influence the load-displacement response;
3. no cracks are formed around the indent or at the indent corners.

Throughout the thesis, the validity of the first assumption was ensured by excluding data from load-displacement responses that exhibited extensive creep. As criterion was adopted that the displacement rate during the unloading should exceed the displacement rate at the end of the hold period by, at least, a factor of five (see Chapter 3). This somewhat arbitrary choice deserves some more attention. Therefore, the ratio between the creep at the end of the hold period and the unloading displacement rate is addressed in more detail in this chapter.

The second assumption is usually met for polymers, as evidenced by the good agreement between modeling and experimental results assuming frictionless contact.\cite{1} However, it is reported that for the contact of a sharp indenter on a compliant elastic surface, the friction influences the load-displacement responses significantly.\cite{2} In the preceding chapters of this thesis, no moduli are presented that were obtained on sticky samples. Some of the very soft EPMs (Chapter 5) exhibited considerable adhesion. However, for those materials no moduli are reported.

The third assumption is ensured by imaging the indents on materials that may exhibit brittle behavior. In this thesis, that applies to the MeMe and EtEt homopolymers at low humidity (Chapter 3), the polystyrenes and superpolystyrenes (Chapter 4) and, possibly, to the polyesters (Chapter 6). Selected indents on these materials were imaged by scanning the Berkovich indenter probe over the surface. No cracking was observed, although for some imaged indents, the indent extended at the indent corners slightly further into the material than expected based on the regular triangular geometry, which may indicate a tiny crack. In this chapter, it is investigated whether the sensitivity of imaging with the indenter is sufficient to reveal the presence of cracks.

For the investigation of the first and second assumption in the list above, samples were investigated that exhibit from the chemical point of view a close resemblance to the random copolymers discussed in Section 3.4. Dynamic DSI proved notably versatile for the study of the glass transition during the study of those copolymers. Therefore, dynamic indentation results for these materials are presented as well. The investigation of the third assumption was conducted on polystyrene.
7.2 Visco-elastic behavior of amorphous copoly(2-oxazoline)s

7.2.1 Random 2-ethyl-2-oxazoline:2-(3-ethylheptyl)-2-oxazoline copolymers

At the glass transition, the mechanical properties of polymers change drastically. The elastic modulus decreases tremendously, and the loss tangent passes through a maximum.\[^3\] These changes in the mechanical behavior are investigated on amorphous random copoly(2-oxazoline)s that are only slightly below their $T_g$. These copoly(2-oxazoline)s were prepared by living cationic ring opening polymerization at a monomer-to-initiator ratio of 100. The polymerization was performed in acetonitrile using methyl tosylate as the initiator, similar to the procedure discussed elsewhere.\[^4\] The monomer units incorporated in the random copolymer are shown in Scheme 7.1. Chemical characteristics of these copolymers are summarized in Table 7.1.

The EHe units have the same number of carbon and hydrogen atoms in the side-chain as the 2-nonyl-2-oxazoline units (see Table 3.1). However, the spatial arrangement differs. In contrast to the poly(2-alkyl-2-oxazoline) with linear alkyl chains longer than five carbon atoms,\[^5\] EHe does not crystallize, as shown by differential scanning calorimetry (DSC). The ethyl groups racemically attached to the heptyl side chains impede alignment of the heptyl chains and thereby prevent crystallization. Figure 7.1 shows the glass transition temperatures observed by DSC for the Et:EHe random copolymers as a function of composition. The glass transition temperature of the copolymers depends linearly on the composition (in weight content), which is in agreement with the Gordon-Taylor model with 1 as the free volume difference ratio.\[^3,6\] For some of the library members, not sufficient material was available for DSC measurements. Therefore, the $T_g$ of the 48 wt.% EHe and the 82 wt.% EHe copolymer were estimated from the linear fit in Figure 7.1 to be 27 °C and 6 °C, respectively.

![Scheme 7.1](image.png)

**Scheme 7.1:** Schematic representation of the monomer units in the poly(2-ethyl-2-oxazoline-r-2-(3-ethylheptyl)-2-oxazoline), Et-r-EHe.
### Table 7.1: Chemical characteristics of the EH-r-Et copolymers.

<table>
<thead>
<tr>
<th>Desired chemical composition (EHe mol%)</th>
<th>Chemical composition (EHe mol%)</th>
<th>Chemical composition (EHe wt.%)</th>
<th>GPC*</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>17700</td>
</tr>
<tr>
<td>10</td>
<td>10</td>
<td>18</td>
<td>14400</td>
</tr>
<tr>
<td>20</td>
<td>18</td>
<td>30</td>
<td>15200</td>
</tr>
<tr>
<td>30</td>
<td>32</td>
<td>48</td>
<td>15700</td>
</tr>
<tr>
<td>40</td>
<td>38</td>
<td>55</td>
<td>16300</td>
</tr>
<tr>
<td>50</td>
<td>46</td>
<td>63</td>
<td>16900</td>
</tr>
<tr>
<td>60</td>
<td>59</td>
<td>74</td>
<td>17700</td>
</tr>
<tr>
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<td>86</td>
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<td>88</td>
<td>94</td>
<td>19300</td>
</tr>
<tr>
<td>100</td>
<td>100</td>
<td>100</td>
<td>16900</td>
</tr>
</tbody>
</table>

* Eluent: N,N-dimethylacetamide with 2.1 g/L LiCl. PS calibration standards.

![Figure 7.1: Glass transition for selected Et-r-EHe copolymers of varying overall chemical composition. The horizontal line indicates the temperature during DSI testing.](image)

The copolymers with a high EHe content were sticky at ambient temperature. Therefore, only the copolymers containing up to 63 wt.% EHe were dropcast for investigation by DSI. The materials were dissolved in chloroform and dropcast. In line with high-throughput experimentation concepts, the dropcasting was performed using a pipetting robot. This
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pipetting resulted in accurately positioned, regularly shaped polymer spots. It was noted that depositing several spots of the same material in one deposition run resulted in some variation in the deposited amount and therefore in the film diameter and thickness, indicating that the volumetric accuracy of handling concentrated chloroform-based polymer solutions with the pipetting robot is not optimal. On the other hand, the deposited volume is not very critical as reliable DSI experiments can also be conducted on small volumes.

After drying, DSI was conducted on these materials at reduced humidity (5.2% RH). The horizontal line in Figure 7.1 indicates the temperature during DSI testing (~25 °C). Various measurement protocols were employed:

1. quasistatic DSI with loading in 10 s, 10 s hold, unload in 2 s (load control);
2. quasistatic DSI with loading in 10 s, 10 s hold, unload in 0.4 s (load control);
3. quasistatic DSI with loading-unloading-reloading-unloading-reloading scheme (open loop);
4. dynamic DSI at various frequencies.

7.2.2 Effect of the unloading rate

Selected load-displacement responses are shown in Figure 7.2. The indentation moduli $E_i$ obtained from the analysis of the unloading responses of several Et:EHe copolymers are shown in Figure 7.3. With increasing EHe content, the material stiffness decreases. The material is still probed at a temperature below its glass transition. However, since the large decrease in the stiffness of amorphous materials at their glass transition sets in gradually,$^{[3,6]}$ $E_i$ already starts to decrease with increasing EHe content, due to the smaller distance to $T_g$. As a sidenote it is mentioned that the number of entanglements per chain can be relatively small due to the modest degree of polymerization, as also discussed in Section 3.4.2. Therefore, the rubbery plateau modulus usually exhibited by amorphous polymers above their $T_g$ (typically ~10 MPa) may be absent for these materials.

Indentation experiments were performed on the polymer spots employing unloading times of either 0.4 s or 2 s (first two loading protocols listed above). The indentation moduli $E_i$ obtained for both unloading times agree relatively well for the (co)polymers containing up to 18 wt.% EHe (Figure 7.3). However, for the copolymer containing 30 wt.% EHe, the indentation moduli obtained employing both unloading times differ appreciably. The difference in $E_i$ observed for both unloading rates allows for an investigation into the limitations of DSI on materials close to their glass transition. If a material exhibits extensive creep, application of the Oliver and Pharr procedure results in unreliable $E_i$ values,$^{[7,8,9]}$ unless the unloading rate is increased sufficiently.$^{[10]}$ The 2 s unloading response analyzed to obtain $E_i$ for the 30 wt.% EHe copolymer is influenced by creep, as the creep rate is large compared to the unloading displacement rate (Table 7.2). The indenter moves during hold at constant load into the material, while during elastic unloading, the material pushes the indenter back,
resulting in a displacement rate with the opposite sign. For sake of readability, the minus sign that formally should be included in Table 7.2 is not shown.

In Figure 7.4, the unloading segments of the load-displacement responses of Figure 7.2 are shown together with the corresponding unloading responses obtained employing an unloading time of 2 s. The offset between the start points of both unloading curves is only small, which is expected as their loading and hold history are equal. However, the curvature of both unloading responses differs considerably. For the unloading in 2 s, the creep influenced the unloading displacement rate, resulting in a nearly vertical initial slope of the unloading response (Figure 7.4). During the analysis the unloading responses were fitted using the conventional power law equation. In order to generate the steep slope at the start of the unloading, the value for the power of the resulting fit, which is annotated in Figure 7.4, is relatively high compared to the value of 2 derived by Sneddon\cite{11} for the contact of a cone onto a flat elastic halfspace. The power values smaller than 2 (Figures 7.4 and 7.5) are attributable to plastic deformation.\cite{12} The large deviation from 2 observed in Figure 7.5 for the 30 wt.% EHe material unloaded in 2 s clearly indicates the visco-elastic response of the copolymer.

The power law fit was performed with the Triboscan software using only part of the unloading response, namely from 95 to 20% of $P_{\text{max}}$. The obtained values were inserted in Microcal Origin to obtain $R^2$ with respect to the full range of the unloading response (Figure 7.4). In this calculation of $R^2$, all deviation between the fit and the original data is attributed to the variable that is plotted on the vertical axis (the load in Figure 7.4). This also explains why the Origin fit does not extend outside the displacement ranges of the unloading responses (Figure 7.4). The $R^2$ values provided in Figure 7.4 are smaller for the 2 s unloading, indicating less optimal fits. However, the difference between the $R^2$ values is not pronounced, indicating that the thus obtained $R^2$ value is not the most sensitive indicator to identify whether analysis results are unreliable due to creep.

Considering that the $E_i$ obtained for the 18 wt.% EHe copolymer upon unloading in 0.4 s was in agreement with that observed upon unloading in 2 s, it is concluded that the effect of creep on this analysis result is low enough.\cite{13} The power value is a very sensitive indicator for influence of creep on the analysis results, as shown in Figure 7.5. Also the criterion on the unloading displacement rate with respect to the creep rate is rather effective to avoid large influences from creep on the analysis results: analysis of load-displacement responses exhibiting a ratio of only four (Table 7.2), less strict than the arbitrary criterion of five adopted in this thesis, already resulted in the same $E_i$ as quicker unloading experiments on the same material.
Table 7.2: Approximate ratio of the initial unloading displacement rate to the creep rate at the end of the hold time. The ratio was evaluated from the last ~1 s of the hold time and the first 0.1 s of the unloading for the indentation experiment performed at 1500 µN.

<table>
<thead>
<tr>
<th>EHe wt.%</th>
<th>Unloading in 0.4 s</th>
<th>Unloading in 2 s</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>84</td>
<td>13</td>
</tr>
<tr>
<td>18</td>
<td>22</td>
<td>4</td>
</tr>
<tr>
<td>30</td>
<td>4</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Figure 7.2: Load-displacement responses for the 30 wt.% EHe copolymer, employing an unloading time of 0.4 s.

Figure 7.3: Indentation moduli obtained for Et-ε-EHe random copolymers employing an experimental protocol with unloading in 2 or 0.4 s. $E_i$ as obtained for the 30 wt.% EHe copolymer by unloading in 2 s is not reliable, as discussed in the text.
Figure 7.4: Unloading responses for the 30 wt.% EHe copolymer upon unloading from (a) 600 µN or (b) 300 µN in 2 s or 0.4 s.

Figure 7.5: The power values obtained in the fit procedure to calculate the $E_i$ values shown in Figure 7.3.
7.2.3 Viscous response and adhesion

Another quasistatic loading protocol was applied onto these copolymers, which is outlined in Figure 7.6. This experiment protocol, which included partial unloading combined with subsequent reloading, resulted in the load-displacement responses shown in Figure 7.7. The latter figure shows that with increasing EHe content, i.e., with decreasing distance to the glass transition:

1. the displacement, in particular the displacement during the hold period, increases;
2. the curvature of the loading response decreases;
3. the overlap between the various loading responses in Figure 7.7 decreases;
4. the overlap between the unloading and reloading responses decreases;
5. a smaller part of the total displacement recovers at unloading;
6. the negative load at the end of the (final) unloading increases.

The first five observations are mainly caused by the increased viscous response. Furthermore, the first, second and fifth observation are partly attributable to a decrease of the yield stress, resulting in a larger plastic deformation. Here it is noted that the yield stress depends on the timescale of testing, i.e., on the viscosity,[14] so both causes mentioned above are related. Decreasing overlap between the various loading responses for the same material, listed as third observation, is a clear expression of the time-dependent behavior. As the loading was conducted in 10 s irrespective of $P_{\text{max}}$, the various loading responses in Figure 7.7 represent various loading rates. The loadings to the smaller $P_{\text{max}}$ allow more time for viscous deformation at the same load $P$. For the Et homopolymer, the lowest $P_{\text{max}}$ experiment resulted in a maximum displacement at the end of the loading of 205 nm, at a load of 345 µN. At the same load of 345 µN, the highest loading rate experiment exhibited a displacement of 200 nm. The displacement value of 205 nm is only 3% higher than the latter value. However, for the 18, 30 and 48 wt.% EHe copolymers, the difference increases due to time-dependent deformation. For these materials, the displacement for the lowest loading rate exceeds the displacement at the same load employing the highest loading rate by 17, 49 and 180%, respectively.

For a perfectly elastic-plastic material, the reloading response should coincide with the preceding unloading response. This material behavior is a key assumption of the Oliver and Pharr method.[7,10] The extent to which this assumption is violated can be assessed by comparing the slope of the unloading and the reloading responses (Figure 7.7). Unload-reload responses of the materials where the loading and unloading responses are difficult to discern in Figure 7.7 are shown in Figure 7.8. The difference between the loading and the reloading responses gets larger with increasing amount of EHe. In line with Section 7.2.2, this indicates that the viscous contribution to the unloading and reloading response increases. However, the increasing difference between the loading and the unloading response with increasing EHe
content should not solely be attributed to the increased time-dependent behavior, as with increasing EHe content the unloading continues effectively to lower loads due to the so-called ‘open loop’ experimental protocol (discussed in more detail in the next paragraph).

Selected unloading responses were fitted using the power law equation. For selected reloading responses, the last ~0.7 s of the reloading segment was fitted using the power law, as well, whereby the power value was restricted to be equal to or larger than 1. From these fits, the slope at $P_{\text{max}}$ was obtained. This slope is a key parameter for the calculation of $E_i$ (Equation 2.1). Typically, the slopes upon reloading were approximately 10, 30 or 70% smaller than those obtained upon unloading, for the 0, 18 and 30 wt.% EHe copolymers. A high slope for the unloading response results in a high $E_i$ (Equation 2.1). This is in line with the relatively high $E_i$ obtained for the 30 wt.% EHe copolymer obtained upon unloading in 2 s (Figure 7.3).

The increasing deviation between the unloading and reloading slopes indicates that the assumption that the unloading is governed by the elastic response becomes more and more problematic when approaching the glass transition.

**Figure 7.6:** Loading scheme employed to obtain the load-displacement responses shown in Figure 7.7. The partial unload and reload took place in 1.5 s.
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Figure 7.7: Loading-unloading-reloading experiments on Et:EHe random copolymers. Data acquired when the tip was not in contact with the material surface has been removed.

Figure 7.8: Unloading and reloading responses for (a) 0 wt.% and (b) 18 wt.% EHe copolymers at the same nominal load (the highest loads shown for these materials in Figure 7.7).
In contrast to the load-displacement responses shown in Figure 7.2 obtained under ‘load control’, the data in Figure 7.7 was obtained using the ‘open loop’ mode. In the load control mode, a feedback assures that the desired load is applied onto the sample surface. In the ‘open loop’ mode, part of the force applied electrostatically to the drive plate in the transducer is used to elastically deform the springs inside the transducer.\[15\] Therefore, the load applied onto the sample surface is the nominal load minus a certain amount that depends on the displacement of the indenter probe. Therefore, in the open loop experiments the load decreases if during the hold period the indenter moves into the material. In Figure 7.7, negative loads are observed upon unloading. This means that the springs in the transducer pull on the tip before the tip actually loses contact with the material.

Figure 7.7 shows that the negative load at the end of the (final) unloading increases with increasing EHe content. Indentation experiments at higher $P_{\text{max}}$ on the same copolymer result in larger pull-off forces, as the higher load results in deeper indents and, therefore, a larger contact area between the indenter probe and the material. For the 48 wt.% EHe copolymer, even in some of the unloading-reloading steps the Berkovich indenter lost contact with the surface.

By contact angle measurements performed as described in ref. 16, it was observed that the surface energy of the random Et:EHe copolymers decreased approximately linearly from 43 mN/m for the Et homopolymers to 33 mN/m for the EHe homopolymer. The surface energy of the EHe copolymer is higher than the ~22 mN/m obtained for the Non homopolymer (see Figure 3.13). This indicates that the branched alkyl side group is less effectively covering the surface than the nonyl side chain. A high surface energy enhances the adhesion. However, the main reasons for the observed stickiness are the proximity of $T_g$ and the modest molar mass of these copolymers.

The work of adhesion can be obtained from the force where the tip loses contact with the substrate. However, for this calculation also the contact area and geometry at the moment of the loss of contact should be known. Therefore, this analysis is usually performed employing a large radius sphere.\[17,18\] Nevertheless, also for the Berkovich indenter probe, a large negative force prior to loss of contact is a qualitative proof that the tip-copolymer adhesion increases. Large adhesion between the tip and the sample will cause friction and a different evolution of the tip-sample contact area during the unloading than assumed by theory. The observed increase in pull-off force with increasing EHe content indicates that also the assumption of frictionless contact between the indenter and the sample gets more and more problematic for these copolymers with decreasing distance to the glass transition.
7.2.4 The loss tangent as function of composition and frequency

Visco-elastic properties of polymers can be studied by subjecting the polymer to a small-amplitude cyclic deformation. At the glass transition of an amorphous polymer, the dissipation of the mechanical energy of such a cyclic deformation is maximum\textsuperscript{[3,6]} The ratio of the viscous response to the elastic response is called the loss tangent, $\tan \delta$.\textsuperscript{[3,19]} For polymers, a time-temperature superposition principle applies; an increase of the test frequency has a similar effect as a decrease of the temperature during testing. Therefore, the loss tangent changes with the testing frequency. For materials close to their glass transition, the change in the loss tangent can be large. Such dynamic experiments can be performed by DSI as well.\textsuperscript{[4,7,18]}

Hayes et al.\textsuperscript{[20]} have measured $\tan \delta$ of polycyanurate, epoxy, polyvinyl acetate and propylene as a function of both testing frequency and temperature by dynamic DSI. In variation to their work where the measurement temperature was varied, here the ‘distance’ to the glass transition is varied by changing the chemical composition. In Figure 7.9, $\tan \delta$ is presented for selected Et:EHe copolymers. It is noted that adhesion also may reduce the accuracy of the dynamic DSI results, therefore $\tan \delta$ obtained for the 55 wt.% EHe copolymer should be used with circumspection. In agreement with theory, Figure 7.9 shows that with decreasing distance to the glass transition, the loss tangent increases.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure7.9.png}
\caption{Loss tangent $\tan \delta$ obtained at a test frequency of 20 Hz as a function of composition for Et:EHe random copolymers. The difference between the glass transition temperature as observed by DSC and the temperature during testing, $T_r$, is indicated as well.}
\end{figure}

The loss tangent increases to higher values than observed for the Et:Non copolymers discussed in Section 3.4 (compare Figure 3.15). This can be attributed to the formation of small crystallites for the latter and the absence thereof for the Et:EHe copolymers. Such
crystallites stiffen the material, resulting in a more elastic response. Furthermore, the $T_g$ of the amorphous phase increases due to its higher Et content (compare Figure 3.12 with 7.1). Since some Non segregated to the crystallites, the Et content and thereby the $T_g$ of the amorphous phase increased.

With increasing test frequencies, the energy dissipation decreases (Figure 7.10). Furthermore, not only for 20 Hz (Figure 7.9) but also for other frequencies, $\tan \delta$ increased with decreasing distance to the glass transition, here corresponding to increasing EHe content.

![Graph showing the loss tangent $\tan \delta$ as a function of testing frequency and chemical composition.](image)

**Figure 7.10:** The loss tangent $\tan \delta$ as a function of testing frequency and chemical composition.

### 7.3 Cracking at the indent corners

Cracking of the material around the indent or at the indent corners invalidates the Oliver and Pharr method.[18] It is noted that, on the other hand, cracking at the indent corners offers the opportunity to study other behavior than elasticity, namely fracture toughness.[18] Usually, these kind of studies are conducted on ceramics or hard metals. In previous chapters, residual indentation imprints were imaged using the indenter tip in order to investigate whether cracking had occurred. However, it should be verified whether this imaging is sensitive enough to identify the occurrence of cracking. The question whether the absence of cracks at the indent corners in the topographic image obtained with the TriboIndenter proves that these cracks are really not there, will be addressed in this section.

Polystyrene is well known for its stress localization, in particular after physical ageing.[21] This stress localization, which is attributable to the large extent of strain softening for aged PS followed by only modest strain hardening as discussed in Section 2.4, may cause the material to exhibit cracking during the indentation experiment. Therefore, PS was chosen for the current investigation. Several spots of PS were deposited onto a glass slide by dropcasting using a pipetting robot. Subsequently, the glass slide containing the PS spots was heated in
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Vacuum to 110 °C, which is 10 °C above the glass transition temperature of PS, and slowly cooled. During cooling, physical ageing took place. Subsequently, indentation experiments were performed on this material and several indents were imaged with the indenter tip. However, no cracking was observed. In order to investigate whether this is due to insufficient instrument sensitivity, imaging by AFM (tapping mode) was conducted on two of these indents. The AFM tips are much sharper than the indenter tips, and this instrument is designed to be very sensitive for surface topology. However, with this instrument, no cracking at the indent corners was observed either (Figure 7.11). In the close-up phase-image at one of the corners, some line-shaped features are observed originating from the indent corner. These are possibly attributable to orientation and local strain-hardening of the polymer induced by the indentation.

Figure 7.11: AFM imaging topologic image of a residual indent on polystyrene. (a) Height and (b) phase information of the indent; close-up on one of the corners, (c) height and (d) phase information. Z-height scale is reduced in order to increase the visibility of possible cracks.

The samples were subjected to several heat treatments consisting of heating above their glass transition and subsequent cooling to room temperature at various cooling rates. Those heat treatments were performed in the framework of an investigation into the effect of the cooling rate on the $E_i$ obtained by indentation and the amount of pile-up at the indent perimeter. After only one of these heat treatments (again: heating to 110 °C followed by slow cooling, in vacuum), cracks were observed upon imaging with the TriboIndenter at the corners of the
indents on one of the two investigated PS spots. The indentation load-displacement responses for both spots are shown in Figure 7.12. The topology images obtained by imaging with the TriboIndenter are shown in Figure 7.13.

An important observation is that the TriboIndenter instrument equipped with this transducer and this Berkovich probe is capable of identifying the presence of cracks. Secondly, extensive cracking is observed, while the differences in the load-displacement responses are only modest (Figure 7.12). Also, the differences in the stiffness at the start of the unloading (Figure 7.14a) and in $E_i$ (Figure 7.14b) are relatively small.

![Figure 7.12](image)

**Figure 7.12:** The indentation load-displacement responses for two PS spots with identical thermal history, one exhibiting cracking and the other exhibiting no or only minor cracking.

![Figure 7.13](image)

**Figure 7.13:** Surface topology obtained by imaging with the TriboIndenter of the indents resulting after the indentations at a maximum load of 5400 µN. (a) Appreciable cracking is observed for spot A (corresponding load-displacement response is shown dashed in Figure 7.12), while (b) on spot B only a minor crack is observed (solid line in Figure 7.12). Z-scale is reduced to improve the visibility of possible cracks.
Figure 7.14: Analysis results of the load-displacement responses shown in Figure 7.12. (a) Slope $S$ at the start of the unloading, for easy comparison with Figure 7.12, $P_{\text{max}}$ is annotated; (b) indentation moduli $E_i$, where it is noted that the values obtained for spot A, which exhibited cracking, are unreliable.

The presence or absence of cracking is the main cause for the difference between the load-displacement responses shown in Figure 7.12. However, it is not the only cause for the difference between the load-displacement, as this difference in cracking behavior itself indicates that both spots were not exactly equal. In this context it is noted that the not-cracking sample was ~60 µm thick, while the PS spot exhibited cracking was 45 µm thick. Possibly, in the thicker sample a tiny amount of toluene remained that did not yet evaporate. Alternatively, there might be some stress in the PS due to the thermal expansion mismatch between the PS and the glass substrate, which is different for both spots due to the different thickness.
However, ascribing in first approximation the difference between both indentation responses to the occurrence of cracking, it is observed that cracking resulted in:

1. a larger displacement at the same load $P_{\text{max}}$;
2. a higher slope $S$ at the start of the unloading (Figure 7.14a);
3. somewhat lower $E_i$ (Figure 7.14b).

By the cracking, elastic strain in the PS adjacent to the indenter probe is released, resulting in a decreased resistance to deformation during the indentation experiment and, therefore, deeper indents. The loss of the elastic strain also decreases the ability of the material to push the indenter back during the unloading step of the indentation experiment, resulting in a reduced displacement during unloading and, therefore, a higher slope at the start of the unloading. As the loss of elastic strain is not accounted for in the Oliver and Pharr analysis, $E_i$ obtained for the spot A samples is not reliable. It is noted that the difference between $E_i$ obtained from indentations exhibiting cracking and indentations not exhibiting cracking is not that large, as the numerical effect of the larger slope $S$ is counteracted by the larger contact area $A_c$ (Equation 2.1).

Interestingly, the cracking did not show up by any abrupt events in the loading responses such as pop-ins. This is in agreement with the observation that on the polystyrene spot exhibiting cracking, cracks were already observed after indentations employing only modest indentation loads $P_{\text{max}}$. Also at a load of 2700 µN, cracking was observed, although at only one of the indent corners.

### 7.4 Conclusions

It was shown that amorphous, not cross-linked polymers of relatively low molar mass close to their glass transition may give rise to unreliable results when the unloading responses are analyzed using the protocol proposed by Oliver and Pharr, due to their large time-dependent deformation. Increasing the unloading rate improved the analysis results. However, also the increased tip-sample friction reduces the accuracy of the analysis results. It was demonstrated that the criterion that the unloading displacement rate should exceed the creep rate by a factor of five is a suitable approach to avoid that the obtained $E_i$ values are affected by creep. Also the value for the power of the fit to the unloading response can be used as an indicator whether creep influenced the unloading response.

The load-displacement responses can clearly visualize the time-dependency of the deformation. The effect of the time-dependent response on the initial slope of the unloading response, which is a key parameter for the analysis procedure, was visualized, showing that the assumption that the unloading response is elastic becomes problematic if the material is tested only just below its glass transition. Furthermore, the pull-off force, where the indenter probe breaks loose from the sample surface, indicates the extent of adhesion.
The frequency-dependency and composition-dependency of the loss tangent of the Et:EHe copolymers was in agreement with the expected behavior based on the DSC results.

A key assumption to the analysis of quasistatic indentation responses is that no cracking occurs around the indent or at the indent corners. The imaging facility of the indentation instrument seems to be sensitive enough to determine whether cracking occurred, at least when a ‘sharp’ Berkovich tip is used. Cracks could be visualized that had resulted in only modest changes in the load-displacement response.

7.5 Experimental

Gel permeation chromatography (GPC). Molar masses were determined using a Shimatzu GPC, equipped with a system controller SCL-10Avp, a LC-10AD pump, a RID-10A refractive index detector, degasser DGU-14A and two PSS GRAM columns, 30 and 1000, at 60 °C utilizing N,N-dimethylacetamide with 2.1 g/L LiCl as eluent at a flow rate of 1 mL/min.

Differential scanning calorimetry (DSC). Thermal transitions were determined by differential scanning calorimetry on a Netzsch DSC 204 F1 Phoenix under a nitrogen atmosphere from −50 °C to 200 °C with a heating rate of 20 K/min (the first heating run to 200 °C, which was followed by a cooling run at 40 K/min, was not considered for the subsequent calculations). Midpoints of the glass transition are reported.

Preparation of the Et:EHe polymer spots for indentation measurements. 20 to 26 mg of each copolymer was deposited in a 96-well sample plate (polypropylene, Greiner Bio-one). Subsequently, 80 µL chloroform was added (Biosolve LTD). After complete dissolution, approximately 4 µL from each solution was pipetted onto a glass slide using an AnalytikJena Fastrans pipetting system (20 µL tips), with a nominal center-to-center spacing of 4.5 mm between the polymer spots. Two identical slides were prepared, and subsequently dried in vacuum at 40 °C for two weeks and then transferred to the TriboIndenter (Hysitron, Inc., MN, USA). These samples resided at low humidity (<7%) for one week before testing at 5.2% relative humidity (RH).

Depth-sensing indentation (DSI). The indentation experiments with the TriboIndenter were performed at 5.2 ± 0.4% RH employing a nanoDMA (1D) transducer and a diamond Berkovich indenter. The relative humidity was measured using a Hygrometer testo 608-H2. Before every indent, the indenter was held in contact with the surface, to allow for piezoactuator stabilization (35 s) and drift correction (40 s), at a contact load of only 0.5 µN to prevent any deformation prior to the indentation experiment. The drift rate (typically 0.1 nm/s) was automatically determined over the last 20 s of the 40 s period.

Quasistatic experiments in load control were performed by lifting the tip 30 nm prior to the measurement, reapproaching the surface (surface detection at a load of 0.5 µN), loading the tip to maximum load in 10 s, holding at maximum load for 10 s and unloading in 2 s or 0.4 s. The maximum load was reduced in steps of 300 µN from 2100 µN to 300 µN. From the 7 measurements (spaced 40 µm apart) per sample, the first two (i.e., the experiments at 2100 and 1800 µN) were left out from the analysis to even further reduce the influence of drift. For the samples containing 30 wt.% EHe, the
indentation experiments performed at 1500 µN and for the 2 s unload also the experiments at 1200 µN exceeded the tip area function calibration range, and are therefore not analyzed either.

Before quasistatic experiments on ‘open loop’ mode, the tip was not lifted but loaded directly. Nominal maximum loads ranging from 2800 to 400 µN were chosen (steps of 400 µN) for the 0, 18 and 30 wt.% EHe copolymers. For the 48 wt.% and 55 wt.% EHe copolymers, lower load levels were chosen, namely 1400 to 200 µN in steps of 200 µN and 700 to 100 µN in steps of 100 µN. The load function is described in Figure 7.6.

**Depth-sensing indentation analysis.** Load-displacement responses were analyzed using the method of Oliver and Pharr\(^7\) by fitting the unloading response from \(0.95 \cdot P_{\text{max}}\) to \(0.20 \cdot P_{\text{max}}\) with the conventional power law form to obtain the slope at the start of the unloading \(S\). Using \(\beta = 1\), the reduced modulus \(E_r\) is then calculated and subsequently, with \(E_{\text{diamond}} = 1140\) GPa, \(\nu_{\text{diamond}} = 0.07\) and \(\nu_{\text{sample}} = 0.4\), \(E_i\) is obtained. The \(R^2\) values obtained by fitting with Microcal Origin software refer to the full unloading curve.

**Dynamic depth-sensing indentation.** Storage moduli \(E'\) and loss tangent \(\tan \delta\) were determined using the TribolIndenter nanoDMA (nano dynamic mechanical analysis) module, whereby an oscillating load (nominally 10 µN) was superimposed over the quasistatic load (nominally 300 µN). The loss tangent \(\tan \delta\) is calculated from the phase lag between the applied load oscillation and the resulting displacement oscillation.\(^{7,18,20}\) The latter was between 0.82 and 2.3 nm in amplitude for the measurements at 20 Hz. The average and standard deviation out of three or four experiments on each duplicate sample, so in total seven or eight measurements, are reported.

**Preparation of the PS polymer spots.** A 9 wt.% solution of PS N5000 in toluene (Biosolve LTD) was prepared. 4 µL of this solution was pipetted onto a glass slide that was placed on a heating plate at ~95 °C, using a AnalytikJena Fastrans pipetting system equipped with 20 µL tips. The center-to-center spacing between the polymer spots was 4.5 mm. The resulting dots were regularly shaped and at least 40 µm high. No extensive ‘coffee-drop’ effect was observed.

**Annealing of the polystyrene.** The glass slide with polystyrene was heated to 110 °C under vacuum in an Heraeus Vacutherm oven. The sample was allowed to cool slowly overnight under vacuum before opening the oven.

**Depth-sensing indentation.** DSI was conducted using a Hysitron TribolIndenter equipped with a 2D transducer and a Berkovich (trigonal pyramid) diamond indenter. Various load levels were used. After loading in 10 s and 10 s hold at \(P_{\text{max}}\), unloading took place in 1 s. Reduced moduli were converted to indentation moduli using a Poisson’s ratio of 0.35.

**Imaging of the polystyrene with the Tribolindenter.** Imaging of the residual imprints with the indenter was conducted at a scan velocity of either 6 or 6.4 µm/s and a setpoint of 2 µN. For imaging, the same Berkovich indenter probe was used as for the indentation experiment.

**Imaging of the polystyrene with by AFM.** Imaging of two residual imprints was conducted by tapping mode AFM using a NT-MDT Solver P47 SMENA AFM. Commercial tapping mode tips (MicroMash) with a typical force constant of 11 N/m were used.

**Optical interferometry.** Film thicknesses were measured using a Fogale Zoomsurf 3D optical interferometer with a 5× objective.
Verification of key assumptions to the analysis method

7.6 References and notes


[13] It seems unlikely that for the 18 wt.% EHe copolymers the initial slope $S$ resulting from the fit to the 2 s unloading response is affected by creep. The indentation experiments were performed at various levels of $P_{\text{max}}$, resulting in different indentation depths $h_{\text{max}}$. The plot of the slope as function of $h_{\text{max}}$ overlapped for both unloading times, indicating that creep can be neglected. Moreover, mathematically a too high slope $S$ also results in an increase in the contact depth and, thus, in the contact area, so that the overall effect on the determined $E_i$ (Equation 2.1) is negligible.


Summary

Mechanical properties of materials can be probed using depth-sensing indentation (DSI), where an indenter of defined geometry is pushed onto a material while its displacement and the exerted force are measured. DSI offers the advantages that only small amounts of material are needed, and that the measurements can be automated. Because of these advantages, this technique is suitable for high-throughput experimentation (HTE) approaches, where a relatively large number of distinct, but related, materials are synthesized and key properties have to be investigated in a time-efficient way in order to obtain structure-(processing)-property relationships for these materials.

The first and second chapter of the thesis review the work carried out in the field of HTE investigation of mechanical properties of polymers. Moreover, challenges in obtaining mechanical properties such as the elastic modulus, the creep properties and the yield stress by indentation are reviewed. It is explained why, depending on the employed analysis protocol, the elastic modulus obtained by indentation exceeds the elastic modulus obtained by conventional testing to some extent. The dependency of the mechanical properties on processing is briefly discussed in order to identify potential influences from the sample preparation method on the indentation results.

The elastic properties of libraries of copoly(oxazoline)s were investigated in a HTE-approach. Poly(oxazoline) chemistry (in particular the recently developed microwave-assisted polymerizations) offers the opportunity to control the side-group and the chain-length (distribution) as well as to prepare block copolymers. Because of this, material properties such as solubility in environmentally friendly solvents, surface energy and material stiffness can be tailored. Therefore, poly(oxazoline)s may be used for several new applications. Chapter three reports a systematic study on the influence of the side-group attached to the oxazoline units on the mechanical properties. The side-groups influenced the glass transition temperature, the hygroscopicity and the occurrence of intermolecular interactions additional to the Van der Waals interactions. As a result, the material stiffnesses at reduced humidity and at ambient humidity depended on the side-group, as well. Moreover, for the combination of the ethyl and the nonyl side-groups, the chemical composition as well as the side group distribution along the polymer chain was varied. The obtained stiffness and the loss tangent could be related to the glass transition temperature and the degree of crystallinity of the materials, which, in turn, depended on their chemical structure.

The small sample amounts required for DSI render the technique suitable for mechanical testing of compounds of which, in the early research stage, only small amounts are synthesized. This is the case for the supramolecular materials investigated in chapter four of this thesis. Supramolecular interactions allow the incorporation of interesting optical, responsive, or self-repairing properties into the material. It was shown that a large range of
mechanical stiffness can be spanned by diblock copolymers assembled using supramolecular metal-ligand interactions consisting of one very stiff block and one more compliant block. Chapter five of the thesis describes an HTE-sample preparation and characterization approach for elastomer materials. The applicability of DSI and Raman spectroscopy as tools to quantify the cross-link density and the conversion of reactive sites of ethylene-propylene-diene rubber (EPDM), respectively, are discussed. For EPDM (without fillers), a good correlation was observed between indentation depths at fixed loading conditions and Shore A hardnsses, which is a common industrial measure for the material hardness.

Exposure of coatings and paints to sunlight and humidity results in chemical changes of the protective and decorative organic coating materials. These chemical changes influence the physical properties, and finally lead to failure (cracking, delamination) of the coating. The studied polyester coatings exhibited an increase of hardness upon exposure to UV light. The increases in hardness could be related to the ageing conditions, and to the chemical changes in the material (polar group formation, chain-scission and cross-linking) that were observed with infrared spectroscopy, gel permeation chromatography and gel-fraction measurements. The hardness increase is largest when oxygen, taken up from the surrounding atmosphere, takes part in the degradation reactions. Careful comparison of the chemical changes and the hardness changes showed that the formation of polar groups is the dominant factor for the hardness increase.

Extensive time-dependent deformation, tip-sample adhesion and cracking at the indent corners can influence the analysis results. It was shown that the indentation data can clearly visualize that the first two problems become more problematic if an amorphous copolymer is tested only just below its glass transition temperature. Furthermore, it was shown that the loss tangent obtained for these copolymers by dynamic indentation exhibited the expected dependency on composition (i.e., proximity to the glass transition) and on frequency. Topographic imaging using the indenter could visualize cracking at the indent corners for cracks that had resulted in only modest changes in the load-displacement responses, indicating that the sensitivity of topographic imaging is good enough to verify whether cracking influenced the indentation results.
Samenvatting

Door middel van indrukkingsspiegel-metingen, in het Engels: *depth-sensing indentation* (DSI), kunnen mechanische eigenschappen van materialen worden onderzocht. Hierbij wordt een indenter met een bekende geometrie op het materiaal gedrukt waarbij de uitgeoefende kracht en de verplaatsing van de indenter gedurende het experiment worden gemeten. Een voordeel van deze techniek is dat hiervoor slechts geringe hoeveelheden materiaal nodig zijn. Een tweede voordeel is dat deze metingen geautomatiseerd kunnen worden. Daarom is het een geschikte techniek voor hoge doorvoer proefneming, in het Engels: *high-throughput experimentation* (HTE). In dergelijke experimenten worden een relatief groot aantal verschillende materialen gesynthetiseerd en geanalyseerd met het doel relaties te leggen tussen de structuur, de processstappen die het heeft ondergaan, en de eigenschappen van de materialen. Vanwege het grote aantal materialen moet dit HTE onderzoek op een efficiënte manier gebeuren wat betreft tijd en inspanning.

De eerste twee hoofdstukken van het proefschrift geven een literatuuroverzicht over mechanische karakterisering van polymeren volgens een HTE aanpak. Het bepalen van mechanische eigenschappen zoals elasticiteitsmodulus, kruip eigenschappen en vloeigrens door middel van DSI stelt een aantal uitdagingen. De literatuur daarover wordt samengevat waaruit duidelijk wordt waarom, afhankelijk van de gekozen analyse methode voor de DSI meetgegevens, de elasticiteitsmodulus verkregen via DSI, enigszins hoger is dan de elasticiteitsmodulus verkregen via conventionele testmethoden. Omdat de methode van materiaalvoorbereiding voor het experiment de DSI resultaten zou kunnen beïnvloeden, wordt ook kort besproken hoe mechanische eigenschappen afhangen van de (thermische) geschiedenis van het materiaal.

De elastische eigenschappen van copoly(oxazoline)s zijn onderzocht volgens een HTE- aanpak (hoofdstuk 3). De monomeersynthese en de polymerisatie, in het bijzonder de recentelijk ontwikkelde polymerisaties onder microgolfbestraling, bieden de mogelijkheid om verschillende zijgroepen in te bouwen, de ketenlengte verdeling te beheersen en blokkopolymeren te maken. Door op deze manier de chemische structuur te veranderen kunnen eigenschappen zoals de oplosbaarheid in milieuvriendelijke oplosmiddelen, de oppervlakte-energie en de elasticiteitsmodulus van het materiaal optimaal afgestemd worden voor diverse nieuwe mogelijke toepassingen. Een systematische studie naar het effect van de zijgroep aan de oxazoline laat zien dat de glas overgang temperatuur en de aanwezigheid van extra intermoleculaire interacties (dus bovenop de Van der Waals interacties), en daardoor ook de elasticiteitsmodulus sterk afhangen van de zijgroep. Ook de mate waarin het materiaal vocht opneemt, resulterend in een afname van de elasticiteitsmodulus bij een toename van de luchtvochtigheid, hangt af van de zijgroep. Voor polymeren met ethyl en nonyl-zijgroepen zijn bovendien de verhouding tussen beide monomeren, en de verdeling van de monomeren over de keten gevarieerd. De gemeten elasticiteitsmodulus en verliesfactor $\tan \delta$ konden
worden verklaard aan de hand van de glasovergang temperatuur en de kristalliniteit van de materialen, die, op hun beurt, afhingen van de chemische structuur.

De beperkte hoeveelheid materiaal benodigd voor DSI maakt deze techniek geschikt voor het testen van mechanische eigenschappen van materialen die in de eerste stadia van het onderzoek slechts op kleine schaal worden gesynthetiseerd. Dit is het geval voor de supramoleculaire materialen onderzocht in hoofdstuk vier van dit proefschrift. De supramoleculaire interacties bieden de mogelijkheid om speciale optische, responsieve of zelf-helende eigenschappen in het materiaal in te brengen. Verschillende supramoleculaire blokcopolymeren zijn onderzocht, waarbij de lengte van de harde en zachte constituenten werd gevarieerd. Hierdoor lieten deze materialen een groot bereik in elasticiteitsmodulus zien.

Hoofdstuk vijf van het proefschrift beschrijft HTE monstervoorbereiding en HTE karakteriseringsmethoden voor elastomeren. De toepasbaarheid van DSI en Raman spectroscopie als gereedschappen om de cross-link dichtheid en de conversie van reactieve groepen van ethyleen-propyleen-diene rubber (EPDM) te kwantificeren is aangetoond. Voor EPDM (zonder vulmaterialen) is een goede correlatie gevonden tussen de indrukkingsdiepte meten onder voorgeschreven belastingscondities, en de Shore A hardheid. De laatste is een in de rubbertechnologie veel gebruikte maat voor de hardheid.

Het blootstellen van deklagen zoals verf aan zonlicht en vochtigheid veroorzaakt chemische veranderingen van de polymeren in de deklaag. Deze chemische veranderingen beïnvloeden de fysische eigenschappen en resulteren uiteindelijk in falen (door scheuren of delamineren) van de deklaag. De hardheid van de polyester deklagen onderzocht in hoofdstuk 6 nam toe bij blootstelling aan UV licht. De toename van de hardheid kon worden gerelateerd aan de verouderingcondities en aan de chemische veranderingen in het materiaal (vorming van polaire groepen, ketenbreuk en cross-linken) die werden waargenomen middels infrarood spectroscopie, gel permeatie chromatographie en gel-fractie metingen. De hardheidstoename was het grootst wanneer zuurstof uit de omringende lucht deelnam aan de degradatietreacties. Door de mate van chemische veranderingen te vergelijken met de hardheidstoename werd duidelijk dat de vorming van polaire groepen de belangrijkste factor is voor de hardheidstoename.

Tijdsafhankelijke vervorming, adhesie tussen de indenter en het monstermateriaal, en scheurvorming tijdens de indentatie kunnen de analyseresultaten beïnvloeden. De indentatie kracht-verplaatsings diagrammen lieten zien dat de eerste twee factoren problematischer worden als een amorf copolymer slechts iets onder zijn glastemperatuur wordt getest (hoofdstuk 7). Verder liet de verliesfactor, verkregen middels dynamische indentatie, de verwachte afhankelijkheid van samenstelling en frequentie zien. Door met de indenter tip over het oppervlak te scanen konden scheuren worden gedetecteerd die slechts tot geringe veranderingen in de kracht-verplaatsings diagrammen hadden geleid. Dit geeft aan dat dit scanen gevoelig genoeg is om eventuele beïnvloeding van de analyseresultaten door deze factor te verwaarlozen als geen scheurvorming waargenomen wordt.
Curriculum Vitae

Hans Kranenburg was born on September 23, 1978 in Zoetermeer, the Netherlands. After completing the gymnasium (pre-university education) at the Gereformeerde Scholengemeenschap Randstad in Rotterdam, he started in 1996 with the Materials Science and Engineering program at Delft University of Technology. The traineeship was conducted at ECN (Energy research Centre of the Netherlands) in Petten on metallic membranes. The master project was conducted in the group of dr. Wim G. Sloof on ‘high temperature oxidation of β-NiAlCr model coating alloys: the effect of reactive elements on growth and adhesion of the oxide layer’. This resulted in 2003 in the master of science degree, with distinction.

After working for a year as material & material damage investigator at Schielab Breda, he started in November 2004 his Ph.D. project under supervision of professor Ulrich S. Schubert. The most important results of this research are described in this thesis.
Publications from the PhD work:


Dankwoord

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I am very happy with the active participation of Hysitron in the Dutch Polymer Institute, as shown by the numerous visits of Oden Warren, Ude Hangen and Jim Burkstrand to Eindhoven and Darmstadt. Thank you for your comments on my presentations at those meetings. Oden and Ude, it was great to have short ‘metal-submeetings’ at the cluster meetings of the Dutch Polymer Institute on how the dislocations and crystallographic orientations show up during indentations in the nanometer-regime. I also thank Hysitron’s engineering department for designing the nice vacuum fixation stage for glass slides.

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