The effect of polar clusters on elastomers cross-linked with (retro-)Diels-Alder chemistry

Diels-Alder chemistry has been used as a tool for the thermoreversible cross-linking of furan-functionalized ethylene/propylene and ethylene/vinyl acetate rubbers. This work presents an investigation on the effect of the rubber polarity on clustering of functional groups, the distribution of the polar bismaleimide cross-linker and the subsequent consequences for the rubber properties in the apolar EPM rubber. SAXS measurements show that the BM cross-linking chemistry occurs in clusters, resulting in a microscopically heterogeneous network. The absence of clusters and the homogeneous distribution of cross-links in EVM provides improved mechanical behavior with respect to EPM.

This chapter is based on: L. M. Polgar, E. Hagting, F. Picchioni and M. van Duin, 'The effect of polar clusters on elastomers cross-linked with (retro-)Diels-Alder chemistry' to be submitted to Polymer 2017.
7.1. Introduction

Rubbers can generally be divided into two classes, based on the amount of unsaturation in their polymer backbone [1]. The most reactive elastomers, such as natural rubber, polyisoprene and butadiene rubber, have a high level of unsaturation in their backbone. Elastomers with low amounts of or no unsaturation, including ethylene-propylene rubber (EPM) and ethylene-vinyl acetate rubber (EVM), have a relatively low reactivity. Elastomers in the latter class distinguish themselves by their outstanding resistance to ozone, weathering, and high temperature [2].

Both EPM and EVM copolymers have a very flexible polymer backbone with a high entanglement density and a relatively low glass transition temperature, which makes them soft and rubbery at room temperature. The major difference between EPM and EVM is their polarity. EPM is a hydrocarbon elastomer, containing only carbon and hydrogen atoms, and thus has a relatively low polarity. The large amount of vinyl acetate in EVM, on the other hand, results in a relatively high polarity. EPM copolymers with 40-55 wt% ethylene and EVM copolymers with 15-45 wt% ethylene are both amorphous at room temperature, due to the random copolymerization of ethylene with propylene or vinyl acetate, respectively, and the consequent absence of long ethylene of vinyl acetate sequences.

Rubbers including EPM and EVM are typically cross-linked to achieve the maximum elasticity and strength. Unfortunately, cross-linking prohibits processing in the melt and thus limits recycling of these materials. Current societal trends towards the limitation of waste and the need for more sustainable materials increase the interest in and the appeal of reversible cross-linking of rubbers [3-8] and resins [9-11]. Thermoreversible cross-linking of maleated EPM and EVM rubbers has successfully been performed using the thermoreversible furan-maleimide DA reaction (Scheme 7.1) [3,12].

Scheme 7.1. Furan-functionalization of maleated EPM and EVM rubber and subsequent thermoreversible cross-linking with bismaleimide via (retro-)DA chemistry.
There are strong indications that the grafting of polar maleic anhydride (MA) groups onto the apolar EPM rubber does not occur in a random fashion [13]. Due to the large difference in polarity, the more polar MA groups are inhomogeneously dispersed throughout the rubber matrix during grafting, resulting in local areas with a high concentration of MA grafts in the resulting EPM-g-MA [13]. This effect is enhanced by polar interactions with already grafted MA groups. These interactions persist in the maleated EPM rubber where the formation of polar clusters high in MA concentration is observed [13,14]. It is assumed that these clusters are maintained upon furan-functionalization and that the BM cross-linker will preferably dissolve into these polar clusters. As a result, the majority of the DA cross-linking is expected to take place in these polar clusters. This will afford cross-linked domains, heterogeneously distributed in the EPM rubber matrix. EVM rubber on the other hand is a more polar polymer, thus there is no driving force to the phase separation of polar MA grafts in maleated EVM. BM cross-linking of EVM-g-furan is therefore expected to result in a more homogenously cross-linked network.

A similar effect is known to occur in polymers with pendant ions [15]. Ionic groups generally segregate into multiplets that in turn form polar clusters [16-19]. Such ionic clusters do not only impart rubber conductivity, but the shape and degree of clustering also has a strong influence on the rubber’s material properties [17,20,21]. The material characteristics of clustered polymers therefore result from the balance between the conformation of the rubber backbone and the electrostatic forces [22-26].

The goal of this work is to study the presence of polar clusters and the effect of the network heterogeneity on the material properties of apolar EPM copolymers and to compare these with polar EVM copolymers. The maleated EPM is expected to cross-link heterogeneously whereas the maleated EVM is expected to form a homogeneously cross-linked network. Since polar clusters are known to play a critical role in controlling the structure and dynamics of the material, any differences between the material properties of these otherwise similar polymers are expected to arise from the (in)homogeneity of the network.

7.2. Experimental

7.2.1. Materials

The parent ethylene-propylene copolymer (EPM, Keltan 3050, 49 wt% ethylene, \(M_n = 50\) kg/mol, PDI = 2.0) and ethylene/vinyl acetate copolymer (EVM, Levamelt 700, 30 wt% ethylene, \(M_n = 35\) kg/mol, PDI = 9) and the analogous maleated EPM (EPM-g-MA, Keltan DES5005, 48 wt% ethylene, 50 wt% propylene, 2.1 wt% MA, \(M_n = 50\) kg/mol, PDI = 2.0) and maleated EVM (EVM-g-MA, 30 wt% ethylene, 69 wt% vinyl acetate, 1.4 wt% MA, \(M_n = 31\) kg/mol, PDI = 17) were kindly provided by ARLANXEO Performance.
Elastomers. The EPM-g-MA and EVM-g-MA precursors were dried in a vacuum oven at 175 °C for one hour to convert any present diacid into the cyclic anhydride [3,27]. Carbon black N550 was kindly provided by Teijin Aramid. Furfurylamine (FFA, Sigma-Aldrich, ≥ 99 %) was freshly distillated before use. 1,1-(methylene-dimethylene)bismaleimide (BM, 95 %), octadecyl-1-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate (99 %), dicumyl peroxide (DCP, 98 %), dioctyl sebacate (DOS, ≥ 97 %), tetrahydrofuran (THF, >99.9 %), toluene (99.8 %), decalin (98 %) and acetone (>99.5 %) were all purchased from Sigma-Aldrich and used as received as reversible cross-linker, antioxidant, peroxide cross-linker, lubricant and solvents, respectively.

7.2.2. Methods

7.2.2.1 Furan functionalization of EPM-g-MA and EVM-g-MA
15 g of EPM-g-MA or EVM-g-MA rubber was dissolved in 150 mL THF after which 3 molar eq. FFA (with respect to MA: 2.1 wt% in EPM-g-MA and 1.4 wt% in EVM-g-MA) was added. The reaction mixture was stirred at room temperature for 5 hr in a closed system and, subsequently, precipitated into a seven-fold of demineralized water under stirring. The furan-functionalized polymer (EPM-g-furan or EVM-g-furan) was obtained as white threads. The polymer product was washed thoroughly in acetone to remove any unreacted FFA and dried under vacuum at 50 °C up to constant weight. Finally, the intermediate amide-acid was compression molded at 175 °C and 100 bar for 15 min to ensure complete conversion to the cyclic imide.

7.2.2.2 Diels-Alder cross-linking of EPM-g-furan and EVM-g-furan
10 g of EPM-g-furan or EVM-g-furan rubber was dissolved in 100 mL THF to which 1000 ppm phenolic antioxidant and 0.50 molar eq. BM (with respect to the furan content) were added. When homogeneous mixtures were obtained, the majority of the solvent was evaporated in the fumehood by blowing over air. The residual solvent was removed in a vacuum oven at 50 °C. Sample bars of the brownish mixtures were obtained by pre-heating the materials in a mold at 140 °C for 5 min and compression molding them at 140 °C and 100 bar for 30 min.

7.2.2.3 Peroxide curing of EPM and EVM
26 g of EPM or EVM rubber was mixed with the DCP peroxide in an internal mixer (Brabender Messenkneder, Type W 30 EHT) at 50 rpm and 50 °C (70% fill factor). After homogenizing the gum rubber for 4 min, 2.0 phr of DCP was added and after 6 more min of mixing, a homogeneous mixture was obtained. Subsequent vulcanization of the obtained mixtures was performed by pre-heating the samples in a mold at 160°C for 5 min and compression molding them at 160°C and 50 bar for 35 min.

7.2.3 Characterization
Gel Permeation Chromatography (GPC) was performed using a series of Viscotek Ralls detector, Viscotek Viscometer Model H502 and Shodex RI-71 Refractive Index
detector using triple detection (refractive index, viscosity and light scattering). The separation was carried out by utilizing a guard column (PL-gel 5 µm Guard, 50 mm) and two columns (PL-gel 5 µm MIXED-C, 300 mm) from Agilent Technologies. THF (containing 0.01 M lithium bromide) was used as eluent with a flow rate of 1.0 mL/min. The number- and weight-averaged molecular weights ($M_n$ and $M_w$, respectively, and the polydispersity index (PDI) = $M_w/M_n$) were calculated relative to polymethylmethacrylate standards.

Elemental Analysis (EA) of the rubber products for the elements N, C and H was performed on a Euro EA elemental analyzer. The oxygen content was calculated via the mass balance. The number of furan groups per chain for the furan containing rubbers (#/chain) was calculated from $M_n$ and the determined nitrogen content in the according to a reported procedure [3,12]. The conversion of the BM cross-linking of EPM-g-furan and EVM-g-furan was determined in a similar fashion and can be used to determine the cross-link density [XLD]$_{EA}$ using the known MA grafting content.

The cross-link density [XLD]$_{FR}$ was determined from equilibrium swelling experiments in decalin for EPM and in toluene for EVM. Rubber samples (approximately 500 mg) were weighed in 20 mL vials and immersed in 15 mL solvent until equilibrium swelling was reached (3 days). The sample was then weighed after removing the solvent on the surface with a tissue ($W_1$) and was finally dried in a vacuum oven at 110 °C until a constant weight was reached ($W_2$). The cross-link density was calculated from the weights of the swollen and dried rubber samples using the Flory-Rehner equation (Eq. 7.1) [28-30].

$$[XLD]_{FR} = \frac{\ln(1-V_R)+V_R+\chi V_R^2}{2V_S\left(0.5V_R-V_R^{1/3}\right)} \text{ with } V_R = \frac{W_2}{W_2+(W_1-W_2)\frac{\rho_R}{\rho_S}}$$  

(Eq. 7.1)

$V_R$ volume fraction of rubber in swollen sample.
$V_S$ molar volume of solvent (106.3 mL/mol and 154.3 mL/mol for toluene and decalin, respectively).
$\chi$ interaction parameter (toluene/EVM: 0.133 [28,29] and decalin/EPM: 0.121 + 0.278$V_R$ [31]).
$\rho_R, \rho_S$ density of the rubber (EVM: 0.930 g/mL and EPM: 0.960 g/mL) and solvent (toluene: 0.870 g/mL and decalin: 0.896 g/mL), respectively.

The cross-link density was also determined from stress-strain curves via the Mooney-Rivlin equation (Eq. 7.2) [32-35]. Using the values for stress versus strain of a rubber sample obtained during tensile testing, a linear proportionality between $\frac{\sigma}{2(\alpha-\alpha^{-2})}$ versus $\frac{1}{\alpha}$ can be obtained from which the parameters $C_1$ and $C_2$ can be determined. The cross-link density can subsequently be determined (Eq. 7.3) [33].
\[
\sigma = 2 \left( C_1 + \frac{C_2}{\Lambda} \right) \left( \Lambda - \frac{1}{\Lambda^2} \right) \quad \text{with} \quad \Lambda = 1 + X \varepsilon 
\]
(Eq. 7.2)

\[
[XLD]_t = \frac{2C_1}{k_B T}
\]
(Eq. 7.3)

\(\sigma\) \hspace{1cm} \text{true stress measured in the strained state of the rubber}

\(C_1, C_2\) \hspace{1cm} \text{characteristic parameters of cross-linked rubber representing entanglements and chemical cross-links, respectively.}

\(\Lambda\) \hspace{1cm} \text{extension ratio}

\(X\) \hspace{1cm} \text{strain amplification factor defined as } \sigma E_0 / \varepsilon \text{ } (X=1 \text{ for rubber gums})

\(E_0\) \hspace{1cm} \text{modulus of the rubber without filler } (E_0 = E \text{ for gums})

\(k_B\) \hspace{1cm} \text{Boltzmann constant}

Small-angle X-ray scattering (SAXS) measurements were performed using an advanced Nano-Star SAXS setup, i.e. a home-made assembly of a NanoStar camera and a Microstar X-ray generator from Bruker AX-S. The collimation line between the rotating X-ray generator and the camera consists of a multilayer optics Montel-P from Incoatec and 3 pin holes of 0.5, 0.3, and 0.5 mm in diameter from Rigaku, spaced at distances of ca. 14, 40, and 62 cm, respectively, from the middle of the optics unit. Passing through the optics the primary beam is mono-chromized for Cu Kα radiation (\(\lambda = 1.542 \, \text{Å}\)) and simultaneously collimated to get a low-divergent beam. Both the optics and the collimation line with the first and the second pin holes are evacuated. The third pin hole, located in the sample chamber of the NanoStar camera, is in air. The SAXS intensity profiles were acquired at room temperature, running the X-ray generator at 45 kV and 60 mA, affording a primary X-ray beam flux at the sample position of \(8 \times 10^8 \text{ photons/(s} \cdot \text{mm}^2)\) and a beam diameter of 0.4 mm. The sample-to-detector distance was set to 105 cm and data were collected for 3 min per rubber sample [36,37].

Tensile tests were performed on an Instron 5565 with a clamp length of 15 mm, according to the ASTM D4-112 standard. Strain rates of 500 mm/min and 5 mm/min were applied. Test samples with a width of \(4.5 \pm 0.1\) mm and a thickness of \(1.0 \pm 0.1\) mm were prepared by compression molding. For each measurement 10 samples were tested and the two outliers with the highest and the lowest values were excluded. Numerical data presented are averages of the other 8 tests. The median stress-strain curve was selected to represent the entire series of a sample in Figure 3. Hardness Shore A was measured using a Bareiss Durometer, according to the ASTM D2240 standard. Cylindrical test samples with a thickness of \(6.0 \pm 0.1\) mm and a diameter of \(13.0 \pm 0.1\) mm were prepared by compression molding. Average values were obtained from 10 measurements. Compression set tests were performed according to the ASTM D931 standard, using a home-made device and the same cylindrical samples. The samples were compressed to 75% of their original thickness for 70 h at room temperature and relaxed for 30 min at 50 °C. Compression molding of all test samples was performed on a Taunus Ton Technik V8UP150A press for 30 min at 140 °C and 100 bar for 30 min.
7.3. Results and discussion

7.3.1. Chemical characterization

The parent EPM and EVM rubbers and their maleated and furan-functionalized analogues were characterized by GPC and EA after thorough extraction of unreacted components and subsequent drying (Table 7.1). The amount of nitrogen present after furan-functionalization of the maleated rubbers is representative for the degree of conversion of grafted maleic anhydride into succinimide. The cross-link densities of the BM cross-linked and DCP cured products as determined by EA, equilibrium swelling and stress-strain testing (Table 7.2).

Table 7.1. Molecular characterization of rubber samples.

<table>
<thead>
<tr>
<th></th>
<th>$M_n$ (kg/mol)</th>
<th>PDI</th>
<th>Elemental content (wt%)</th>
<th>Conversion (%)</th>
<th>#/chain</th>
</tr>
</thead>
<tbody>
<tr>
<td>EPM</td>
<td>53</td>
<td>2.0</td>
<td>&lt;0.01, 86.67, 13.33 → 0.0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>EVM</td>
<td>35</td>
<td>9.0</td>
<td>&lt;0.01, 64.41, 9.19 → 26.4</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>EPM-g-MA</td>
<td>54</td>
<td>2.0</td>
<td>&lt;0.01, 84.70, 14.30 → 1.0</td>
<td>-</td>
<td>11</td>
</tr>
<tr>
<td>EVM-g-MA</td>
<td>31</td>
<td>17</td>
<td>&lt;0.01, 65.40, 9.61 → 25.0</td>
<td>-</td>
<td>4.4</td>
</tr>
<tr>
<td>EPM-g-furan</td>
<td>55</td>
<td>2.1</td>
<td>0.27, 84.80, 14.20 → 0.7</td>
<td>93</td>
<td>10</td>
</tr>
<tr>
<td>EVM-g-furan</td>
<td>31</td>
<td>17</td>
<td>0.20, 66.37, 9.52 → 23.9</td>
<td>98</td>
<td>4.3</td>
</tr>
</tbody>
</table>

Table 7.2. Cross-link densities as determined from elemental analysis, equilibrium swelling and tensile testing.

<table>
<thead>
<tr>
<th></th>
<th>Elemental content (wt%)</th>
<th>[XLD]$_{EA}$ (mol/mL)</th>
<th>[XLD]$_{FR}$ (mol/mL)</th>
<th>[XLD]$_{MR}$ (mol/mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BM cross-linked EPM-g-furan</td>
<td>0.36, 83.65, 12.52 → 3.5</td>
<td>1.11$_{10^{-4}}$</td>
<td>7.31$_{10^{-5}}$</td>
<td>2.11$_{10^{-4}}$</td>
</tr>
<tr>
<td>BM cross-linked EVM-g-furan</td>
<td>0.42, 65.16, 9.34 → 25.08</td>
<td>1.01$_{10^{-4}}$</td>
<td>8.81$_{10^{-5}}$</td>
<td>1.41$_{10^{-4}}$</td>
</tr>
<tr>
<td>DCP cured EPM</td>
<td>&lt;0.01, 85.72, 12.95 → 1.3*</td>
<td>-</td>
<td>8.91$_{10^{-5}}$</td>
<td>1.51$_{10^{-4}}$</td>
</tr>
<tr>
<td>DCP cured EVM</td>
<td>&lt;0.01, 63.78, 9.00 → 27.22</td>
<td>-</td>
<td>8.41$_{10^{-5}}$</td>
<td>1.11$_{10^{-4}}$</td>
</tr>
</tbody>
</table>

* Decomposition products of DCP are cumyl alcohol and acetophenone.

Grafting of MA onto EPM and EVM does not affect $M_n$ because imidization only affects the grafted MA units, but not the polymer chains. The PDI of EVM increases, suggesting branching via a combination of intermediate EVM macro-radicals. The conversion of grafted MA to imide is high (> 90%). The cross-link density of the BM cross-linked EPM and EVM is similar because they have a similar degree of furan-functionalization. Since the cross-link density is one of the main variables affecting the properties of cross-linked rubbers [38], the similarity in cross-link density of the BM cross-linked EPM-g-furan and EVM-g-furan allows for a fair comparison between them.

For both BM cross-linked elastomers the cross-link density determined from EA closely corresponds to that determined by equilibrium swelling. The cross-link densities determined from the stress-strain curves, however, are significantly larger.
than those determined from EA and equilibrium swelling. This may be due to inherent differences in the mode of deformation of the polymer chains between both methods. While the polymer chains are fully stretched in a tensile test, no chain stretching occurs during the equilibrium swelling experiments [34]. Differences in how loosely the cross-links or entanglements are embedded in the network structure may therefore affect the determined cross-link density [39]. Entanglements therefore appear to significantly contribute to $[\text{XLD}]_{\text{MR}}$. Normally, when the cross-link density is obtained from either equilibrium swelling or stress-strain curves, it includes both true chemical cross-links and permanently trapped chain entanglements while temporary entanglements that can unfold in the swollen or strained state are neglected [40-42]. The difference between the cross-link densities determined by the different methods appears to be relatively small for the BM cross-linked EMP-g-furan. This may be related to the inhomogeneity of the cross-linked network. If the cross-linking points are more sparsely divided throughout the rubber matrix, they are less capable of trapping entanglements than a more homogeneously cross-linked network such as the BM cross-linked EVM-g-furan of the peroxide cure EPM and EVM. As a result, an inhomogeneously cross-linked network with a certain amount of cross-links may appear to be less cross-linked than a homogeneously cross-linked network with the same number of cross-links [43]. Finally, the thermoreversible character of the BM cross-links may add to the observed discrepancies as during a swell test, the polymer is left for three days during which the dynamic, thermoreversible cross-links may open and close, allowing for the disentanglement of previously trapped entanglements.

7.3.2. Polar clusters

The structure of polar and ionic clusters has been extensively studied, primarily using SAXS [43,44]. The starting EPM and EVM rubbers are assumed to be fully homogenous as no SAXS scattering was observed [27]. SAXS measurements of the various functionalized EPM and EVM samples were performed to investigate the presence of polar clusters, their size and structure (Figure 7.1). For all EPM samples a peak is observed in the SAXS profile, which implies that these samples contain aggregates that differ in electron density from the polymer matrix [45]. For EPM-g-MA this scattering peak is observed at a scattering vector ($q$) of 0.057 Å$^{-1}$ for the EPM-g-MA precursor, which is in good agreement with literature data for similar materials [14,27]. The broad scattering peak indicates micro-phase separation of the grafted anhydride groups into MA-rich domains, which is driven by the large polarity difference between the polar MA grafts and the apolar EPM polymer backbone [27]. For EVM-g-MA and EVM-g-furan such a scattering peak is not observed, which confirms the assumption that the polar vinyl acetate co-monomers in EVM impede the formation of polar clusters.
SAXS scattering remains absent upon BM cross-linking of EVM-g-furan. For EPM-g-furan however, BM cross-linking results in a significant increase in scattering intensity and a shift of the peak to a lower q value of 0.03 Å⁻¹. These differences are associated with an increase in the cluster size and the Bragg spacing, which is the distance d between the clusters according to $q = 2\pi/d$ [46,47]. The Bragg spacing was found to increase from 11.2 nm to 20.9 nm upon cross-linking EPM-g-furan, implying that clusters in the former are more closely packed. This increase in Bragg spacing upon cross-linking is related to the increased size of the polar clusters in the matrix. The related SAXS peak is known to shift to lower q values upon such an increase in cluster size [14,44,48]. The reason is that the structure of the polymer matrix is tightened during cross-linking. As a result, nodules are unable to return to their original position. Insertion of the (rigid) BM cross-linking agent into the polymer may also help to increase the average distance between the chains, resulting in larger Bragg spacing [45,49].

The SAXS scattering observed for the functionalized EPM samples arises from both thermal, time-dependent fluctuations in cluster concentrations as a result of Brownian motion (ergodic contributions) and as a result of the inhomogeneous distribution of cross-links (non-ergodic contributions) [50]. These dynamic and static scattering contributions can be separated to obtain a more quantitative view by subtracting the scattering intensity of the corresponding non-cross-linked polymer, assuming the latter solely reflects the dynamic scattering contribution [43]. A morphological model can then be used to interpret the SAXS profiles, yielding the characteristics of the clusters. The Yarusso and Cooper (YC) model [48] was found to be superior in interpreting SAXS data of EPM-g-MA [14,44,51] (Figure S7.1). This hard-sphere model describes the polar clusters as spherical particles with radius $R_1$, surrounded by a polymeric layer with restricted-mobility with radius $R_2$ (Figure 7.2) [44,48]. The particles are arranged in a liquid-like order with a distance of closest approach of $2R_2$. The average volume of an element containing one scattering particle is defined as $V_p =$...
Finally, $\Delta \rho$ is the difference in electron density between the scattering polar clusters and the EPM matrix [27]. Here the YC model was successfully used to fit the SAXS patterns of EPM-g-MA, EPM-g-furan and BM cross-linked EPM-g-furan (Table 7.3). The fit parameters were all obtained with $R^2$ values above 0.99.

**Figure 7.2.** Schematic representation of a YC model spherical, polar domain in (BM cross-linked [furan-functionalized]) EPM-g-MA with $R_1$ the radius of the cluster and $R_2$ the radius of the polymeric layer with restricted-mobility surrounding this cluster.

**Table 7.3.** Parameters from the fit of SAXS patterns of functionalized EPM samples with the Yarussso & Cooper model.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$R_1$ (Å)</th>
<th>$R_{CA}$ (Å)</th>
<th>$R_{CA} - R_1$ (Å)</th>
<th>$V_\rho$ ($\text{Å}^3$)</th>
<th>$\Delta \rho$ (e/Å$^3$)</th>
<th>d (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EPM-g-MA</td>
<td>22.3</td>
<td>44.1</td>
<td>21.8</td>
<td>4.65 $\times$ 10$^4$</td>
<td>0.35</td>
<td>112</td>
</tr>
<tr>
<td>EPM-g-furan</td>
<td>23.9</td>
<td>47.9</td>
<td>24.0</td>
<td>5.72 $\times$ 10$^4$</td>
<td>0.28</td>
<td>120</td>
</tr>
<tr>
<td>BM cross-linked EPM-g-furan</td>
<td>43.2</td>
<td>77.9</td>
<td>34.7</td>
<td>3.38 $\times$ 10$^5$</td>
<td>0.47</td>
<td>209</td>
</tr>
</tbody>
</table>

A relatively small increase in cluster size $R_1$ is observed upon the furan-functionalization of EPM-g-MA. This is remarkable as the size of the added FFA is similar to the initially grafted MA. When all grafted MA groups are phase-separated from the EPM matrix (which is very likely given their large difference in polarity), $\Delta \rho$ can provide information about the composition of the scattering particle [14]. While the furan-functionalization of EVM-g-MA affords a small increase in the overall electron density, the increased cluster volume will yield a lower electron density per cluster volume element $\Delta \rho$. Formation of DA cross-links in polar clusters results in a significant increase in the electron density because of the very high polarity of the BM cross-linker. This compensates for the increased cluster volume and results in an increase in $\Delta \rho$. The thickness of the restricted-mobility layer ($R_1 - R_{CA}$) also increases with the size of the polar clusters ($R_1$).

In conclusion, SAXS showed that the presence of polar clusters in (BM cross-linked) EPM-g-furan and their absence in (BM cross-linked) EVM-g-furan samples. This confirms that the cross-links are spatially more homogeneously distributed in BM cross-linked EVM-g-furan than in BM cross-linked EPM-g-furan.
7.3.3. Material properties

The material properties of rubbers (with phase-separated domains) are highly dependent on the cross-link density and the structure of the cross-linked, microphase-separated domains. The cross-link density of the BM cross-linked EPM-g-furan and EVM-g-furan elastomers and of the DCP cured references are all roughly $8 \times 10^{-5}$ mol/mL (Table 7.2). Since both the EPM and EVM copolymers used in this study are amorphous at room temperature, the differences between their mechanical properties can provide information on the effect of the homogeneity of cross-linking.

The stress-strain curves of EPM and EVM are typical for non-cross-linked rubbers with an extremely high elongation at break and a very low tensile strength [3,12]. Despite the intrinsic differences between the chemical structure of EPM and EVM, the tensile strength increases and the elongation at break decreases upon cross-linking of both materials (Figure 7.3A). The effect of BM cross-linking is more pronounced for EVM-g-furan than for EPM-g-furan. This may be because the non-cross-linked EPM-g-furan already has polar clusters that can act as physical cross-links in a tensile test.

A qualitative comparison of the shapes of the stress-strain curves of the BM cross-linked EPM-g-furan and EVM-g-furan at different strain rates (Figure 7.3B) can give some insight in the effect of the heterogeneity of the network [52]. At both strain rates, the BM cross-linked EPM-g-furan shows an initial accumulation of stress with a relatively low increase in strain at increased stress loads. This stress localization in the cross-linked clusters eventually leads to rupture of the physical interactions in these clusters as is indicated by the flattening incline to the same stress-strain slope as the BM cross-linked EVM-g-furan. The overall more gradual inclination of the stress-strain slope of the BM cross-linked EVM-g-furan indicates that the applied stress is distributed more evenly over the network.
Figure 7.3. Median stress-strain curves of A: EPM-g-furan and EVM-g-furan (dashed), their BM cross-linked products (solid) and DCP cured EPM and EVM references (dotted) at a similar cross-link density and a strain rate of 500 mm/min and B: BM cross-linked EPM-g-furan and EVM-g-furan at strain rates of 500 mm/min (solid) and 5 mm/min (dashed).

The effect of cross-linking, entailing a characteristic increase in hardness, Young’s modulus and tensile strength and a decrease in elongation at break and compression set [53-56], is evident for both peroxide curing of EPM and EVM and BM cross-linking of EPM-g-furan and EVM-g-furan (Figure 7.4). Overall, the BM cross-linked EPM-g-furan has a higher Young’s modulus and a lower tensile strength and elongation at break than the BM cross-linked EVM-g-furan (Figure 7.4A). The Young’s modulus and tensile strength of the BM cross-linked EPM-g-furan and EVM-g-furan are increased with respect to their DCP cured references. Finally, the relative increase in hardness and decrease in compression set upon BM cross-linking is larger for EVM-g-furan than for EPM-g-furan (Figure 7.4B).

Figure 7.4. A: Tensile properties and B: hardness and compression set of EPM-g-furan and EVM-g-furan, their BM cross-linked products and DCP cured EPM and EVM references with a similar cross-link density. The error bars indicate ± 1 standard deviation.

The homogeneous distribution of cross-links in the EVM-g-furan rubber allows for a more gradual breakage of cross-links and initially more loss of mechanical strength when it is exposed to stress. This gradual breakage of cross-links eventually results in a higher tensile strength and elongation at break with respect to the heterogeneously BM cross-linked EPM-g-furan. Polymers with heterogeneous networks such as the BM
cross-linked EPM-g-furan display lower stability to extension because chain segments between two or more cross-links in clusters may be too short to deform or store elastic energy in these materials [57]. Their cross-links are closely packed in polar clusters and can only cooperatively act as a single cross-linked supernode with a low individual ability for elastic-energy storage [43,58,59]. For a network consisting of highly cross-linked zones embedded in a matrix of a less cross-linked polymer, stress will accumulate in these zones of elevated functionality (Figure 7.5). Contrary, a network with a uniform cross-link distribution will be able to transfer applied stress more efficiently so that all the chains in the network will bear an equal stress load [60,61]. The decreased effectiveness of such heterogeneously dispersed cross-links [62] may therefore explain the lower tensile strength and elongation at break of the BM cross-linked EPM-g-furan with respect to the EVM-g-furan. The observed differences would be even more evident if the molecular weights of the two elastomers were the same (50 kg/mol for EPM-g-furan versus 30 kg/mol for EVM-g-furan) since yield stress typically increases with molecular weight due to the greater number of entanglements per molecule [63].

The observed smaller relative difference in hardness and compression set upon BM cross-linking of EPM-g-furan with respect to EVM-g-furan may also be a result of its more inhomogeneous distribution of cross-links. The associated broader distribution of chain-lengths between entanglements is already present in the non-cross-linked precursor as a result of the inhomogeneous distribution of functional groups. The broader distribution of mesh sizes [43] in the BM cross-linked EPM-g-furan with respect to the EVM-g-furan thwarts easy network penetration, affording a relative higher enhancement of the rubber’s hardness for the EVM-g-furan [43].

Finally, previous studies on the thermoreversibly cross-linking of the same EPM and EVM polymers showed that the retention of the material properties upon reprocessing in the melt is somewhat higher for the BM cross-linked EPM-g-furan
than for EVM-g-furan (97, 90, 95, 86 and 107% versus 83, 89, 93, 74 and 73% for the hardness, Young's modulus, tensile strength, elongation at break and compression set, respectively) [3,12]. This difference may also be related to the network heterogeneity of the former.

7.4. Conclusions

Two commercially available, maleated elastomers (EPM-g-MA and EVM-g-MA) were thermoreversibly cross-linked via Diels-Alder chemistry in a straightforward, two-step approach of furan-functionalization and subsequent bismaleimide cross-linking. SAXS measurements showed the presence of clusters in the apolar EPM elastomers and their absence in the polar EVM elastomers indicating phase-separation of the polar MA/furan groups in the former. DA cross-linking of EPM-g-furan with polar BM takes predominantly place in such polar clusters, resulting in an inhomogeneously cross-linked network. Differences in material properties between the two cross-linked elastomers can be attributed to the homogeneity of their cross-linked networks as they are compared at the same cross-link density. The advantage of the uniform cross-linking in EVM-g-furan appears to be an improved stability in mechanical behavior, resulting in a higher tensile strength and elongation at break.

7.5. References

[34] Somhatsompop N. Polym Polym Compos 1999;7:41.
Supplementary information Chapter 7

Figure S7.1. Parameters for Yarruso-Cooper model fits to the experimental SAXS profiles of A: EPM-g-MA, B: EPM-g-furan and C: BM cross-linked EPM-g-furan.