It is demonstrated that the proof of concept for using Diels-Alder chemistry as a tool for the thermoreversible cross-linking of functionalized EPM-g-MA gum rubber is not limited to laboratory scale using a solvent route as presented in the previous chapters. The use of a laboratory internal mixer (30 cm$^3$) is the first step towards an industrial process as it greatly reduces the processing time and allows for a solventless process for the furan-functionalization and BM cross-linking of EPM rubber. The resulting products have the same performance as those made on laboratory scale and have similar thermoreversible cross-linking behavior. Practical compounds were also prepared by mixing thermoreversibly cross-linked EPM with carbon black and mineral oil on a batch mixer. As expected, this resulted in an increase in hardness, Young’s modulus and tensile strength and a decrease in elongation at break and compression set without affecting the thermoreversible character of the cross-links. The pendant furan groups of the (non)cross-linked EPM-g-furan were found to interact with the carbon black filler which explains the high gel content and material properties of the EPM-g-furan. Finally, crystalline EPM rubber comounds were prepared. These show excellent material properties, which are retained over multiple reprocessing cycles.

This chapter is based on: L. M. Polgar, J. Keizer, R. Blom, B. Niemeijer, F. Picchioni and M. van Duin, ‘Recyclable EPM rubber compounds based on thermoreversible Diels-Alder chemistry’ to be submitted to Rubber Chemistry and Technology 2017.
8.1. Introduction

Elastomeric materials can be found everywhere in modern day life in products such as car tyres, seals and roof linings. Rubbers are suitable for so many applications, because they are generally elastic, though, strong and durable [1-3]. The main components in rubber products are cross-linked elastomers that are capable of quick recovery to their original dimensions after elongation or compression [1]. Unfortunately, cross-linking of elastomers is usually an irreversible process, which makes the recycling of rubber products practically impossible. This is the main reason why many rubber products are discarded after use, being burned for energy or sent to landfills. Some reuse of rubber products is found in re-treading tires or shredding rubber waste to be used as filler for playground surfaces. It is more desirable to be able to recycle these products in a cradle-to-cradle fashion, obtaining rubber products with the same material properties as the original products [4]. A lot of effort has therefore been devoted to the devulcanization of cross-linked rubbers [5-9]. Devulcanization often involves harsh mechanical, thermal and/or chemical treatments. An alternative solution is found in thermoreversible cross-linking of rubbers [10-16]. Thermoreversibility allows for the rubber to be reprocessed at intermediate temperatures that are high enough to temporarily break the cross-links without inducing thermal degradation through chain scission. In this way the desirable qualities of thermosets (high performance) and thermoplastics (recyclability) are combined. A good example is the thermoreversible cross-linking of functionalized ethylene/propylene copolymer rubbers (EPM) with bismaleimide (BM) through reversible Diels-Alder (DA) chemistry [10].

EP(D)M rubbers have a saturated main chain and show high resistance against weather and heat aging and have low swell in aqueous media. The main applications of EP(D)M rubbers are in the automotive industry, cable insulation and building and construction industry [2]. With a market size of 1100 kton in 2015 [17], the replacement of EPDM with a thermoreversibly cross-linked EPM would have a huge impact on society. To meet this demand however, rubbers are generally produced in large volumes and with small economical margins. As a result, production costs are a leading factor for innovation in the industry. Up to now, examples of such thermoreversibly cross-linked rubber that are produced on an industrial scale are limited [18]. The furan-functionalization of maleated EPM and the subsequent DA cross-linking in small-scale laboratory processes, described in previous research, involve the use of large amounts of organic solvents (at least 10 times the batch size) and take much time per batch (roughly one week including dissolving and drying). In order to avoid this long and wasteful process and to take a first step towards industrial production, the use of an internal mixer for the furan-functionalization and cross-linking of the rubber compound is investigated.
Rubber products are usually compounded with (reinforcing) fillers. Carbon black is widely used as a filler in elastomers to modify their mechanical properties, i.e. the strength, fracture behavior, abrasion and failure properties are improved [19]. About 90% of the worldwide production of carbon black is used by the tire industry where the carbon black enhances tear strength and improves modules and wear characteristics of the tires. Moreover, the addition of carbon black usually reduces the costs of (EPDM) rubber products as it is a relatively cheap material obtained by the partial combustion or thermal decomposition of hydrocarbons (usually as a by-product of partially burned products from refineries). In addition, rubber products typically contain (oil) plasticizer to adjust the viscosity and hardness of the compound. The addition of reinforcing fillers such as carbon black has many complicated effects in any rubber compound, both on macro and micro scale [20,21]. It is therefore important to investigate whether compounding thermoreversibly cross-linked rubber with filler and plasticizer has the same beneficial effects on the material properties and whether it affects the thermoreversible character of the rubber.

The first part of this study involves the production of BM cross-linked EPM rubber compounds with carbon black and mineral oil using an internal mixer and an investigation of any interaction between the different components in the resulting compounds. For this part of the study amorphous EP(D)M rubbers are used to simplify the characterization with swelling tests. The second part of this study involves the evaluation of the material properties of the thermoreversibly cross-linked rubber compounds and the retention of their properties upon reprocessing. Since an increase in the ethylene of peroxide cured EP(D)M rubbers is known to result in improved rubber performance due to the presence of crystalline domains, this second part also includes a comparison between amorphous and crystalline EPM elastomers to study the effect of the crystallinity on the material properties of thermoreversibly cross-linked rubber compounds.

### 8.2. Experimental

#### 8.2.1. Materials

The EPM copolymer (K3050, 49 wt% ethylene), the maleated EPM rubbers (EPM-g-MA, DE5005, 49 wt% ethylene, 2.1 wt% MA and EPM-g-MA-cr, K2708R, 73 wt% ethylene, 0.8 wt% MA), the EPDM reference rubbers with 5-ethylidene-2-norbornene (ENB) as diene (ENB-EPDM, K8550C, 48 wt% ethylene, 5.5 wt% ENB and ENB-EPDM-cr, K8570C, 66 wt% ethylene, 5.0 wt% ENB) and Sunpar 2280 oil were kindly provided by ARLANXEO Netherlands. Carbon black N550 and N772 were kindly provided by Teijin Aramid. Furfurylamine (FFA, Sigma-Aldrich, ≥ 99%) was freshly distilled before use. 1,1-(Methylene-di-4,1-phenylene)bismaleimide (BM, 95%), di(tert-butylperoxyisopropyl)benzene (98%), octadecyl-1-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate (99%), and decalin (98%) were all purchased from
Sigma-Aldrich and used as received as reversible cross-linker, peroxide cross-linker, phenolic anti-oxidant and solvent, respectively. The aliphatic bismaleimide with a 12 carbon spacer (BMC12) was synthesized from maleic anhydride (MA, >99%, Sigma-Aldrich) and 1,12-diaminododecane (>98%, Sigma-Aldrich), according to a published procedure [22,23].

8.2.2. **Methods**

8.2.2.1. **Furan-functionalization of EPM-g-MA rubber**

The maleated rubber precursors were dried in a vacuum oven for one hour at 175 °C to convert any diacid present into cyclic anhydride [10,24]. 22 g EPM-g-MA was fed to an internal mixer (Brabender Messenkneder, Type W30 EHT, 30 cm³) to reach a fill factor of 80% and it was homogenized at 50 rpm for 3 min. After some preliminary experiments a temperature of 128 °C was chosen as the minimum temperature to obtain a coherent batch of maleated EPM on such a small scale. Meanwhile, a spatula tip of the inhibitor (3–4 mg) was added. Next, 1.25 eq. of FFA (based on MA content, 0.57 g for EPM-g-MA and for 0.22 g EPM-g-MA-cr) was slowly added to the rubber melt and allowed to react for 3 min. The mixer was then stopped and opened and the resulting EPM-g-furan product was removed and cooled.

8.2.2.2. **Furan-functionalization, compounding and cross-linking of EPM-g-MA rubber**

The furan-functionalization, mixing with carbon black and oil and BM cross-linking was combined in 1 process. First a filler/oil pre-mix of 70 parts per hundred rubber (phr) of carbon black N550 and 70 phr N772 with 50 phr Sunpar 2280 oil was prepared. After functionalizing 10 g of EPM-g-MA with FFA for 3 min (see 8.2.2.1.) the set temperature of the mixer is increased to 180 °C to ensure complete conversion of the amide-acid intermediate to the imide, the evaporation of the excess of FFA (bp = 145 °C) and for the subsequent melting and good dispersion of the BM cross-linker (T_m = 176 °C). After homogenizing the EPM-g-furan for 3 min when 180 °C was reached, 19 g of the dry filler/oil mixture is added. When the torque was stable again (after typically 2-3 min), the BM cross-linker was added (0.2 to 1.5 molar eq. based on furan content). Mixing was continued for 2 min before the compound was removed from the mixer. Sample bars of the obtained products 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 bars for 15 min. Compression molding was performed on a Taunus Ton Technik V8UP150A press, equipped with a temperature controller. The resulting sample bars were thermally annealed in an oven at 50°C for a minimum of 72 h to ensure complete cross-linking.

8.2.2.3. **Compounding and peroxide curing of ENB-EPDM rubber**

10 g of ENB-EPDM was fed to the internal mixer and homogenized at 50 rpm and 70 °C for 4 min. Then, 19 g of the dry filler/oil mixture is added (see 8.2.2.2.). When the torque was stable (after typically 2-3 min), 1 phr of pure peroxide was added slowly...
to the mixture. The rubber compound was mixed for 4 more min until it was removed from the mixer. This rubber compound was then vulcanized by pre-heating in a mold at 160 °C for 5 min and compression molding at 160 °C and 50 bars for 35 min.

8.2.3. Characterization
The conversion of EPM-g-MA to EPM-g-furan was followed by Fourier Transform Infrared spectroscopy (FT-IR) and elemental analysis (EA). FT-IR spectra were recorded on a Perkin-Elmer Spectrum 2000. Rubber films with a thickness of 0.1 mm were compression molded at 150 °C and 100 bar for 30 min, thermally annealed to ensure maximum DA cross-linking and measured in a KBr tablet holder. Measurements were performed over a spectral range from 4000 to 600 cm⁻¹ at a resolution of 4 cm⁻¹, co-averaging 32 scans. Deconvolution was used to quantify the areas under the individual FT-IR peaks (R² > 0.95). The differences in relative peak areas were used to calculate the reaction conversions. The methyl rocking vibration peak at 723 cm⁻¹ was used as an internal reference, as it originates from the EPM backbone and is not affected by chemical modification. The decrease of the absorbance of the C=O symmetrical stretch vibration of the anhydride groups at 1856 cm⁻¹ was used to calculate the conversion of the reaction from EPM-g-MA to EPM-g-furan, according to a reported procedure [10]. The decrease of the characteristic C-O-C symmetrical stretch vibration of the furan groups at 1013 cm⁻¹ was used to determine the conversion of the cross-linking reaction in the same way. EA for the elements N, C and H was performed on a Euro EA elemental analyzer. The nitrogen content was related to the furan-functionalization according to a reported procedure [10].

GPC was performed using triple detection (refractive index, viscosity and light scattering), using a consisting of a Viscotek Ralls Viscometer Model H502 and Shodex RI-71 Refractive Index detector. The separation was carried out 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 at 30 ºC. THF 99+%, stabilized with butylated hydroxytoluene was used as the eluent at a flow rate of 1.0 mL/min. The samples were filtered over a 0.45 µm PTFE filter prior to injection. Four GPC measurements were performed on each sample. Data acquisition and calculations were performed using Viscotek OmniSec software version 4.6.1, using a refractive index increment (dn/dc) of 0.052. Molecular weights were determined based on a universal calibration curve generated from narrow polydispersity polystyrene standards (Agilent and Polymer Laboratories).

Equilibrium swelling experiments were performed in decalin. The rubber sample (approximately 500 mg) was weighed in 20 mL vials (W₀) 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 (W₁) and was dried in
a vacuum oven at 110 °C until a constant weight was reached ($W_2$). The gel content of the rubber is defined as $W_2/W_0 \times 100\%$. For the reinforced rubber compounds $W_0$, $W_1$ and $W_2$ were corrected for the presence of carbon black and $W_0$ was corrected for the presence of oil to enable the calculation of the rubber gel content. The cross-link density $[\text{XLD}]_{\text{gum}}$ was calculated from $W_1$ and $W_2$ using the Flory-Rehner equation (Eq. 8.1) [25-27]. For the reinforced rubber compounds a correction for the adsorption of decalin by the carbon black is performed via the Kraus correction (Eq. 8.2) to obtain the cross-link density of the rubber compound $[\text{XLD}]_c$ [28].

$$[\text{XLD}]_{\text{gum}} = \frac{\ln(1-V_R)+V_R+\chi V_R^2}{2V_S\left(0.5V_R-V_R^{1/3}\right)} \quad \text{with} \quad V_R = \frac{W_2}{W_2+(W_1-W_2)\frac{\rho_{\text{EPM-g-furan}}}{\rho_{\text{decalin}}}}$$

(Eq. 8.1)

$$[\text{XLD}]_c = \frac{[\text{XLD}]_1}{1+K \phi} \quad \text{with} \quad K = 0.0179 \cdot V_{oa} + 2.29 \quad \text{and} \quad \phi = \frac{f_{cb}\rho_{\text{comp}}W_g}{\rho_{\text{cb}}W_1}$$

(Eq. 8.2)

$V_{oa}$ Oil absorption volume of unit weight by 50/50 ratio (94 mL/100 g for decalin on N550 [30,31]).
$f_{cb}$ Weight fraction of carbon black in the dried residue (0.483).
$W_g$ Weight of rubber present in the dried residue (g).
$\rho_{\text{comp}}$ Density of the dried residue (1.4 g/mL as a weighted average).
$\rho_{\text{cb}}$ Density of the carbon blacks (1.8 g/mL for a 50/50 ratio N550/N770 [2]).

UV spectroscopy measurements were performed on an AQUAMATE Thermo Spectronic UV Spectrophotometer. Calibration curves were constructed from two series of samples with increasing concentrations of EPM-g-MA and EPM-g-furan in hexane, which were mixed with the carbon black by stirring for 24 h at 80 °C. The carbon black was then removed from the slurry using an ultracentrifuge at 4500 rpm for 10 min and the concentration of rubber in the centrifugate was measured using UV spectroscopy. Extraction experiments were performed on a FOSS Soxtec 2043 at 170 °C using THF as solvent with 4 h boiling and 30 min rinsing. After extraction both the beakers containing the extraction solution and the thimbles containing the residue were placed in an oven at 50 °C for at least 8 h to evaporate all solvent and finally weighed. The same full extraction procedure was also performed with 3 empty thimbles to correct for any loss of weight. All measurements were performed in triplo. Thermographic analysis (TGA) of the dried Soxtec residues was performed using a Mettler Toledo TGA/SDTA851e connected to an auto robot TS0801RO with a Mettler Toledo TS0800GC1 Gas Control unit. The samples were heated from 20 °C to 500 °C at 10 °C per minute under nitrogen to crack the rubber part of the residue, while leaving the carbon black unaffected.
The cure kinetics were studied using a Monsanto ODR 2000 Rheometer at temperatures of 50 or 180 °C according to ISO 3417:2008, yielding elastic torque versus time curves. Hardness was measured using a Bareiss Durometer, according to the ASTM D2240 standard. Square test samples of 5x5 cm and a thickness of 2.0 ± 0.1 mm were prepared by compression molding. Average values were obtained from 10 measurements. Tensile tests were performed on an Instron 5565 with a clamp length of 15 mm, according to the ASTM D412 standard. A strain rate of 500 ± 50 mm/min was applied. Test samples of 45 mm long, 5 mm wide and 1 mm thick 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. Data presented are averages of the other 8 tests. The median stress-strain curves in the figures were selected to represent the entire series of a sample. Compression set tests were performed according to the ASTM D931 standard, using a home-made device and cylindrical samples with a thickness of 6.0 ± 0.1 mm and a diameter of 13.0 ± 0.1 mm, which were prepared by compression molding. The samples were compressed to 75% of their original thickness for 70 h at room temperature and relaxed for 30 min at 50 °C.

8.3. Results and discussion

8.3.1. The preparation of thermoreversibly cross-linked EPM-g-furan

In the previous study the EPM-g-furan product was compression molded at 180 °C and 100 bar for 15 min to ensure conversion of the intermediate amide acid into the imide [32]. Three experiments were performed to determine whether (high temperature) compression molding is still required after the modification on an internal mixer (Figure 8.1). First, EPM-g-MA and FFA were mixed in the internal mixer at 128 °C and 50 rpm for 7 min and the product was separated in two parts. One part was compression molded at 180 °C and 100 bar for 15 min as in the previous study (i) and the second part was compression molded at 80 °C and 100 bar for 15 min (ii). Compression molding at a temperature of 80 °C proved to be high enough to obtain a homogeneous film for FT-IR spectroscopy and low enough to prevent conversion of amide acied (characteristic peaks at 1550 and 1650 cm⁻¹) to the imide. Finally, another reaction between EPM-g-MA and FFA was performed in the mixer at 128 °C for 3 min and heating the mixer to 180 °C for another 3 min, after which the product was compression molding at 80 °C and 100 bar for 15 min (iii). No significant amounts of anhydride ($\tilde{\nu}^{\text{as}}_{\text{CO}} = 1856$ cm⁻¹) are observed for any of the three furan-functionalized samples. However, the large peaks at 1550 and 1650 cm⁻¹ present in sample ii indicate the presence of amide acids and confirm that higher temperatures are required to irreversibly convert these into imides. Such amide peaks are not present in samples i and iii. This clearly demonstrates that heating the material to 180 °C in an internal mixer suffices to achieve the desired conversion amide acids into imide.
Figure 8.1. FT-IR spectra of EPM-g-MA and 1 eq. of FFA after 7 min in an internal mixer at 128 °C and compression molding at 180 °C and 100 bar for 15 min (i, black) or at 80 °C and 100 bar for 15 min (ii, red) and after 3 min in an internal mixer at 128 °C and 3 min at 180 °C and compression molding at 80 °C and 100 bar for 15 min (iii, blue).

The furan-functionalization of EPM-g-MA in the internal mixer yielded a brownish product that appears similar to the product obtained via the solvent-based procedure followed in previous studies [32]. To determine the minimum amount of FFA required for the maximum conversion (an excess of 3 eq. FFA was used in the solution process [32]), the amount of FFA that was added to the internal mixer was varied from 0 to 1.5 molar equivalent (based on the MA content). The characteristic furan peaks at 1504, 1073 and 1013 cm\(^{-1}\) [10] were clearly visible in the FT-IR spectra. The conversion of EPM-g-MA to EPM-g-furan was determined from the decrease in the anhydride peak area at 1856 cm\(^{-1}\) as measured by FT-IR and from the nitrogen content using EA (Table 8.1). Overall high conversions are a result of the fast reaction between primary aliphatic amines and cyclic anhydride groups [33]. Complete conversion was achieved upon the addition of a small excess of FFA. The addition of 1.25 eq. of FFA was used for all other furan-functionalization experiments in the internal mixer described in this study.

Table 8.1. Anhydride conversion upon the addition of different amounts of FFA as determined by infrared spectroscopy and elemental analysis.

<table>
<thead>
<tr>
<th>FFA added (eq.)</th>
<th>Anhydride conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>FT-IR</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0.50</td>
<td>47</td>
</tr>
<tr>
<td>1.00</td>
<td>85</td>
</tr>
<tr>
<td>1.25</td>
<td>100</td>
</tr>
<tr>
<td>1.50</td>
<td>100</td>
</tr>
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</table>
The thus developed furan-functionalization process of EPM-g-MA in an internal mixer (3 min reaction at 128 °C and 3 min heating to 180 °C) was followed by the addition of 0.5 eq. of BM (based on the furan content) and mixing for another 2 min at 180 °C. The insolubility of the sample in decalin confirms that the material was cross-linked. The obtained cross-link density of $7.4 \times 10^{-5} \pm 0.5 \times 10^{-5}$ mol/mL is comparable with cross-link densities obtained from FT-IR and EA measurements ($6.9 \times 10^{-5}$ and $7.7 \times 10^{-5}$ mol/mL, respectively) and in the same order of magnitude as the cross-link densities of sulfur vulcanized or peroxide cured EP(D)M gum rubber ($10^{-5} - 10^{-4}$ mol/mL) [34-38].

For some polymers the high shear forces and temperatures applied when processed in an internal mixer are known to lead to degradation reactions, such as chain scission or long chain branching [39-41]. This can have a detrimental effect on the material properties of the polymers [42]. GPC measurements were performed on EPM-g-MA before and after processing in an internal mixer at 180 °C for 10 min (Table 8.2). $M_n$ remains the same and $M_w$ and PDI slightly increase upon processing under these conditions. This suggests that some branching took place and no significant chain degradation.

<table>
<thead>
<tr>
<th>EPM as received</th>
<th>EPM after processing</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M_n$ (kg/mol)</td>
<td>54 ± 4</td>
</tr>
<tr>
<td>$M_w$ (kg/mol)</td>
<td>126 ± 12</td>
</tr>
<tr>
<td>PDI (-)</td>
<td>2.3 ± 0.2</td>
</tr>
<tr>
<td></td>
<td>54 ± 6</td>
</tr>
<tr>
<td></td>
<td>146 ± 19</td>
</tr>
<tr>
<td></td>
<td>2.7 ± 0.3</td>
</tr>
</tbody>
</table>

In conclusion, the furan-functionalization and BM cross-linking steps performed in solution as described in the previous study [32] were combined and upscaled to an internal mixer process without the use of solvent. This resulted in complete anhydride conversion and a similar cross-link density in a much shorter time (10 min instead of 3 days) with a smaller excess of FFA reagent (1.25 eq. instead of 3 eq.) and probably without significant degradation of the polymer.

### 8.3.2. Thermoreversibly cross-linked EPM-g-furan compounds

Carbon black is the most used reinforcing filler in the rubber industry and is commonly used in EPDM compounds. The 70/50/70 formulation used for the compounding of EPM-g-furan in this study is in the same range as commonly added amounts of carbon black (50-150 phr) and oil (20-70) for commercial EPDM rubbers [43-45].
8.3.2.1. Cross-link density

In rubber technology, cross-linking is typically studied using rheological measurements [46-48]. These yield so-called rheometer curves that present the torque as a measure for the extent of cross-linking versus time at a specific cure temperature. Rheometer curves have been measured for EPM-g-MA, EPM-g-furan and BM cross-linked EPM-g-furan rubber compounds (Figure 8.2). Time sweeps of the thermally annealed samples were determined at 180 °C until a constant torque was obtained (Figure 8.2A). The samples were then quenched to prevent the premature formation of cross-links before re-measuring them at 50 °C (Figure 8.2B). The usual initial drop in torque (caused by shear thinning of the polymer upon heating and shearing) was skipped (first 30 s) to show only the effect of a constant temperature on the material. For the measurements at 180 °C the torque of all samples further appears to decreases to a plateau over time. This decrease in torque is strongest for the BM cross-linked EPM-g-furan. This may be due to de-cross-linking via the retro-DA reaction, which is known to be prevalent at this temperature [10,49]. For the measurements at 50 °C the torque of the BM cross-linked EPM-g-furan clearly increases over time with respect to the non-cross-linked EPM-g-furan and EPM-g-MA. This may be due to the formation of cross-links via the DA reaction which is known to be prevalent at this temperature [10,50,51]. The torque of the non-cross-linked EPM-g-furan also appears to slightly increase over time at 50 °C.

![Figure 8.2](image-url). Rheometer curves of EPM-g-MA, EPM-g-furan (both without cross-linker) and BM cross-linked EPM-g-furan at A: 180 °C and B: at 50 °C directly after quenching them from 180 °C. The lines are for illustrative purposes only.

Equilibrium swelling experiments on compounds of EPM-g-MA, EPM-g-furan and BM and BMC12 cross-linked EPM-g-furan were performed to determine their gel and sol fractions and their cross-link densities (Table 8.3). A peroxide cured ENB-EPDM was used as a reference compound. The EPM-g-MA rubber almost entirely dissolves in decalin at room temperature with a small fraction of elastomer still bound to the carbon black filler. Remarkably, the gel fraction of the non-cross-linked EPM-g-furan is
significantly higher than that of the EPM-g-MA compound. This indicates that a significant amount of the EPM-g-furan elastomer is bound to the carbon black. On the other hand, a significant amount of the BM and BMC12 cross-linked EPM-g-furan elastomers has dissolved, resulting in a gel content that is lower than that of the peroxide cured reference sample. Nevertheless, their Kraus corrected cross-link densities are in the order of $5 \times 10^{-5}$ mol/mL, confirming that these compounds are indeed cross-linked with network densities on the low side of commercially applied EPM and EPDM rubber products ($10^{-5}$ to $10^{-2}$ mol/mL) [34,35,52]. The high sol fraction of the BM cross-linked EPM-g-furan may be a result of the reversible character of the cross-links that are in a constant dynamic equilibrium and allow part of the polymer to dissolve over time. This effect may be enhanced by the shifting of the equilibrium due to the continuous extraction of BM during the swelling test. The cross-link density of this gel fraction of the peroxide cured ENB-EPDM reference compound was found to be similar to that of the BM cross-linked EPM-g-furan.

**Table 8.3.** Gel content and cross-link density as determined from equilibrium swelling experiments in decalin of compounds of EPM-g-MA, EPM-g-furan, BM cross-linked EPM-g-furan and peroxide cured ENB-EPDM.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Gel content (%)</th>
<th>Apparent cross-link density (mol/mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EPM-g-MA</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>EPM-g-furan</td>
<td>23</td>
<td>$9.5 \pm 1.7 \times 10^{-6}$</td>
</tr>
<tr>
<td>BM cross-linked EPM-g-furan</td>
<td>79</td>
<td>$9.3 \pm 0.5 \times 10^{-5}$</td>
</tr>
<tr>
<td>BMC12 cross-linked EPM-g-furan</td>
<td>74</td>
<td>$7.5 \pm 0.4 \times 10^{-5}$</td>
</tr>
<tr>
<td>1 phr peroxide cured ENB-EPDM</td>
<td>98</td>
<td>$8.6 \pm 0.3 \times 10^{-5}$</td>
</tr>
</tbody>
</table>

8.3.2.2. Polymer-filler interaction

Carbon black consists of elemental carbon that is coalesced into particle aggregates and agglomerates that are highly porous and have a huge surface area [19,45]. This results in physical interactions with polymers as they get caught in the pores and small parts of multiple chains get absorbed by the carbon black particles [19,28]. The absorbed part of rubber on the carbon black surface is commonly referred to as bound rubber [20]. Bound rubber acts as additional physical cross-links and thereby affects the properties of the polymers. This may be the reason for the discrepancy between cross-link densities determined from equilibrium swelling and stress-stain curves (Table 8.3). The high gel content of the non-cross-linked EPM-g-furan also suggests that it has a higher bound rubber content than EPM-g-MA. Interactions between pendant furan groups on polymers and carbon nanotube fillers are described in literature [53-55]. The surface of carbon nanotubes resembles that of carbon black [56]. Interactions of a similar nature may take place in these EPM-g-furan compounds [57,58]. Furthermore, the BM cross-linkers may also interact with the carbon black
filler in a similar fashion, especially since the solubility parameter of BM of 27.6 (MPa)\(^{0.5}\) more closely resembles that of the carbon black, which is typically between 30 and 40 (MPa)\(^{0.5}\), than that of the EPM-g-furan rubber of 16.0 (MPa)\(^{0.5}\) [59,60]. Such an interaction could impede the (thermoreversible) BM cross-linking of the elastomer. Several experiments were performed to investigate such interactions.

Five solutions of EPM-g-MA and EPM-g-furan in hexane ranging from 0.2 to 1.0 g/L were measured by UV spectroscopy before mixing them with carbon black for 24 h at room temperature. The carbon black was separated from the solution by centrifuging before re-measuring the UV spectrum of these solutions. Reference experiments in which carbon black was mixed in hexane showed no UV peaks after centrifuging. UV absorption is correlated to the concentration of the polymers via the Lambert-Beer law. A decrease in concentration after mixing with and removing carbon black was observed for all samples. The UV absorption at 220 nm was found to be the \(\lambda_{\text{max}}\) for both compounds and was found to decrease with 4.8% for EPM-g-MA and 13.4% for EPM-g-furan (Figure 8.3). This demonstrates that the amount of EPM-g-furan extracted by the carbon black is higher than the amount of PM-g-MA, indicating that that despite the low degree of functionalization, the interaction between carbon black and EPM-g-furan is more prevalent than between carbon black and EPM-g-MA. Similar experiments were performed for different concentrations of BM in hexane (Figure S8.1). These showed no decrease in BM concentration after mixing with and removing carbon black from the mixtures, suggesting that there is no absorption of BM on the carbon black under these conditions.

![Figure 8.3. UV absorption at 220 nm of EPM-g-MA and EPM-g-furan in hexane before (closed symbols, solid lines) and after mixing with carbon black (CB) for 24 h at room temperature (open symbols, dashed lines).](image)

Soxtec extraction experiments of EPM-g-MA and EPM-g-furan and BM cross-linked EPM-g-furan gum rubbers confirm that these EPM rubbers completely dissolve in THF and that the thermoreversible character of the cross-links allows for complete dissolution under the extraction conditions (the boiling point of THF is 78 °C). Although the retro-DA reaction is not dominant at this temperature, rinsing with clean
solvent could result in a shift of the equilibrium by continuously extracting temporarily uncross-linked parts of the polymer and, mainly, BM cross-linker. This also explains the lower gel fraction of the rubber compounds when determined via Soxtec extraction with respect to equilibrium swell tests. Soxtec extraction and TGA of the extraction residue however, both show that a significant amount of elastomer is still retained together with the carbon black (Figure 8.4 and Table S8.1). The retained fraction of polymer after extraction may be a result of an interaction with the carbon black. The shape of the TGA curves is similar for all tested extraction residues and thermal degradation of the polymers was observed around 400°C (Figure S8.2). A reference TGA experiment on pure carbon black resulted in a weight loss of less than 0.1 wt%.

![Figure 8.4. Amount of bound rubber determined via Soxtec extraction and TGA. The error bars indicate ± 1 standard deviation.](image)

The large discrepancy between the rubber fraction in the extraction residue and the TGA weight loss of those residues is a result of the intrinsic differences between both methods as non-volatile degradation products are retained on the TGA sample. Besides that, the experiments are performed at different temperatures. The effect of temperature on the bound rubber content which may be enhanced if there are thermoreversible interactions such as the DA reaction between the rubber and the filler. Nevertheless, the different measurements indicate the same trend. The bound rubber fraction of all modified elastomers is higher than that of EPM. This may be because irregularities in the modified elastomer chains are more likely to get ‘stuck’ (bound) to the carbon black filler. The amount of retained rubber of the non-cross-linked EPM-g-furan is significantly higher than that of EPM-g-MA. This increased value suggests an increased interaction between the pendant furans and the carbon black filler. The addition of BM to the compound does not result in an increase in bound rubber content for EPM-g-MA compound. For the EPM-g-furan however, higher bound rubber contents are observed upon the addition of BM. Nevertheless, the bound rubber content is still lower than that of the peroxide cured ENB-EPDM of which less than 2 wt% is dissolved during the extraction process.
In conclusion, rheometer time sweeps, equilibrium swelling, UV spectroscopy, Soxtec extraction and TGA experiments all indicate that there is an increased bound rubber content for the non-cross-linked EPM-g-furan compound with respect to the EPM-g-MA compound. This may be a result of an interaction between the pendant furan groups and the carbon black filler. The BM cross-linking reaction appears not to be directly interfered by this interaction as the resulting products are still cross-linked.

8.3.2.3. Material properties of BM cross-linked EPM-g-furan
Compounding the EPM gum rubbers with carbon black and oil has the expected effect on the material properties [19] as the compounds appear to have an increased hardness, Young's modulus, tensile strength and elongation at break and a decreased compression set with respect to their corresponding gum rubbers (Figure 8.5). The non-cross-linked EPM-g-furan compound has an increased hardness, Young's modulus and tensile strength and a decreased in elongation at break and compression set with respect to its EPM-g-MA precursor. This difference is larger than that between the two corresponding gum rubbers, confirming the interaction between the pendant furan groups of EPM-g-furan and the carbon black filler as these effects on the properties are usually attributed to an increased cross-link density. BM cross-linking of the EPM-g-furan compounds results in an even more pronounced increase in hardness, Young's modulus and tensile strength and a decrease in elongation at break and compression set. This effect is characteristic for cross-linking rubbers [61,62]. The lower cross-link density of the BMC12 cross-linked EPM-g-furan (Table 8.3) also results in a decreased hardness, Young's modulus and tensile strength and an increased elongation at break and compression set with respect to the BM cross-linked EPM-g-furan (data not shown for brevity). This contradicts with previously reported results on EPM-g-furan rubber gums cross-linked with the same BMs [23]. The higher “effectivity” of the aromatic cross-linker in the rubber compounds may be because the majority of the compound consists of carbon black that is also mostly aromatic. This may result in a better miscibility of the aromatic cross-linker in the compound. Finally, the tensile strength of the peroxide cured rubber compound is relatively low with respect to values found in literature [63]. This may be because the use of 1 phr of peroxide in the absence of coagents is not be enough to yield a fully cross-linked system [64].
Although the thermoreversibly cross-linked EPM-g-furan compound clearly displays the properties of a cross-linked rubber [61,62], the peroxide cured ENB-EPDM reference compound with a similar cross-link density has a higher hardness, Young’s modulus, tensile strength and elongation at break and a lower compression set. The difference in properties between the two polymers may be a result of the larger molecular weight of the ENB-EPDM (85 kg/mol) with respect to the EPM-g-MA (50 kg/mol) [65-67]. The peroxide-initiated grafting process of MA onto EPM is known to result in a certain amount of chain degradation due to unwanted side-reactions [68], resulting in a limitation of the chain length of the EPM-g-MA rubber. This is also the reason why these amorphous EPM-g-MA rubbers do not meet the requirements for peroxide cured EPDM compounds that are typically used in products such as single ply roof membranes (tensile strength of 9 MPa and the elongation at break of 200%) [69]. Therefore, low molecular weight, amorphous EP(D)M elastomers are rarely used in rubber products. They are used in some applications such as conveyor belts, but in these cases it requires the addition of fibers to reinforce the rubber compound. The material properties of these relatively short amorphous EPM-g-MA rubbers can be enhanced by using different BM cross-linkers [23] or by the addition of multifunctional cross-linking aids [70]. Another way to tune the material properties of such EPM rubbers is by increasing the ethylene content and thereby increasing the degree of crystallinity of the elastomer [1].

8.3.2.4. Crystallinity of the rubber matrix

Low molecular, crystalline EPM elastomers have several applications in the building and construction sector as well as in the wiring and cabling sector. If the ethylene/propylene ratio in EPM rubbers exceeds 1.5 the elastomer becomes crystalline resulting in a more rigid material [2]. The effect of the crystallinity on the properties of the thermoreversibly cross-linked rubber compounds is studied by
comparing the amorphous EPM-g-MA containing 49 wt% ethylene with the more crystalline EPM-g-MA-cr containing 73 wt% of ethylene. Peroxide cured ENB-EPDM containing 53 wt% of ethylene and ENB-EPDM-cr containing 66 wt% of ethylene are used as irreversibly cross-linked reference compounds. The Kraus corrected cross-link densities of these materials after the addition of different amounts of cross-linker have been determined to allow for a comparison of the properties of these materials at the same cross-linking density (Figure 8.6).

![Figure 8.6.](Image)

The apparent cross-link density of both crystalline EP(D)M rubbers increases to a higher level upon the addition of cross-linker than that of their amorphous EP(D)M analogues. This is probably related to the presence of crystalline domains in these samples. Both peroxide cured ENB-EPDM reference samples display a continuous increase in apparent cross-link density upon the addition of peroxide. This increase in cross-link density levels off at higher peroxide concentrations due to degradation in side reactions [71,72]. Such a correlation is also observed upon the addition of small amounts of BM to EMP-g-furan. However, the cross-link density does not increase any further upon the addition of more than an equimolar amount of BM with respect to the furan groups. An optimum in cross-link density was also observed in a previous study on similar gum rubbers [23,70] and was explained by the capping of pendant furan-groups with the excess of cross-linker. In this case however, the apparent cross-link density does not decrease upon the addition of an excess of BM. This may be due to partial absorption of BM onto the surface of the carbon black filler.

Samples with cross-link densities of around $1.7 \times 10^{-4}$ mol/mL have been used to study the effect of the crystallinity of the elastomer and the type of cross-linking on the material properties of these rubber compounds (Figure 8.7). Overall, it appears that
the material properties of the crystalline BM cross-linked EPM-g-furan-cr more
closely resemble the properties of the non-crystalline, peroxide cured ENB-EPMD
reference compound. However, the relative difference with the crystalline reference
compound is similar. This discrepancy may be due to a non-covalent interaction
between pendant furan groups on the EPM-g-furan and the carbon black filler that
impede the formation of covalent, thermoreversible cross-links between these furan
groups and the BM cross-linkers.

Figure 8.7. A: Hardness and compression set at and B: Young’s modulus, tensile strength and
elongation at break of BM cross-linked amorphous and crystalline EPM-g-furan and peroxide
cured ENB-EPDM reference all with an apparent cross-link density of around 1.7×10^{-4} mol/mL. The
error bars indicate ± 1 standard deviation.

The more crystalline BM cross-linked EPM-g-furan-cr and ENB-EPDM-cr rubber
compounds have a higher hardness, Young’s modulus, tensile strength and elongation
at break and a lower compression set that their amorphous EPM-g-furan and ENB-
EPDM analogues. The reason for this is that the crystalline polyethylene domains act
as additional physical cross-links. These yield more resistance against deformation
and require more force to stretch the rubber compound and to disrupt the crystalline
regions, resulting in an increase in hardness, Young’s modulus and tensile strength.
Normally, crystalline EP(D)M rubbers have somewhat inferior compression set at 23
°C. The relaxation after compression in this study however was performed at a
temperature of 50 °C. This results in an enhanced compression set for both crystalline
EP(D)M rubber compounds. The increased elongation at break of the compounds with
the crystalline elastomers is a result of stretching of the polymers out of their
crystalline domains [1,73-75]. This phenomenon becomes evident when comparing
the stress-strain curves (Figure 8.8). The initial steep increase in stress upon straining
the crystalline EP(D)M compounds required to disrupt the crystalline regions is
followed by a more gradual increase as a result of the stretching of the polymers. As a
result, the tensile strength and elongation at break of EPM-g-furan-cr and ENB-EPDM-
cr rubber compounds are larger than those of the amorphous EPM-g-furan and ENB-
EPDM, respectively.
Figure 8.8. Median stress-strain curves of BM cross-linked compounds of amorphous (red) and crystalline (blue) EPM-g-furan and peroxide cured compounds of amorphous and crystalline ENB-EPDM references. All samples have an apparent cross-link density of around $1.7 \times 10^{-4}$ mol/mL.

8.3.2.5. Reprocessing and retention of the material properties.

Finally, the thermoreversibly cross-linked EPM-g-furan-cr compounds were reprocessed by cutting compression moulded samples in small pieces, feeding these into the internal mixer and mixing them at 130 °C and 50 rpm for 3 min (until the stable torque indicated that a homogeneous mixture was obtained). The reprocessed material obtained from the internal mixer was compression molded at 150 °C and 50 bars for 30 min and the apparent cross-link density (Table 8.4) and the material properties of the resulting homogeneous samples were determined (Figure 8.9). This process was repeated three times and the retention of the different properties with respect to the original BM cross-linked EPM-g-furan-cr compound was found to be > 90% for every reprocessing step (Figure S8.3).

Figure 8.9. A: Hardness and compression set and B: Young’s modulus, tensile strength and elongation at break of BM cross-linked EPM-g-furan-cr compounds after reprocessing in an internal mixer for up to three times. Error bars indicate ± 1 standard deviation.
Table 8.4. Apparent cross-link density as determined from equilibrium swelling for compounds of BM cross-linked EPM-g-furan-cr compounds after reprocessing in an internal mixer for up to three times.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Apparent cross-link density (mol/mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Original BM cross-linked EPM-g-furan-cr</td>
<td>1.6 ± 0.2 × 10^{-5}</td>
</tr>
<tr>
<td>1x reprocessed BM cross-linked EPM-g-furan-cr</td>
<td>1.8 ± 0.4 × 10^{-4}</td>
</tr>
<tr>
<td>2x reprocessed BM cross-linked EPM-g-furan-cr</td>
<td>1.6 ± 0.5 × 10^{-4}</td>
</tr>
<tr>
<td>3x reprocessed BM cross-linked EPM-g-furan-cr</td>
<td>1.7 ± 0.5 × 10^{-4}</td>
</tr>
</tbody>
</table>

The thermoreversibly cross-linked EPM-g-furan-cr compound shows hardly any loss of apparent cross-link density or material properties upon reprocessing for up to at least three times. The hardness, Young's modulus, tensile strength and elongation at break all remain relatively constant with respect to the original BM cross-linked EPM-g-furan-cr. Remarkably, the hardness and Young's modulus appear to increase and the elongation at break and compression set appear to decrease after the first reprocessing cycle. These changes in properties correspond to a material with a higher cross-link density. The properties deteriorate slightly and the hardness, Young's modulus and tensile strength increase and the elongation at break and compression set decrease with respect to the original EPM-g-furan-cr compound after subsequent reprocessing cycles.

The initial increase in cross-link density and corresponding effect on the material properties upon reprocessing may be caused by a more optimal mixing of the compound that takes place during the extra 3 min in the internal mixer. The smaller error bars determined for every material property after reprocessing also indicate this effect. Reference experiments performed to reproduce the original compound using longer mixing times also showed a similar effect on the properties (higher cross-link density and the corresponding effect on the properties). However, these longer mixing times are likely to induce a certain amount of degradation [39-41], especially upon applying the high shear forces to the freshly added, cross-linked rubber before heating it up and de-cross-linking (it takes approximately 30 s for the rubber to reach the mixing temperature). In conclusion, the high retention of properties upon reprocessing of the thermoreversibly cross-linked EPM-g-furan-cr compounds demonstrates that compounding these gum rubbers with high amounts of carbon black (140 phr) and oil (50 phr) does not have a negative effect on their recyclability. It even appears that the retention of material properties upon reprocessing is higher for the compounds than for the gum rubbers [10]. A more in depth study of the interactions between the components in the compound is required to fully understand the reasons behind this.
8.4. Conclusions

EPM-g-MA elastomers were furan-functionalized with FFA and BM cross-linked in a fast, solventless process using an internal mixer. High anhydride conversions were obtained according to FT-IR and EA analysis. Equilibrium swelling of the EPM-g-furan product with BM indicates that the material was cross-linked. The resulting cross-link density of $7.3 \times 10^{-5}$ mol/mL approaches the typical range of cross-link densities for sulphur vulcanized and peroxide cured EPDM rubber. According to GPC measurements of EPM-g-MA before and after processing in the internal mixer, no significant chain degradation took place.

The furan-functionalization and BM cross-linking process in the internal mixer was successfully combined with mixing with carbon black and oil in a one-step process. Compounding appeared not to directly interfere with the DA reaction as the compounded EPM-g-furan rubbers are still cross-linkable with BM as was shown, amongst others, by rheometer experiments. The increase in torque observed at low temperatures demonstrated the formation of cross-links whereas de-cross-linking via the retro-DA reaction was observed at high temperatures. Equilibrium swelling tests, UV spectroscopy, Soxtec extraction and TGA all indicated that there is an interaction between the pendant furan groups and the carbon black filler. This interaction resulted in an increase in hardness, Young’s modulus and tensile strength and a decrease in elongation at break and compression set of the non-cross-linked EPM-g-furan with respect to the EPM-g-MA. Even so, the material properties of the BM cross-linked products were inferior to those of peroxide cured EPDM reference compounds with the same cross-linking density as a result of its lower molecular weight. The low molecular weight of EPM-g-MA is an intrinsic result of side-reactions taking place during the peroxide-initiated grafting process of MA onto EPM. The properties can be improved however, by using a more crystalline EPM-g-MA (with higher ethylene content). The crystalline BM cross-linked EPM-g-furan-cr showed an increased hardness, Young’s modulus, tensile strength and elongation at break and a decreased compression set with respect to its amorphous analogue. Furthermore, these properties were retained upon reprocessing for up to three cycles. The fact that the reprocessability of the compounds is better than that of the gum rubbers may also be a result of the (reversible) interaction between pendant furan groups and carbon black that act as additional physical cross-links but that are more easily opened during reprocessing than the DA cross-links.

8.5. References


Supporting information Chapter 8

Figure S8.1. UV absorption at 220 nm of hexane with different concentrations of BM before (closed symbols, solid line) and after mixing with carbon black for 24 h at room temperature and removing it via ultracentrifuge (open symbols, dashed line).

Table S8.1. Retained fraction of rubber after Soxtec extraction by weighing and according to TGA.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Bound rubber content</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Soxtec</td>
</tr>
<tr>
<td>EPM</td>
<td>0.17 ± 0.02</td>
</tr>
<tr>
<td>EPM-g-MA</td>
<td>0.26 ± 0.03</td>
</tr>
<tr>
<td>EPM-g-MA with BM</td>
<td>0.27 ± 0.03</td>
</tr>
<tr>
<td>EPM-g-furan</td>
<td>0.30 ± 0.02</td>
</tr>
<tr>
<td>EPM-g-furan with BM</td>
<td>0.40 ± 0.03</td>
</tr>
<tr>
<td>EPDM</td>
<td>0.47 ± 0.04</td>
</tr>
<tr>
<td>peroxide cured ENB-EPDM</td>
<td>0.98 ± 0.03</td>
</tr>
</tbody>
</table>
Figure S8.2. TGA results of the SOXTEX extraction residues of different rubber compounds with and without BM.

Figure S8.3. Retention of properties of BM cross-linked EPM-g-furan-cr upon up to three times reprocessing with respect to the original material.