The use of Diels-Alder chemistry for thermoreversible cross-linking of rubbers: the next step towards recycling of rubber products?

A proof of principle for the use of Diels Alder thermoreversible chemistry as cross-linking tool for rubber products is demonstrated. A commercial ethylene-propylene rubber grafted with maleic anhydride has been thermoreversibly cross-linked in two steps. The pendant anhydride moieties were first modified with furfurylamine to graft furan groups to the rubber backbone. Secondly, these pendant furans were cross-linked with a bismaleimide via a Diels-Alder coupling reaction. The material properties of the resulting Diels-Alder cross-linked rubbers are similar to a peroxide cured ethylene/propylene/diene rubber (EPDM) reference. The newly formed Diels-Alder cross-links break at elevated temperatures (>150 °C) via the retro-Diels-Alder reaction and can be reformed by thermal annealing at lower temperatures (50-70 °C). Reversibility of the system was proven with infrared spectroscopy and mechanical properties. Recyclability was also shown in a practical way, i.e. by cutting a cross-linked sample into small parts and compression molding them into new samples displaying comparable material properties, which is not possible for conventionally cross-linked rubbers. The physical properties of the resulting products are similar to sulphur- and peroxide cured EPDM references and superior compared to their non-cross-linked precursors.

2.1. Introduction

Ethylene/propylene/diene rubbers (EP(D)M) are one of the most used synthetic rubbers and can be found in automotive sealings, roofing and window profiles. Cross-linked EPDM compounds with reinforcing filler and plasticizer have relatively high moduli, strength and elasticity, and they are renowned for their good temperature, chemical, ozone and stress cracking resistance [1,2]. EPDM rubbers are commonly available, relatively low-cost and can easily be formulated into compounds with an additional set of useful properties such as outstanding ozone-, weather-, and temperature resistance [3,4]. Unfortunately, the excellent properties of these cross-linked rubber compounds are associated with the practical impossibility to reprocess these materials after their product life [5]. This is a critical issue, for example, in the automotive industry, as from January 2015 onwards new European legislation obliges the recycling of 95 wt% of all materials in used cars [6]. Meanwhile, billions of rubber tires (taken here merely as a paradigmatic example) are scrapped every year, the bulk of which (~50%) is incinerated for a low-grade and undesirable form of energy recovery that cannot be achieved without pollution [7,8]. The rest is dumped as landfill or stockpiled, placing yet another burden on the environment [9,10]. A long term solution is therefore required for the recycling of rubber products.

Sulfur vulcanization and peroxide curing are currently the main industrial cross-linking techniques in the rubber industry. These yield irreversible chemical cross-links, preventing melt reprocessing [4,9]. Considerable efforts have been devoted to the de-vulcanization of a variety of cross-linked rubbers [11-14]. For iso-based rubbers such as natural rubber and butyl rubber such reclaiming processes have been commercially practiced for decades [15-17]. Rubbers like EPDM with the unsaturations in the side-group are less reactive and therefore more difficult to recycle. Nevertheless, some workable reclaiming processes have been developed for these materials [18,19]. These processes combine thermal and mechanical treatment for selective cleavage of the sulfur cross-links. Unfortunately, they also cause a considerable amount of chain scission of the main polymer chain, which is detrimental for the performance of the recyclate [18,20]. For this reason, the amount of devulcanized material that can be reused in new products is limited to approximately 25% [18,19].

A more desirable way of recycling cross-linked rubbers would be using a ‘cradle to cradle’ approach that does neither involve an additional (chemical) processing step nor results in any degradation of the product after recycling. Such a material should behave similarly to permanently cross-linked rubbers at service conditions, while the reversibility of the cross-links would impart the processability and complete recyclability of a thermoplastic at high temperatures. A technical solution is found in the commercially produced thermoplastic elastomers and thermoplastic vulcanizates.
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[21-23]. Another approach to achieve recyclability is via rubber networks with reversible cross-links that respond to an external stimulus [24,25]. Although numerous external stimuli to control the degree of cross-linking can be imagined, the most feasible stimulus (also from the viewpoint of future industrial applications) is temperature. The formation of cross-links at relatively low service temperatures is required for good mechanical behavior, while their cleavage at high temperatures (similar to processing temperature of original non-cross-linked compound) allows for recycling of the material.

Generally, reversible cross-linking in polymeric systems can result from relatively weak interactions, such as ionic, hydrogen bonding or crystallinity [26]. Unfortunately, such rubbers cannot indefinitely hold stress without creep [27]. The use of stronger covalent cross-linking could result in enhanced mechanical performance. Some specific materials can be reversibly cross-linked by making use of so-called dynamic covalent networks via polycondensation reactions [28] or by reversible network topology freezing via transesterification reactions [27,29,30]. The disadvantage of these approaches is the necessity of designing and synthesizing new polymers rather than modifying existing rubbers that already have the desired properties.

Techniques to thermoreversibly cross-link rubbers involve hydrogen bonding, ionic interactions and covalent bonding such as via thermo-activated disulfide rearrangements [31,32]. Recently, thermoreversible cross-linking via Diels-Alder (DA) chemistry was developed [33-39]. DA chemistry can be applied to a broad range of polymers and represents a popular choice, especially since the DA reaction allows for relatively fast kinetics and mild reaction conditions [36,40-42]. Their low coupling and high decoupling temperatures make furan and maleimide excellent candidates for reversible polymer cross-linking [33,37-39,43-45]. Bis-maleimides and bis-furans have already been used as cross-linking agents with several furan- or maleimide-functionalized polymers, respectively [37,38,46-48]. Aim of the present work is to provide a proof-of-principle for the use of Diels-Alder chemistry as a thermoreversible cross-linking tool in a rubber product. The proposed approach (Scheme 2.1) is briefly discussed below.

The reactivity of saturated hydrocarbon elastomers, such as ethylene/propylene rubbers (EPM) has to be increased. A commercially relevant example that facilitates this is the peroxide-initiated free-radical grafting of maleic anhydride (MA) [33,49-54]. Thermoreversible cross-linking of such maleated EPM rubbers (EPM-g-MA) have been studied using hydrogen bonding, ionic interactions and covalent bonding [31,32]. A furan can be grafted onto such a maleated rubber by inserting furfurylamine (FFA) into the pendant anhydride to form an imide [55,56]. The furan moieties that are thus attached to the rubber backbone can then participate in
thermoreversible DA chemistry as an electron-rich diene [57,58]. The electron-poor bis-maleimide is a suitable dienophile for this cross-linking reaction [38,45,59]. To the best of our knowledge, thermoreversible cross-linking of industrial rubbers such as EPM via furan/maleimide Diels-Alder chemistry represents a novelty in the open literature (Scheme 2.1).

Scheme 2.1. Furan grafting and bis-maleimide cross-linking of industrial EPM-g-MA rubber.

2.2. Experimental

2.2.1. Materials
EPM (Keltan 3050, 50 wt% ethylene, $M_n = 50$ kg/mol, PDI = 2.0), an EPDM with a medium ethylidene (ENB-EPDM, Keltan 8550C, 53 wt% ethylene, 5.5 wt% ENB) and maleated EPM (EPM-g-MA, Keltan DE5005, 49 wt% ethylene, 2.1 wt% MA, $M_n = 50$ kg/mol, PDI = 2.0) were kindly provided by ARLANXEO Netherlands B.V. Furfurylamine (FFA, Sigma-Aldrich, ≥99%) was freshly distillated. Aliphatic bismaleimides (BM) were synthesized from di-dodecylamine (Sigma-Aldrich, >98%) and maleic acid anhydride (MA, Sigma-Aldrich, >99%) according to a reported procedure [60]. A ‘model’ DA adduct was used for characterization by $^1$H-NMR and the calibration of infrared (IR) and spectroscopy. It was synthesized by refluxing 2-octadecylsuccinic anhydride (2-ODSA, Sigma-Aldrich) and FFA in tetrahydrofuran and purified by recrystallization [33]. Bis(t-butylperoxy-i-propyl) benzene (Perkadox 14-40, AkzoNobel), Octadecyl-1-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate (99%), tetrahydrofuran (THF, >99.9%), decalin (98%) and acetone (>99.5%) were all bought from Sigma-Aldrich and used as peroxide curative, phenolic antioxidant and solvents, respectively.

2.2.2. Methods
2.2.2.1. Functionalization with furan
Prior to the reaction, EPM-g-MA was dried in a vacuum oven for one hour at 175 °C to convert any diacids into anhydrides [32]. Typically, 45.0 g EPM-g-MA rubber (9.6 mmol MA) was dissolved in 500 mL THF at room temperature. 2.8 g of freshly distillated FFA (28.9 mmol; 3.0 eq. based on MA content in EPM-g-MA) was then added to the 10 wt% rubber solution. The reaction mixture was stirred for 5 h in a
closed system at room temperature and then precipitated by pouring it slowly into a tenfold amount of acetone (5 L) under mechanical stirring, yielding the polymer product as white threads. The product (EPM-g-furan) was dried to constant weight in an oven at 35 °C. Subsequently, the now slightly yellowish product was briefly compression molded at 175 °C and 100 bar to ensure the conversion of all intermediate maleimide acid products to imide products (Figure S2.1).

2.2.2.2. **Bismaleimide cross-linking and reprocessing**

Typically, 40.0 g of EPM-g-furan rubber (8.6 mmol furan content) and 1000 ppm phenolic anti-oxidant (~40 mg) were dissolved in 500 mL THF at room temperature. 1.48 g BM (4.3 mmol, 0.5 eq. based on furan content in EPM-g-furan) was added to the 10 wt% solution. The reaction mixture was stirred until it was homogeneous and the solvent was evaporated at 50 °C. The product was compression molded for 30 min at 175 °C and 100 bar. The resulting plaque or bars were thermally annealed for three days at 50 °C. 'Reprocessed' sample bars were prepared by cutting or grinding these bars into small pieces (± 50 mm³) and compression molding them into new coherent samples with the same dimensions under the same conditions.

2.2.2.3. **Peroxide and sulfur cross-linking**

ENB-EPDM was homogenized in a Brabender (W 30 EHT) at 50 rpm and 70% fill factor. 1.25 phr of peroxide or 1.88 phr of a standard (80% pure) sulfur system was added and mixed with the rubber for 3 min at 70 °C. The resulting compound was vulcanized by compression moulding for 30 min at 175 °C and 100 bar.

2.2.3. **Characterization**

2.2.3.1. **Chemical analysis**

The rubber samples were analyzed by Fourier transform infrared (FT-IR) using a Perkin-Elmer Spectrum 2000 with a diamond crystal for ATR. 1.0 mm thick rubber films were compression molded for 10 min at 150°C and 100 bar and measured in a KBr tablet holder (transmission). Ground samples and powders were measured using an ATR setup of Greasy Specac (reflection). Measurements were performed over a spectral range from 4000 to 600 cm⁻¹ at a resolution of 4 cm⁻¹, averaging 32 scans. Deconvolution (R² > 0.95) was used to integrate the areas under the individual FT-IR peaks. The methyl rocking vibration (ν\text{CH}_3 = 723 cm⁻¹), originating from the EPM backbone, remains unchanged upon modification and was used as an internal reference. A calibration curve of mixtures of EPM-g-MA and EPM-g-furan showed that the EPM-g-MA content was directly proportional (R² = 0.97) to the decrease in absorbance of the C=O symmetrical stretch vibration of the anhydride groups (ν\text{CO} = 1856 cm⁻¹). The difference in relative peak areas was used to calculate the reaction conversion from EPM-g-MA to EPM-g-furan.
Likewise, a calibration curve was constructed to determine the conversion of EPM-g-furan from FT-IR analysis. Mixing various amounts of the ‘model’ Diels-Alder adduct with EPG-g-MA resulted in a linear increase of the in-plane bending vibration of the DA adduct ($\delta^{ip}_{DAring} = 1190 \text{ cm}^{-1}$) [34,57]. As this peak has some overlap with neighboring rubber peaks, the relative decrease in the C-O-C symmetric stretch vibration of the furan rings ($\bar{\nu}^{s}_{COC} = 1013 \text{ cm}^{-1}$) was used to calculate the conversion upon appearance of $\delta^{ip}_{DAring}, \delta^{ip}_{CH_3}$ was used as an internal reference. The resulting conversions were used to calculate the amount of formed DA adduct.

After thorough washing and drying, Elemental Analysis (EA) for N, C and H was performed on the rubber samples with a Euro EA elemental analyzer. The amount of N increases upon modification with furfurylamine and further increases upon subsequent cross-linking with the bis-maleimide. The molar contents were derived from the measured mass percentages. The molar N content in EPM-g-furan is equal to that of the furan groups (Scheme 2.1). The molar ratio of MA-grafted monomer to the non-grafted EPM monomers in the EPM-g-MA precursor ($7.69 \times 10^{-3}$) was compared with the molar ratio N:EPM of the EPM-g-furan samples to determine the conversion.

Since the molar amount of MA grafted onto the EPM-g-MA is lower (0.72 mol% MA per monomer) than the sensitivity of the NMR apparatus (> 1%), a model system with a shorter aliphatic chain with respect to the MA group (2-ODSA) was used to perform a more accurate $^1$H-NMR analysis. 2-ODSA was modified with FFA under the same conditions as the EPM-g-MA and heated to 150 °C for 15 min. The subsequent formation of the succinic anhydride was determined from EA, mass spectrometry, $^1$H and $^{13}$C-NMR.

Mass spectra were recorded on a LTQ Orbitrap XL spectrometer (ThermoFisher Scientific) with ESI or APCI ionization in positive mode. HRMS-ESI$^+$ (m/z): $\{M+H3O\}^+$ calculated for the amide acid (C$_{27}$H$_{47}$NO$_4$.H$_3$O$^+$), 468.37; found, 468.38. $\{M+H3O\}^+$ calculated for the succinimide (C$_{27}$H$_{46}$NO$_3$.H$_3$O$^+$), 450.36; found, 450.36. $\{M+H\}^+$ calculated for the succinimide (C$_{27}$H$_{46}$NO$_3^+$), 432.35; found, 432.35. HRMS-APCI$^+$ $\{M+H\}^+$ calculated for the amide acid (C$_{27}$H$_{48}$NO$_4^+$), 450.36; found, 450.36. $\{M+H\}^+$ calculated for the succinimide (C$_{27}$H$_{46}$NO$_3^+$), 432.35; found, 432.35.

$^1$H-NMR spectra were recorded on a Varian Mercury Plus 400 MHz using DMSO-d$_6$ as a solvent. $^1$H-NMR spectra of samples at elevated temperature were recorded on a Varian Mercury Plus 500 MHz using DMSO-d$_6$ as a solvent. The assignment of the peaks was performed using the NMRPredict Desktop software of MestreNova. Chemical shifts are reported in ppm with the resonance solvent signal as the internal reference (DMSO, d$_6$: $\delta = 2.50$ ppm, CDCl$_3$: $\delta = 7.26$ ppm for $^1$H and CDCl$_3$: $\delta = 77.16$ ppm for $^{13}$C). Data are reported as follows: chemical shifts, multiplicity, coupling
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constants (Hz), relative integration and location. $^1$H-NMR (400 MHz, CDCl$_3$): $\delta = 7.32$ (s, 1H, CHO-fur), 6.30 (d, $J = 5$ Hz, 2H, fur), 4.66 (s, 2H, CH$_2$N), 2.92-2.75 (m, 2H, CH$_2$CO), 2.39 (d, $J = 14$ Hz, 1H, CHCO), 1.92 (m, 2H, CH$_2$CH), 1.53 (s, 1H, CHO-fur), 1.36 (m, 2H, CH$_2$), 1.22 (br s, 28H, CH$_2$), 0.85 (t, $J = 7$ Hz, 3H, CH$_3$) ppm. $^{13}$C-NMR (400 MHz, CDCl$_3$): $\delta = 183.6$ (C=O), 178.9 (C=O), 142.4 (C=O, fur), 134.9 (CHO-fur), 110.4 (CHO-fur), 108.9 (CH=CHO, fur), 39.9 (CH=CO), 35.0 (CH$_2$-CO), 31.9 (CH$_2$-N), 31.2 (CH$_2$-CH), 29.7 - 22.7 (16CH$_2$), 14.1 (CH$_3$) ppm.

The modified 2-ODSA was cross-linked with BM in deuterated DMSO directly in a NMR tube. The formation of the DA-adduct was complete for this model system as can be seen from the complete disappearing of the representative BM peak at 7.00 ppm and the appearing of the corresponding new peaks at 3.66 and 3.82 ppm (Figure 2.1).

Dodecyl bismaleimide: $^1$H-NMR (400 MHz, DMSO-d$_6$): $\delta = 7.00$ (s, 4H, C=C), 3.37 (t, $J = 7$ Hz, 4H, CH$_2$N), 1.46 (t, $J = 14$ Hz, 4H, CH$_2$CH$_2$N), 1.23 (br s, 16H, CH$_2$) ppm.

Diels-Alder adduct: $^1$H-NMR (400 MHz, DMSO-D$_6$): $\delta = 7.71$ (s, 1H), 6.31 (d, $J = 1$ Hz, 1H, 2 Hz), 6.19 (dd, 3 Hz and 20 Hz, 1H), 3.82 (dd, 5 Hz and 4 Hz, 1H), 3.66 (dd, 14 Hz and 11 Hz, 1H) ppm

![Figure 2.1](image_url). $^1$H-NMR spectra of 2-ODSA-g-furan and BM directly after mixing and emphasis on the changes in peak configuration of the same mixture after keeping it at 50 °C for 1 h.
2.2.3.2. Cross-link density determination

The cross-link density ([XLD] \textsubscript{s} in mol/mL) was determined from swelling experiments in decalin [5]. Approximately 500 mg of dried, cross-linked sample was weighed into a 20 mL vial and immersed in 15 mL decalin until equilibrium swelling (3 days) was reached (W\textsubscript{1}). Subsequently, the swollen samples were dried in a vacuum oven at 80 °C until a constant weight was reached (W\textsubscript{2}). The weights of the swollen and dried samples were used to calculate the apparent cross-link density using the Flory-Rehner equation (Eq. 2.1) [61,62].

\[
[XLD] \textsubscript{s} = \frac{\ln(1-V_R)+V_R+\chi V_R^2}{2V_S(0.5V_R-V_R^{1/3})} \text{ with } V_R = \frac{W_2}{W_2+(W_1-W_2) \cdot \rho_{EPDM-g-furan} / \rho_{decalin}}
\]

- \(V_R\) Volume fraction of rubber in swollen sample.
- \(V_S\) Molar volume of solvent (decalin: 154 mL/mol at room temperature).
- \(\chi\) Flory-Huggins interaction parameter (decalin-EPDM: 0.121 + 0.278\(V_R\)) [63].
- \(\rho\) Density (860 kg/m\(^3\) for EPM-g-furan and 896 kg/m\(^3\) for decalin)

Another way to determine the cross-link density ([XLD] \textsubscript{t} in mol/mL) is from the results of a tensile test. The resulting stress-strain curve contains the data required for the Mooney-Rilvin equation (Eq. 2.2) [64,65].

\[
\sigma = 2 \left( C_1 + \frac{C_2}{\Lambda} \right) \left( \Lambda - \frac{1}{\Lambda^2} \right) \text{ with } \Lambda = 1 + X \varepsilon
\]

- \(\sigma\) True stress measured in the strained state of the rubber
- \(C_1, C_2\) Characteristic cross-linked rubber parameters
- \(\Lambda\) Extension ratio
- \(X\) Strain amplification factor defined as \(\sigma E_0 / \epsilon \) (X=1 for rubber gums)
- \(E_0\) Modulus of the rubber without filler \(\text{ (E_0=E for gums)}\)

A limitation of the Mooney-Rilvin equation is its invalidity at large strains, affording accurate determination of the cross-link density to only hold in the tensile elongation range of 30-150% [66]. Using the values for stress and strain of a rubber obtained with tensile testing within this range a linear proportionality between \(\frac{\sigma}{2(a-a^{-2})} vs \frac{1}{a}\) is obtained from which parameters \(C_1\) and \(C_2\) can be determined. Based on kinetic theory the, cross-link density can subsequently be determined (Eq. 2.3) [67].

\[
[XLD] \textsubscript{t} = \frac{2C_1}{k_B T}
\]

- \(k_B\) Boltzmann constant
- \(T\) Temperature

2.2.3.3. Thermal and mechanical analysis

Thermogravimetric analysis (TGA) was performed in a Mettler-Toledo analyzer (TGA/SDTA851e) using an air flow 100 mL/min [68]. 10 mg of sample was loaded in a
70 µL α-Al₂O₃ crucible and the temperature was increased from 30 to 900 °C at 10 °C/min. Blank curve correction using an empty crucible was performed.

The samples for Dynamic Mechanical Thermal Analysis (DMTA) and tensile testing were prepared by compression molding 450 mg rubber product into rectangular bars of 4.5 cm long, 5 mm wide and 1 mm thick. The DMTA analysis of the bars was conducted on a Rheometrics Scientific Solid Analyzer (RSA II) in air using a temperature ramp experiment in the ‘film fiber’ mode. A clamp length of 23 mm, an oscillation frequency of 1 Hz and a strain of 0.7% were applied. Samples were heated and cooled in cycles from 20 °C to 150 °C or 180 °C and back, using heating and cooling rates rate of 2 °C/min and 0.05 °C/min, respectively.

Tensile tests were performed on an Instron 5565 with a clamp length of 15 mm according to the ASTM D 4112 standard for ‘Vulcanized and thermo-elastic tension’. A strain rate of 500 ± 50 mm/min was applied. For each measurement, 10 samples were tested and the two outliers with the highest and the lowest values were excluded for calculating the result average. For each set of samples, one median graph was selected as a characteristic for the entire series. Hardness Shore A was measured using a Bareiss Durometer according to the ASTM D 2240 standard. Samples with a thickness of 2 ± 0.1 mm were used for these tests. Average values were obtained from the average ± standard deviation of 10 measurements. Compression set tests were performed at room temperature for 70 h on an Instron 4301-H0135 model and relaxed for 30 min at 50 °C. The tests were performed according to the ASTM D 931 standard for ‘Rubber property – compression set’. Each measurement was performed in duplo, using cylindrical samples with a thickness of 6 ± 0.1 mm and a diameter of 13 ± 0.1 mm.

2.3. Results and discussion

2.3.1. Chemical Analysis
2.3.1.1. Modification and cross-linking
The preparatory heating of EPM-g-MA (spectra not shown) clearly resulted in the complete conversion of the hydrolyzed di-acids into anhydride rings as the typical acid peak ($\nu_{CO} = 1710$ cm$^{-1}$) was absent and the characteristic anhydride peak ($\nu_{CO}^{as} = 1856$ cm$^{-1}$) was present.

The modification of these anhydrides into imide moieties with pendant furan groups and the subsequent cross-linking of this EPM-g-furan rubber with bis-maleimide were followed by transmission FT-IR (Figure 2.2). The most illustrative result for the conversion are the nearly complete disappearance of $\nu_{CO}^{as}$ at 1856 cm$^{-1}$, the appearance of $\nu_{CO}^{s}$ at 1710 cm$^{-1}$ and the appearance of C-N stretching vibration of the maleimide
Furthermore, the splitting of the C-C aliphatic stretching peak ($\tilde{\nu}_{\text{CC}} = 1050 \text{ cm}^{-1}$) into the COC furan peaks ($\tilde{\nu}_{\text{COC}}^{\text{as}} = 1073 \text{ cm}^{-1}$ and $\tilde{\nu}_{\text{COC}}^{\text{s}} = 1013 \text{ cm}^{-1}$), the appearance of the C=C stretching vibration of the furan ring ($\tilde{\nu}_{\text{CC}} = 1504 \text{ cm}^{-1}$) and of the deformation vibration band of the furan ring at 599 cm$^{-1}$ clearly indicate the presence of furan groups on the polymer, after precipitation and washing in acetone [34,57]. The furan ring stretching peaks at 1436 and 1345 cm$^{-1}$ could not be identified as they were hidden by the large overlapping CH$_2$-vibrations of the rubber backbone [34]. The absence of a peak at 1530 cm$^{-1}$ strongly indicates that any remaining amide-acid has been irreversibly converted into closed imide rings by the heating treatment after the reaction [31,69]. The incorporation of BM results in the appearance of $\delta_{\text{Daring}}^{\text{ip}}$ at 1190 cm$^{-1}$ and of the characteristic succinimide bands ($\tilde{\nu}_{\text{CNC}}^{\text{s}} = 1385 \text{ cm}^{-1}$, $\delta_{\text{HNC}}^{\text{ip}} = 1311 \text{ cm}^{-1}$ and $\delta_{\text{OCN}}^{\text{as,oop}} = 620 \text{ cm}^{-1}$) [70,71]. Meanwhile $\tilde{\nu}_{\text{COC}}^{\text{s}}$ of the furan-related absorptions decreases upon cross-linking. The $\tilde{\nu}_{\text{CO}}$ carbonyl band is also enhanced by a second absorption around 1770 cm$^{-1}$, attributed to the succinimide ring resulting from the cycloaddition [58].

**Figure 2.2.** FT-IR absorption spectra of A: EPM-g-MA and modified EPM-g-furan and B: of the EPM-g-furan precursor and the Diels-Alder cross-linked EPM-g-furan.
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The FT-IR and EA results were used to calculate the number of modified and cross-linked groups on the rubber chain as a measure for the cross-link density (Table 2.1). The EA results are in good agreement with those from FT-IR deconvolution.

<table>
<thead>
<tr>
<th>Table 2.1. Reaction conversion according to Elemental Analysis and FT-IR.</th>
<th>Elements (wt%)</th>
<th>Conversion (%)</th>
<th>Average no functional groups per chain</th>
</tr>
</thead>
<tbody>
<tr>
<td>N, C, H*</td>
<td>EA; FT-IR</td>
<td>EA, FT-IR</td>
<td></td>
</tr>
<tr>
<td>EPM-g-MA</td>
<td>&lt;0.01, 84.7, 14.3</td>
<td>-</td>
<td>11; 11†</td>
</tr>
<tr>
<td>EPM-g-furan</td>
<td>0.3, 84.8, 14.2</td>
<td>93; 96</td>
<td>10; 10</td>
</tr>
<tr>
<td>BM cross-linked EPM-g-furan</td>
<td>0.4, 84.2, 14.0</td>
<td>80; 72</td>
<td>9; 8</td>
</tr>
</tbody>
</table>

* The remainder of the weight is assumed to consist of oxygen.
† The initial number of functional groups is derived from the molecular weight of the rubber (50 kg/mol) and its weight percentage of MA (2.1 wt%).

According to the calculations, the product has 8 cross-links per rubber chain of approximately 50 kg/mol. However, EPM-g-MA rubber is known to form polar clusters enriched with anhydride groups [52]. If the formed cross-links would concentrate in these clusters, the average amount of cross-links per rubber chain would not be a good estimate for the cross-link density. The density of such cross-linked domains would be smaller and the chance of intramolecular cross-linking within the same polymer chain would increase. These two different scenarios (uniform and non-uniform distribution of cross-linking bonds) can be conveniently distinguished by determining the cross-link density from tensile tests and swelling experiments (Figure 2.3) [72].

**Figure 2.3.** Cross-link densities as determined from swell tests using Flory-Rehner and tensile tests using Mooney-Rivlin.

The apparent cross-link density of 2.07 \( \times 10^{-4} \) mol/mL for the BM cross-linked EPM-g-furan corresponds to roughly 10 cross-links per chain. This value is in the same order of magnitude as the number of functional groups per chain determined from chemical
analysis (Table 2.1). This suggests that there is a random and uniform distribution of the cross-links throughout the material. Furthermore, this value corresponds to the typical cross-link densities of sulfur- and peroxide cured EPDM-gums (1·5·10^{-4} mol/mL) that are found in literature [73,74]. Such values are characteristic for loosely cross-linked, rubbery networks. The results from both the swell test and tensile tests confirm the similarity in cross-link density for the initial and reprocessed BM cross-linked EPM-g-furan. In addition to that, this cross-link density of the BM cross-linked samples seems to be similar to the sulphur- and peroxide cured EPDM samples that are used as a non-reversibly cross-linked reference. The small discrepancy between the values determined by these two methods is not surprising when one makes allowance for the fact that the mechanical test is also related to the number of physical “trapped” entanglements (not measured in a solvent) in the system [75,76].

2.3.1.2. De-cross-linking by retro-Diels-Alder

The de-cross-linking of the BM cross-linked EPM-g-furan product was followed by transmission FT-IR (Figure 2.4). Some characteristic furan peaks such as \(\nu_{\text{CC}}^s\) and \(\nu_{\text{COC}}^s\) at respectively 1504 and 1013 cm\(^{-1}\) decrease upon cross-linking and to increase after de-cross-linking. The \(\nu_{\text{COC}}^s\) peak for example, is clearly visible in the spectrum of EPM-g-furan. It can be seen to decrease upon the addition of bis-maleimide cross-linking agent (cross-linked EPM-g-furan). Directly after compression moulding the rubber sample at 150 °C, this peak increases again as the furan groups are decoupled (de-cross-linked EPM-g-furan). After one week of thermal annealing of the sample at 50 °C, the peak disappears again (re-cross-linked EPM-g-furan). This phenomenon indicates cross-linking and de-cross-linking via a reversible DA reaction between the grafted furan groups and the added bis-maleimide cross-linking agents [77].

![Figure 2.4. FT-IR absorption spectra of EPM-g-furan and DA (de/re-)cross-linked EPM-g-furan.](image-url)
Solubility tests were used to see the effects of cross-linking and de-cross-linking (Figure 2.5). EPM-g-furan is soluble in decalin (5 wt%) at room temperature. The same material cross-linked with BM is clearly insoluble under the same conditions. The thermoreversibility of the cross-linking reaction was shown by dissolving the product during 1 h of heating to 175 °C.

Figure 2.5. Non-cross-linked, BM cross-linked and de-cross-linked EPM-g-furan in decalin.

2.3.2. Mechanical testing
Several typical material properties of the modified and cross-linked rubbers were determined to get a ‘fingerprint’ of the material. Ideally, the thermoreversibly cross-linked material should have mechanical properties similar to irreversibly cross-linked rubbers with the same cross-link density. Additionally, it should be possible to grind or cut the used thermoreversibly cross-linked material, break the existing cross-links by increasing the temperature and to compression mold the reprocessed material with the same material properties. It is evident that when an EPDM rubber is reversibly sulphur- or peroxide cured, remolding the cut pieces under the same conditions does not yield a coherent sample (Figure 2.6).

Figure 2.6. Sample bars of rubber and (re-)cross-linked rubber used for mechanical testing.

2.3.2.1. Dynamic Mechanical Thermal Analysis
The temperature response of the rubber’s mechanical behavior was tested by DMTA. The moduli of the samples were measured, while heating and cooling at a controlled
rate for up to eight cycles. Temperature cycles from 20 °C to 150 °C were performed on all samples (Figure 2.7A). The system’s slow kinetics however required a cooling rate of 0.05 °C/min and a maximum temperature of 180°C to observe a significant temperature response (Figure 2.7B).

Figure 2.7. DMTA cycles from 20 °C to 150 °C A: at 2 °C/min for EPM-g-MA, EPM-g-furan, BM cross-linked EPM-g-furan and the same cross-linked sample after reprocessing and B: at 0.05 °C/min of the cross-linked bars directly after compression moulding and thermal annealing.

At a heating and cooling rate of 2 °C/min, the loss modulus (E") appears to remain constant for nearly all measurements (not shown). The storage modulus (E’) therefore largely determines the response of the phase angle and therewith the elasticity of the rubber (Figure 2.7A). All depicted heating curves show a decrease in storage modulus typical for such non-cross-linked, amorphous rubbers [4]. This makes sense for the non-cross-linked, amorphous EPM-g-MA and EPM-g-furan, which soften significantly upon heating. The related loss of form and elasticity make any further measurements on EPM-g-MA at temperatures above 100 °C impossible. The non-cross-linked EPM-g- furan samples did not enter the flow regime up to 150 °C and could be returned to their original shape and properties upon cooling at the same rate.

The cross-linked samples show higher moduli with only a modest decrease upon heating. Heating curves of covalently cross-linked rubbers typically show stable modulus plateaus with a slight increase with temperature [3,78]. Softening at elevated temperatures for the thermoreversibly cross-linked rubbers is contributed to de-cross-linking via retro-DA reactions [34,57,79]. The modulus of the rubber networks can be recovered completely to their original value (93% ± 10%) after cooling. Up to eight consecutive heating and cooling cycles were performed without any negligible loss in storage and loss modulus. This indicates that no (or very little) degradation or side-reactions take place when heating or cooling in the temperature range of 20 to 150 °C. This was confirmed as the products do not show any weight loss up to 300 °C according to TGA measurements. Likewise, the storage and loss moduli of the cross-linked samples that were cut to pieces and compression molded again were similar.
(96% ± 10%) to that of the originally cross-linked samples. This indicates that recycling of these materials does not influence their material behavior significantly.

A very low heating rate of 0.05 °C/min was applied to identify the softening temperature of these various samples (Figure 2.7B). The non-cross-linked EPM-g-furan samples (red) simply “melt” with increasing temperature. Meanwhile, the cross-linked material that was thermally annealed at 50 °C for 5 days (black) retains its high modulus upon heating up to approximately 150 °C, where it starts decreasing steeply. This strong drop in the storage modulus signifies the softening of the material, which is contributed to de-cross-linking via the retro-DA reaction. The de-cross-linked sample was re-measured directly without prior thermal annealing (blue). Its modulus starts to increase above 80 °C. This increase is contributed to the DA cross-linking reaction that is more efficient at higher temperatures [33]. Above 150°C, the modulus drops more steeply and the material softens again as the retro-DA reaction is favored over the DA cross-linking reaction at higher temperatures [33]. Since the DMTA shows flow ≤ 150 °C, mixing and shaping of these thermoreversibly cross-linked rubbers can be easily achieved with the standard mixing and processing equipment used for traditionally vulcanized rubber compounds. On the other hand, this implies that the application temperature of these thermoreversibly cross-linked materials is factually limited to 100 °C, where the modulus decrease is still within 10% of the original value (Figure 2.7B). It must be stressed however that a more exact temperature window for application should be established when using the rubber gum in combination with the fillers normally added to rubber compounds.

The fact that a temperature increase of 0.05 °C/min was required to observe the increase in modulus demonstrates that the DA reaction kinetics in this system are much slower than that of other systems described in literature [33,40,43]. These slow reaction kinetics are preliminarily attributed to the low concentration of grafted furan groups and bis-maleimide cross-linkers, the high viscosity in the rubber bulk and the nature (chemical structure) of the rubber matrix. The low degree of functionalization, combined with the limited mobility in the polymer matrix, make it difficult for the diene and dienophiles to approach each other.

2.3.2.2. Tensile testing

Tensile tests were performed on the various EPM samples. The median stress-strain curves show that the thermoreversibly, BM cross-linked rubber, before and after reprocessing, yields at higher stresses and lower strains than their non-cross-linked EPM-g-MA and EPM-g-furan precursors (Figure 2.8A). This distinction is illustrative for the different behaviors of cross-linked and non-cross-linked rubbers as is illustrated by the peroxide and sulfur cured EPDM samples [80,81]. The tensile strength, the Young’s modulus and the elongation at break were determined from these tensile tests and averaged over 8 measurements (Figure 2.8B).
Figure 2.8. Tensile test results for EPM-g-MA (1), EPM-g-furan (2), BM cross-linked EPM-g-furan (3) and reprocessed, BM cross-linked EPM-g-furan (4) together with sulfur (5) and peroxide (6) cured EPDM. A: Median stress-stain graphs and B: the corresponding Young’s modulus, tensile strength and elongation at break.

Firstly, a difference in elongation at break between the non-cross-linked EPM-g-MA and the modified EPM-g-furan is observed (Figure 8B). This difference could be explained by synergetic effects of the pendant, conjugated furan groups [82]. Their increased rigidity, π-stacking stabilization and a very low degree of radical cross-linking between the furans could be enough to decrease the rubber’s elasticity to a certain extent. Secondly, the cross-linked samples show significantly higher tensile moduli and lower elongation at break values compared to their non-cross-linked precursors. This is typical as high tensile moduli and low elongation are indicative for rubbers with high cross-linking densities [3,83]. Thirdly, it appears that the recycled cross-linked rubbers retain these characteristic properties. This indicates that these cross-linked rubbers can be reshaped or recycled regardless of their high modulus and low elongation, which are characteristic features for thermosets. Lastly, the peroxide and sulfur cured samples have slightly higher Young’s moduli than the BM cross-linked ones and are therefore slightly more cross-linked [72,84]. Nevertheless, important mechanical properties such as the tensile strength and elongation at break of the BM cross-linked samples are at least as good as those of the peroxide and sulfur cured samples.

2.3.2.3. Hardness tests and compression set
The hardness and compression set at 23 °C are also characteristic material properties for rubbers (Figure 2.9). When going from the EPM-g-MA and EPM-g-furan precursors to the BM cross-linked EPM-g-furan, the hardness increases and the compression set decreases. This clearly indicates the conversion of a viscous polymer into an elastic network that occurs upon cross-linking. The hardness and compression set of reprocessed samples of respectively 44 Shore A and 5% are comparable to those of the original BM cross-linked samples. The hardness and compression set of the sulfur
and peroxide cross-linked EPDM rubbers were 60 and 61 Shore A and 5% and 8% respectively. Although these irreversibly cross-linked samples have higher hardness values, indicating a higher cross-link density, their compression set is slightly inferior to the BM cross-linked samples.

![Figure 2.9. Hardness and compression set results for non-cross-linked EPM-g-MA and EPM-g-furan, BM cross-linked EPM-g-furan and irreversibly peroxide and sulfur cured EPDM rubbers.](image)

### 2.4. Conclusions

A commercial EPM-g-MA rubber was thermoreversibly cross-linked in a simple two-step approach. The maleated rubber was first modified with furfurylamine to graft furan groups onto the rubber backbone. The resulting pendant furans show reactivity as Diels-Alder dienes. An aliphatic bis-maleimide was used as cross-linking agent, resulting in a thermoreversible bridge between two furan moieties. Both reactions were successful with good conversion according to infrared spectroscopy, elemental analysis, swelling and solubility tests.

Reversibility of the cross-linking was proven by infrared spectroscopy, solubility tests and DMTA measurements. It was demonstrated in a practical way by cutting cross-linked product into small pieces and compression moulding these into new coherent samples with the same properties. This was shown to be impossible for conventional sulfur and peroxide cross-linked EPDM rubbers. The kinetics of the cross-linking and de-cross-linking reactions was preliminarily investigated with DMTA measurements. The DA chemistry provides the cross-linked rubber product with an application window of at least 20 °C to 150 °C. The mechanical properties and the temperature response of the resulting cross-linked products are superior compared to their non-cross-linked precursors and similar to that of covalently cross-linked rubber.
The presented results provide a new route for the (reversible) cross-linking of (EPM) rubbers via a (retro)Diels-Alder reaction, which complements the toolbox of rubber recycling. They pave the way towards the application of such cross-linking strategies (and the recyclability these might entail) for a variety of rubber products.

2.5. References

Thermoreversible cross-linking of EPM

Supplementary information Chapter 2

**Figure S2.1.** ATR-IR spectra of the conversion of di-carboxylic acid into anhydride, the formation of the amide acid upon reaction with a primary amine and its (irreversible) conversion into succinimide upon heating.

**Figure S2.2.** NMR spectra of 2-ODSA-g-furan and BM after keeping it at 50°C for 1h (zoomed-in HSQC spectrum of the peaks corresponding to the Diels-Alder adduct) and after heating it to 150°C for 30 minutes directly before measuring.