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**Influence of the chemical structure of cross-linking agents on properties of thermally reversible networks**

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**Abstract:** It is well-known that the properties of cross-linked rubbers are strongly affected by the cross-link density. In this work it is shown that for thermoreversibly cross-linked elastomers, the type and length of the cross-linker also have a significant effect. A homologous series of diamine and bismaleimide cross-linkers was used to cross-link maleic-anhydride-grafted EPM irreversibly and furan-modified EPM thermoreversibly, respectively. Bismaleimide cross-linkers with a polarity close to that of EPM and a relatively low melting point have a better solubility in the rubber matrix, which results in higher chemical conversion and, thus, higher cross-link densities at the same molar amount of cross-linker. Samples cross-linked with different spacers (aromatic and aliphatic spacers of different lengths) were compared at the same cross-link density to interpret the effects on the material properties. The rigid character of the short aliphatic and the aromatic cross-linkers accounts for the observed increase in hardness, Young’s modulus and tensile strength with respect to the longer, more flexible aliphatic cross-linkers. In conclusion, the structure of the cross-linking agent can be considered as an alternative variable in tuning the rubber properties, especially for thermoreversibly cross-linked rubber.

**Keywords:** cross-linking; cross-linker; elastomer; material properties; POC-16; rubber; structure-property; thermoreversible.

**Introduction**

Cross-linked elastomers are defined as polymeric networks that are capable of absorbing large deformations in a reversible manner. In the rubber industry elastomers are usually cross-linked to improve and engineer the physical and chemical properties of the rubber end-products [1–3]. The cross-links prevent flow and provide the rubber products with a high degree of elasticity and toughness even far above their glass-transition temperature. Typical cross-linked rubber products are tires, seals, roofing foil and cable...
and wire insulation. The type of elastomer, the cross-linking chemistry, the compounding ingredients, such as filler and plasticizer, and the cross-linking technology are some of the factors to consider when designing rubber compounds for a specific application [4–6]. The cross-link density is considered one of the main variables, which significantly influence the material properties of the rubber end-products [7–9].

At this moment, the two most commonly used methods to cross-link elastomers are sulfur vulcanization and peroxide curing [2]. The major drawback of these methods is that the formed cross-links are irreversible and prevent reprocessing of production scrap and rubber products after use. As a result, most rubber products end up as down-graded products, at a landfill or in an incinerator [10, 11]. For some unsaturated, sulfur-vulcanized rubbers a certain extent of devulcanization can be achieved [10, 12, 13]. Unfortunately, such devulcanization processes are less effective for rubbers with a low degree of unsaturation in their side groups, such as ethylene/propylene/diene rubber (EPDM) [14]. Although the low level of unsaturation results in excellent heat, weathering, oxidation and ozone resistance, it also makes EPDM less susceptible to sulfur vulcanization and subsequent devulcanization [6]. Peroxide curing does not require unsaturation because of its free-radical reaction mechanism, making it useful for the cross-linking of fully saturated polymers, such as EPM rubber. However, peroxide-cured rubbers cannot be de-cross-linked at all [3].

For rubbers with saturated backbones, such as EPM, a certain degree of functionality can be introduced to make them more reactive [15]. An example is the free-radical grafting of maleic anhydride (MA) on the rubber backbone, which yields a more reactive, maleated rubber (EPM-g-MA) [16–18]. Such functionalized elastomers are more susceptible to a broader array of different cross-linking techniques, including thermoreversible cross-linking [11]. Thermoreversible cross-linking of chemically modified elastomers such as EPM-g-MA has been studied before [19–21]. An interesting method is the thermoreversible, covalent cross-linking of polymers containing pendant furan groups with bismaleimide (BM) functionalities via the reversible Diels-Alder (DA) reaction [22–25]. EPM-g-MA can be thermoreversibly cross-linked using DA chemistry after incorporating furan functionalities [20, 26, 27] and coupling the electron-rich furan dienes [28] with the electron-poor BM [29–31].

A limitation in applying this approach for EPM-g-MA rubber is the low amount of MA functional groups that can be grafted on the EPM rubber due to the low solubility of polar MA in EPM in apolar EPM rubber and the competition with chain degradation [32]. Cross-linking a maleated EPM (containing 2 wt% MA) with BM yielded a maximum cross-link density of 2 \times 10^{-4} \text{ mol/mL}, which limits the flexibility and applicability of the system [33]. However, a variation in the chemical structure of the spacer between the two maleimide groups of the BM cross-linking agent in terms of length and flexibility could also influence the material properties [34, 35]. There is a great variety in BM cross-linking agents, either commercially available or synthesizable from their respective diamines [36–38]. A benefit of such an approach is that a comparison can be made with the irreversible cross-linking of EPM-g-MA with the diamine precursors (Scheme 1).

Cross-links are usually simplified on a macromolecular scale as simple nodes and the details of cross-link structure are usually disregarded. Still, the effect of the cross-linker spacer that connects the polymer chains has been studied for both sulfur and peroxide curing [39–42]. Vulcanization with sulfur results in a distribution of monosulfidic, disulfidic and polysulfidic cross-links which is difficult to control, but known to affect the dynamic properties and heat resistance of sulfur-vulcanized rubber [7, 43]. Peroxide curing results in random carbon-carbon cross-links. Additional cross-linking can be achieved using multifunctional co-agents [39, 40]. Unfortunately, these conventional cross-linking systems do not truly allow for a systematic variation of the cross-link spacer and a subsequent study of the effect on the properties [4].

In this study the effects of the spacer of diamine and BM cross-linking agents and the amount of cross-linker on the material properties of irreversibly and thermoreversibly cross-linked EPM rubber is systematically investigated. The homologous series of diamines and BM used in this study includes cross-linkers with aromatic and aliphatic spacers of different lengths (Scheme 1). By comparing the samples at the same cross-link density, the effect of the variation of the spacer of the different cross-linking agents on the chemical reactivity and properties of the cross-linked rubber can be interpreted separately.
Scheme 1: Reaction overview of irreversible cross-linking of EPM-g-MA with diamines, modification of EPM-g-MA with furfurylamine to EPM-g-furan and thermoreversible cross-linking of EPM-g-furan with bismaleimides.

Experimental

Materials

Maleated EPM (EPM-g-MA, 49 wt% ethylene, 49 wt% propylene, 2.1 wt% MA, $M_n = 50$ kg/mol, PDI = 2.0) was provided by ARLANXEO Performance Elastomers. Prior to use, the EPM-g-MA precursor was dried in a vacuum oven at 175 °C for 1 h to convert any diacid present into cyclic anhydride. Furfurylamine (FFA, Aldrich, ≥ 99%) was freshly distilled prior to use. Carbon black N550 was kindly provided by Teijin Aramid.

Maleic anhydride (MA, > 99%), 1,4-diaminobutane (DAC4, > 99%), 1,6-diaminohexane (DAC6, > 98%), 1,8-diaminooctane (DAC8, > 98%), 1,12-diaminododecane (DAC12, > 98%), acetic anhydride (≥ 98.0%), trimethylamine (≥ 99%), sodium sulfate (≥ 99%), N,N’-(1,3-phenylene)bismaleimide (BMPh1, > 97%), 1,1’-(methylenedi-4,1-phenylene)bismaleimide (BMPh2, > 95%), m-phenylenediamine (DAPh1, ≥ 99%) and 4,4’-diaminodiphenylmethane (DAPh2, ≥ 97.0%), octadecyl-1-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate (phenolic anti-oxidant, > 99%), dimethylformamide (DMF, Sigma-Aldrich, ≥ 99.8%), decahydronaphthalene (decalin, > 98%), tetrahydrofuran (THF, > 99.9%), acetone (> 99.5%), deuterated chloroform (CDCl3, “100%”) and deuterated DMSO (DMSO-d6, “100%”) were all purchased from σ-Aldrich and used as received.

Methods

Synthesis of aliphatic bismaleimides

The aliphatic bismaleimides with a 4, 6, 8 or 12 carbon spacer (BMC4, BMC6, BMC8 and BMC12, respectively) were synthesized from MA and DAC4, DAC6, DAC8 and DAC12, respectively according to a published procedure [36]. The diamine (0.25 mol) was added under stirring to an opaque solution of MA (49.0 g, 0.50 mol) in 150 mL freshly distilled DMF. The resulting yellow solution was then stirred at 100 °C for 30 min. Acetic anhydride
dride (102.0 g, 1.0 mol), nickel(II) acetate (0.5 g, 2 mmol) and triethylamine (10.0 g, 98.8 mmol) were added to the reaction mixture. The resulting dark brown mixture was stirred at 90 °C for 30 min after which it was cooled down to 40 °C. The mixture was then poured into 2 L of ice water and stirred for 10 min. The precipitate was filtered over a Buchner funnel, washed twice with 1 L water and stirred in 2 L water for 1 h, after which it was filtered off and washed twice with 1 L water. The product was dissolved in 700 mL acetone and dried with sodium sulfate. The sodium sulfate was filtered off at 50 °C over a preheated Buchner funnel. Then, the solution was refluxed overnight with 25 g of carbon black, which was removed by filtering twice over a Buchner funnel. Recrystallization in acetone yielded pale yellow crystals which were filtered over a Buchner funnel and washed with cold acetone.

Diamine cross-linking

Fifteen gram of EPM-g-MA (3.2 mmol MA content) was dissolved in 120 mL THF and 2 mg phenolic anti-oxidant was added. Subsequently, 0.1 – 1.0 eq. (based on MA content of EPM-g-MA) of the diamine (DAC4, DAC6, DAC8, DAC12, DAPh1 or DAPh2) was dissolved separately in approximately 20 mL THF. For irreversible cross-linking of EPM-g-MA, the diamine solution was added to a stirred rubber solution at room temperature, resulting in a viscous gel that cannot be stirred anymore after a few seconds, especially for the aliphatic cross-linkers. The viscous gel is transferred to a petri-dish and the majority of the solvent is evaporated in the fume hood by blowing over air. The residual solvent was removed in a vacuum oven at 35 °C and the resulting product was compression molded at 150 °C and 100 bar for 15 min to convert any diacid present into cyclic anhydride, yielding test samples with the desired dimensions [33]. It was noted that the diamine cross-linking reaction is very fast and that compression molding must be performed immediately after the addition of the diamine to yield smooth and homogeneous samples. The irreversible character of the formed cross-links makes it impossible to improve the homogeneity of the samples afterwards. Upon the addition of large amounts of some specific diamines (namely DAC4 and DAC12) it proved impossible to obtain homogeneous samples at all.

Bismaleimide cross-linking

The EPM-g-MA precursor was converted into EPM-g-furan according to a reported procedure [33]. Typically, 40.0 g of EPM-g-furan (8.6 mmol furan content) and 40 mg anti-oxidant were dissolved in 500 mL THF. 0.1–1.0 eq. (based on furan content of EPM-g-furan) of the bismaleimide (BMC4, BMC6, BMC8, BMC12, BMPh1 or BMPh2) was dissolved in THF and added to the 10 wt% rubber solution under stirring. In contrast to the irreversible cross-linking (see previous paragraph), no gelation was observed. Again, the majority of the solvent was evaporated in the fume hood by blowing over air. The residual solvent was removed in a vacuum oven at 50 °C and the resulting product was compression molded at 150 °C and 100 bar for 1 h. The resulting products were thermally annealed in an oven at 50 °C for 7 days.

Characterization

Bismaleimide synthesis

Mass spectra were recorded on an LTQ Orbitrap XL spectrometer (ThermoFisher Scientific) with ESI or APCI ionization in positive mode. HRMS-ESI+ (m/z): {M + H}+ calculated for BMC4 (C_{12}H_{12}N_{2}O_{4}·H)+, 249.087; found, 249.087. {M + H}+ calculated for BMC6 (C_{14}H_{16}N_{2}O_{4}·H)+, 277.118; found, 277.118. {M + H}+ calculated for BMC8 (C_{16}H_{20}N_{2}O_{4}·H)+, 305.150; found, 305.150. {M + H}+ calculated for BMC12 (C_{20}H_{28}N_{2}O_{4}·H)+, 361.212; found, 361.212. 1H-NMR spectra were recorded on a Varian Mercury Plus 400 MHz spectrometer. All bismaleimides were obtained with yields of approximately 15–40% without any residual diamine (< 1%) after purification. The low yields compared to the literature [36, 37] are attributed to larger losses due to more rigorous purification.
Chemical shifts are reported in parts per million with the resonance solvent signal as the internal reference (2.50 for DMSO-d$_6$ and 7.26 for CDCl$_3$). NMR data are reported as follows: chemical shifts, multiplicity, coupling constants (hertz), relative integration, and location.

- DAC4 (CDCl$_3$); $\delta = 2.60$ ppm (m, 4H, NH$_2$CH$_2$), 1.40 ppm (m, 4H, NH$_2$CH$_2$CH$_2$), 1.21 ppm (br s, 4H, NH$_2$CH$_2$).
- DAC6 (CDCl$_3$); $\delta = 2.68$ ppm (t, 4H, NH$_2$CH$_2$), 1.44 ppm (m, 4H, NH$_2$CH$_2$CH$_2$), 1.32 ppm (m, 4H, NH$_2$CH$_2$CH$_2$CH$_2$), 1.24 ppm (br s, 4H, NH$_2$CH$_2$).
- DAC8 (CDCl$_3$); $\delta = 2.67$ ppm (t, 4H, NH$_2$CH$_2$), 1.42 ppm (m, 4H, NH$_2$CH$_2$CH$_2$), 1.30 ppm (m, 8H, NH$_2$CH$_2$CH$_2$CH$_2$), 1.20 ppm (br s, 4H, NH$_2$CH$_2$).
- DAC12 (DMSO-d$_6$); $\delta = 2.64$ ppm (t, 4H, NH$_2$CH$_2$), 1.41 ppm (m, 4H, NH$_2$CH$_2$CH$_2$), 1.28 ppm (br m, 16H, NH$_2$CH$_2$CH$_2$CH$_2$), 1.23 ppm (br s, 4H, NH$_2$CH$_2$).
- DAPh1 (DMSO-d$_6$); $\delta = 6.34$ ppm (s, 4H, C$_6$H$_4$), 4.16 ppm (s, 4H, NH$_2$CH$_2$).
- DAPh2 (DMSO-d$_6$); $\delta = 6.79$ ppm (d, 4H, N–C$_6$H$_4$), 6.45 ppm (d, 4H, CH$_2$–C$_6$H$_4$), 4.18 (4H, NH$_2$), 3.32 (s, 4H, CH$_2$).
- BMC4 (CDCl$_3$); $\delta = 6.65$ ppm (s, 4H, HC=CH), 3.52 ppm (t, 4H, NCH), 1.55 ppm (t, 4H, t, 4H, NCH).
- BMC6 (CDCl$_3$); $\delta = 6.70$ ppm (s, 4H, HC=CH), 3.49 ppm (t, 4H, NCH), 1.55 ppm (t, 4H, NCH), 1.30 ppm (br s, 4H, NCH, CH$_2$).
- BMC8 (CDCl$_3$); $\delta = 6.70$ ppm (s, 4H, HC=CH), 3.50 ppm (t, 4H, NCH), 1.50 ppm (t, 4H, NCH), 1.30 (br s, 8H, CH$_2$).
- BMC12 (CDCl$_3$); $\delta = 6.65$ ppm (s, 4H, HC=CH), 3.50 ppm (t, 4H, NCH), 1.55 ppm (t, 4H, NCH), 1.25 ppm (br s, 16H, CH$_2$).
- BMC12 (DMSO-d$_6$); $\delta = 7.00$ ppm (s, 4H, HC=CH), 3.37 ppm (t, 4H, NCH), 1.46 ppm (t, 4H, NCH), 1.23 ppm (br s, 16H, CH$_2$).
- BMPh1 (CDCl$_3$); $\delta = 7.56$ ppm (d, 4H, C$_6$H$_4$), 741 ppm (d, 4H, HC=CH).
- BMPh2 (CDCl$_3$); $\delta = 7.30$ ppm (d, 8H, C$_6$H$_4$), 6.84 ppm (d, 4H, HC=CH), 4.04 ppm (s, 2H, CH$_2$).

**Cross-link density determination**

The cross-link density ([XLD]) in mol/mL was determined from equilibrium swelling experiments in decalin [14]. Approximately 500 mg of dried, cross-linked sample was weighed into a 20 mL vial ($W_s$) and immersed in 5 mL decalin until equilibrium swelling was reached. The sample was dabbed with a tissue to remove any solvent from the surface and then weighed ($W_s$). Subsequently, the swollen samples were dried in a vacuum oven at 80 °C until a constant weight was reached ($W_s$). The weights of the swollen and dried samples were used to calculate the cross-link density using the Flory-Rehner equation (1) [44].

$$[XLD] = \frac{\ln(1 - V_s) + V_s + \chi V_s^3}{[2V_s(0.5V_s - V_s^{1/3})]}$$

$V_s$ volume fraction of rubber in swollen sample: $W_s / (W_s + (W_i - W_s)\rho_{EPM-g-furan}/\rho_{decalin})$
$V_s$ molar volume of solvent (decalin: 154 mL/mol at room temperature).
$\chi$ interaction parameter (decalin-EPDM: 0.121 + 0.278V$_s$) [45].
$\rho$ density (0.860 g/mL for EPM-g-MA and EPM-g-furan and 0.896 g/mL for decalin).

**Material testing**

Tensile tests were performed on an Instron 5565 with a gauge length of 15 mm according to the ASTM D 4-112 standard for ‘Vulcanized and thermoelastic tension’. A strain rate of 500 ± 50 mm/min was applied. Samples used for the tensile tests were prepared by compression molding 450 mg rubber into rectangular bars of 4.5 cm long, 5 mm wide and 1 mm thick. For each measurement 10 samples were tested and the two outliers with the highest and the lowest values were excluded for calculating the result averages. Stress-stain curves shown in figures are median curves. Hardness Shore A was measured using a Bareiss Durometer according to the ASTM
Table 1: Solubility parameters, melting points and estimated flexibilities of the different cross-linking agents.

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$^a$The flexibility ranges from relatively flexible to rigid as indicated by ++ to −−.
density was measured and no significant changes were observed during thermal annealing (only DAC8 results are shown as a representative example). This confirms that diamine cross-linking of EPM-g-MA is thermally irreversible. For the BM cross-linked EPM-g-furan samples de-cross-linking takes place at the elevated temperature during compression molding (150 °C), as can be seen from the instantaneous decrease in cross-link density directly after compression molding (starting cross-link density is ~10^{-4} mol/mL for all samples). During annealing the cross-link density of the BM cross-linked EPM-g-furan samples increases slowly over time, indicating that re-cross-linking takes place as expected. Hence, for further studies these samples were thermally annealed for a full week to ensure the highest cross-link density and constant properties.

**Reactivity**

The cross-link density of peroxide-cured EP(D)M rubber is known to increase linearly as a function of the peroxide content and to level off at higher peroxide contents due to degradation side-reactions [52–54]. Such linear correlations are also observed for the cross-link density of EPM-g-MA cross-linked with diamine and EPM-g-furan cross-linked with BM (Fig. 2a). However, at higher levels of cross-linking agent added, a maximum and a subsequent decline in the cross-link density is observed for both the irreversibly (diamine) and thermoreversibly (BM) cross-linked EPM systems. This optimum can be explained by the capping of pendant anhydride/furan-groups in the rubber with excess cross-linker, i.e. a cross-linker molecule (diamine or BM) is connected with only one functional group to a polymer chain, while its second functional group is not connected (Fig. 2b).

For both EPM rubbers the first addition of cross-linker does not immediately result in an increase in cross-link density as measured with the equilibrium swelling experiments, because the first cross-links are used to convert the soluble polymer sample in an insoluble gel. Since the functionality of the EPM-g-MA and EPM-g-furan polymers is ~10 per chain, the gel point is reached after ~20% conversion. Only beyond the gel point a gel is present that can be swollen. Theoretically, the cross-linked rubbers are expected to have a maximum cross-link density upon the addition of equimolar amounts of cross-linker (cross-linker/[rubber functional group] molar ratio = 0.5). The experimental data show that this is indeed the case, confirming that the efficiency of both the diamine and BM cross-linking is close to 100%. However, both the gel point and the maximum cross-link density of the BM cross-linked EPM-g-furan are shifted to higher cross-linker/functional group ratios with respect to the diamine cross-linked EPM-g-MA. This can be explained by the relatively slow and less efficient reaction between maleimides and furan compared to the extremely fast and efficient
reaction between primary amines and cyclic anhydride [55], which was also evident from the absence of gelation compared to the instantaneous gelation, respectively, during sample preparation in solution. In addition, the thermoreversible character of the DA cross-links may also contribute to the shift. Whereas diamine cross-linking of EPM-g-MA results in covalent imide cross-links that cannot rearrange [21], the DA cross-links are in a dynamic equilibrium with the pendant furan groups in which not every connection is permanently closed. Even at room temperature, there is an active shift from exo to endo configurations of the DA adducts proceeding via the retro-DA reaction [56, 57]. Since the reaction is in equilibrium, not all reactants form the DA adduct and the reaction equilibrium is driven towards adduct formation at higher BM concentrations. The dynamic character of the equilibrium reaction also implies that a capped BM could detach, uncapping the furan-group and allowing it to react with another, already attached BM, yielding a cross-link. In conclusion, the cross-link density goes through a maximum as a function of the cross-linker concentration for diamine and BM cross-linking, as is also known for hydrosilane cross-linking of rubber [15, 58, 59], whereas for sulfur and peroxide cross-linking of rubber the cross-link density simply increases with the amount of cross-linker [54]. This means that the degree of functionalization of the starting polymer factually limits the cross-link density and as a consequence, the material properties of the cross-linked products [60]. This is of course not desirable from the point of view of possible future industrial applications. Indeed, when designing a new product using this material, a range of different properties should be easily accessible in order to fine tune the design for a given application. This could be achieved by using different cross-linkers, characterized by a different chemical structure. In this context we used different diamines (irreversible cross-linking) or BMs (reversible cross-linking).

The effect of adding different amounts of the various diamine and BM cross-linkers on the cross-link density was studied up to the saturation limit reached upon stoichiometry to allow a better comparison between them (Fig. 3). First, a slow buildup of the cross-link density is observed for all cross-linking agents. This is because the polymers only become insoluble after the gel point has been reached. Then a fairly linear relationship between the cross-link density and the functional group/cross-linker molar ratio is observed. For both the diamine and BM cross-linkers the addition of aliphatic cross-linkers results in higher cross-link densities than the addition of the same amount of aromatic cross-linker. For the diamine cross-linkers, this is related to the higher nucleophilic character and basicity of aliphatic diamines with respect to aromatic diamines (pKb ~ 3 vs. ~ 9). As the amine connects with its lone electron pair to a positively charged carbonyl of the cyclic anhydride, a more basic diamine will react faster and, thus, more efficiently.
BM cross-linking of EPM-g-furan does not occur during solution mixing, but takes place in the rubber bulk at elevated temperatures during thermal annealing. The solubility parameter of the EPM rubber matrix ($\delta_{EPM} = 15.7 \text{ MPa}^{0.5}$) is relatively low due to its apolar, hydrocarbon backbone and increases only slightly upon maleation ($\delta_{EPM-g-MA} = 15.9 \text{ MPa}^{0.5}$) or furan-functionalization ($\delta_{EPM-g-furan} = 16.0 \text{ MPa}^{0.5}$). For the BM cross-linkers the aliphatic BMs have a relatively low solubility parameter and the BMC8 and BMC12 also have a relatively low melting point compared to the aromatic BMs. Consequently, the aliphatic BMs will have a relatively high solubility in the EPM matrix, which thus explains the observed higher reactivity (Fig. 1). Longer spacers in the aliphatic BMs result in lower solubility parameters and lower melting points and, thus, in increased solubility in EPM, which again explains the observed enhanced reactivity. In conclusion, the solubility, as determined by the solubility parameter and the melting point, determine the chemical reactivity. Finally, it can be speculated that the flexibility of the BM cross-linker can also contribute. If one maleimide end of the BM molecule has formed the DA adduct, the other maleimide group will have higher mobility and freedom to move around when attached to a more flexible spacer (long aliphatic > short aliphatic > aromatic). This will make it easier for the free maleimide end to “reach” furan groups that are further away and, subsequently, will have a higher probability to form a cross-link. The rigidity of the aromatic spacers may also explain why samples cross-linked with BMC4 show an overall higher cross-link density than those cross-linked with BMPH2, despite their similar solubility parameter and the greater length of BMPH2. In contrast to BM cross-linking of EPM-g-furan the diamine cross-linking of EPM-g-MA takes place during mixing in a homogeneous solution and, thus, the solubility of the diamines in the bulk rubber matrix will not affect the reactivity. In addition, the diamine cross-linking of EPM-g-MA is extremely fast compared to the BM cross-linking of EPM-g-furan. As a combined result, the subtle effects of the variation in the spacer as observed for BM cross-linking of EPM-g-furan are not observed for the diamine cross-linking of EPM-g-MA. As a consequence, it is expected that the material properties of the thermoreversibly cross-linked system are also more susceptible to variations in the type cross-linker used.

Material properties

Mechanical and elastic properties of materials represent their response to external stress or strain at a particular temperature and time scale. For rubbers products these properties are mainly determined by the type of elastomer, the cross-link density and, to some extent, the cross-link structure [8]. Numerous studies on rubber vulcanizates have provided general relationships between physical properties and the cross-link density [3, 7–9]. In general, the hardness and the modulus increase more or less linearly with the cross-link

![Fig. 3](https://example.com/fig3.png)
density, whereas the elongation at break and the compression set follow an exponential decrease. The tensile strength shows a more complex behavior, going through a maximum, if a wide range of cross-link densities is studied. At low cross-link density the tensile strength usually just increases with cross-link density. A full overview of the results of the diamine cross-linked EPM-g-MA and the BM cross-linked EPM-g-furan can be bound in the supplementary Tables S1 and S2, respectively. For both the diamine cross-linked EPM-g-MA and the BM cross-linked EPM-g-furan samples the material properties follow these general relations versus the cross-link density (Fig. 4). This shows that the details of the cross-linking reaction, such as the amount of cross-linker and the chemical conversion are only of importance in the sense that they determine the cross-link density, which in its turn determines the properties, as for the traditionally cross-linked rubber systems. It also implies that the thermoreversible character of the BM cross-linked EPM-g-furan does not influence the general effect of the cross-link density on the rubber properties.

Overall, the relative experimental error in all properties determined for the diamine cross-linked EPM-g-MA samples (averages of 8%, 19%, 18%, 33% and 20% for hardness, Young’s modulus, tensile strength, elongation at break and compression set, respectively) is significantly larger than the relative error in the properties of the BM cross-linked EPM-g-furan (averages of 2%, 6%, 11%, 13% and 18% for hardness, Young’s modulus, tensile strength, elongation at break and compression set, respectively). The large standard deviations for the diamine cross-linked EPM-g-MA products are probably related to the inhomogeneity of these samples. Within these error margins similar correlations were found for the diamine cross-linked EPM-g-MA and the BM cross-linked EPM-g-furan (Fig. 4). However, the Young’s modulus, the tensile strength, the compression set and the elongation at break at high cross-link density of all BM cross-linked EPM-g-furan samples were found to be relatively high compared to the diamine cross-linked EPM-g-MA samples. The relatively high modulus, tensile strength and elongation at break of the BM cross-linked EPM-g-furan may be the result of stress relaxation of the reversibly cross-linked polymer chains that could alleviate critical stresses which cause material failure [20, 61]. The retro-DA reaction may take place under the stress of deformation, allowing for stress relaxation of the chains. The free end of the BM would then re-cross-link at a different location, rather similar to the mechanism of ion-hopping for ionomers in which cross-links disengage and reconnect at other cross-linking sites so that the cross-link density remains unaltered while allowing stress relaxation and relief of local stresses [20, 62, 63]. This effect is also observed in sulfur cross-linking as reversion of polysulfidic cross-links allows them to adapt to the configuration by irreversibly transforming into shorter cross-links [4, 64]. The higher compression set of the BM cross-linked EPM-g-furan may also be the result of the ability of the polymer chains to adapt and relocate under stress [3, 4, 19, 61]. Since the total
cross-link density remains constant as a result of the fast de-cross-linking/re-cross-linking, the effect on the hardness is small. Polysulfidic cross-links are also suggested to show a similar mechanism of stress relief as a result of the lability of polysulfidic cross-links, that can split up under stress and reform (yield mechanism), which would relief local stresses and postpone failure of the sample [3].

No correlations between the structure of the cross-linker and the properties were observed for the diamine cross-linked EPM-g-MA samples. This may partly be related to the relatively large experimental error in the properties of these systems. But it also implies that the effects, if any, of variation of the spacer of...
the cross-linkers on the properties irreversibly cross-linked EPM elastomer is rather small. For the BM cross-linked samples, though, such correlations were more clearly observed, as will be discussed below.

While the effect of the cross-link density on the material properties has frequently been reported in the literature [3, 7–9, 54], the effect of systematically changing the structure of the cross-linker is not very well known. Unfortunately, the large set of material properties of the BM cross-linked EPM-g-furan provided in Table S2 does not allow for a direct interpretation in terms of cross-link structure, since varying amounts of cross-linker have been used and the cross-linking efficiency was shown to be dependent on the details of the rubber/cross-linker combination, resulting in a large variation of cross-link densities. In order to discuss the effects of the cross-link structure independently of the cross-link density, the properties of the BM cross-linked EPM-g-furan samples with different BM cross-linkers will be compared at the same “medium” cross-link density of $6 \times 10^{-5}$ mol/mL (Fig. 5) by fitting the various material properties as function of the cross-link density using the known general relationships mentioned above.

For the BM cross-linked EPM-g-furan samples the aromatic cross-linkers appear to yield significantly higher hardness than the aliphatic cross-linkers (Fig. 5b). Cross-linkers with short aliphatic spacers also appear to result in significantly larger hardness than cross-linkers with long aliphatic spacers. The same trends are observed for the Young's modulus and, to a lesser extent, for the tensile strength (Fig. 5b and c, respectively). Finally, longer aliphatic spacers seem to yield higher elongations at break than shorter aliphatic spacers (Fig. 5d), while for the compression set no significant correlations with the spacer structure are observed (Fig. 5e). Although the mobility of the cross-linked chains is known to become increasingly restricted at higher cross-links densities [8, 9, 39, 65, 66], these systematic correlations were observed not only at the “medium” cross-link density of $6 \times 10^{-5}$ mol/mL, but over the whole range of cross-link densities between $2 \times 10^{-5}$ and $1 \times 10^{-4}$ mol/mL.

The observed trends seem to correlate with the flexibility of the cross-linker. The parameters in Table 1 indicate that the flexibility increases with longer aliphatic spacers and from aromatic to aliphatic spacers. The higher hardness, Young’s modulus, tensile strength and somewhat lower elongation at break of the EPM-g-furan cross-linked with more stiff and rigid (short aliphatic and aromatic) cross-linkers may be due to an increase the resistive force of the material against deformation [35]. It has been speculated that for sulfur-vulcanized rubber the flexibility of the sulfur cross-link (mono-, di and polysulfidic) may affect these rubber properties [3]. Stress relaxation and local stress relief caused by the dynamic equilibrium and the mobility of BM cross-linkers, as discussed above, may also play a role. Since the DA reaction is a pericyclic reaction with an aromatic transition state, the conjugated, aromatic BM cross-linkers may lower the energy barrier of the transition state and, thus, increase the reaction rate of both the DA and retro-DA reactions. The cross-linking/de-cross-linking mechanism would, thus, be more prevalent in samples cross-linked with aromatic BM, resulting in an increase in Young’s modulus and tensile strength. Finally, longer and more flexible (aliphatic) cross-linkers allow the polymer network to stretch more, resulting in cross-linked rubbers with a higher elongation at break as is also known for polysulfidic cross-links [35]. Since varying the cross-linking agent appears to have a different effect on the material properties than simply varying the cross-link density, the choice of the appropriate cross-linker can be used as an additional parameter to tune the material properties of thermoreversibly cross-linked elastomers for specific applications.

Conclusions

A homologous series of various diamine and bismaleimide cross-linkers with aromatic and aliphatic spacers of different lengths between the maleimide groups was used to cross-link EPM-g-MA irreversibly and EPM-g-furan thermoreversibly, respectively. For both systems a maximum in the cross-link density was observed upon the addition of roughly an equimolar amount of cross-linker. This maximum is caused by capping of the available functional groups on the rubber with the excess of cross-linker. The EPM-g-MA/diamine system required a lower molar amount of cross-linker to reach the same cross-link density compared to the EPM-g-furan/BM system. This is ascribed to the extremely fast reaction between primary amines and cyclic anhydride
with respect to the much slower Diels-Alder reaction and the reversible character of the latter. Because BM cross-linking of EPM-g-furan is relatively slow and occurs only at elevated temperatures in the bulk rubber, enhanced solubility of the BM cross-linkers in the EPM rubber matrix, as a result of lower polarity and/or lower melting point (BMC12 > BMC8 > BMC6 > BMC4 > Bmpz2 > BMPH1), results in a higher cross-link density. For diamine cross-linking of EPM-g-MA this is not observed, since cross-linking already occurs during mixing in the homogeneous solution. The rubber properties, such as hardness, Young’s modulus, tensile strength, elongation at break and compression set, of both the diamine/EPM-g-MA and BM/EPM-g-furan cross-linked rubbers correlate with the cross-link density with trends well-known in rubber chemistry and technology. Although the trends were found to be similar, the rubber properties of all diamine cross-linked EPM-g-MA were found to be relatively inferior compared to the BM cross-linked EPM-g-furan. This is probably due to large heterogeneity of the former samples and the thermoreversible character of the latter. Normalizing the various properties of BM cross-linked EPM-g-furan to a cross-link density of 6.10⁻⁵ mol/mL allowed a further interpretation of the effect of the cross-linker spacer. Variations in the spacer of the diamine cross-linker do not significantly influence the material properties of irreversibly cross-linked EPM rubbers. For the BM cross-linked EPM-g-furan, however, a clear effect of the flexibility of the spacer (long vs. short aliphatic and aromatic vs. aliphatic) was observed. This implies that choosing the appropriate cross-linker is an additional parameter that can be used to tune the material properties of thermoreversibly cross-linked elastomers for specific applications.

In summary, it is shown that these EPM rubbers, thermoreversible cross-linked via (retro) Diels Alder chemistry, not only provide a practical route towards recycling, but also provide more scientific insight in the effect of the cross-link spacer on the cross-linking reactivity and the rubber properties. This system paves the way towards the design of sustainable rubber products according to the corresponding guidelines also form a societal point of view. Our understanding of this system is certainly advanced even if, in view of future design toolbox needed for specific applications, a more comprehensive structure-property relationship should be investigated. Factors such as the use of multifunctional cross-linkers (including their chemical structure) and possible influence of fillers on proposed chemistry should be carefully investigated.

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References

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