

Cross-linking of rubber in the presence of multi-functional cross-linking aids via thermoreversible Diels-Alder chemistry

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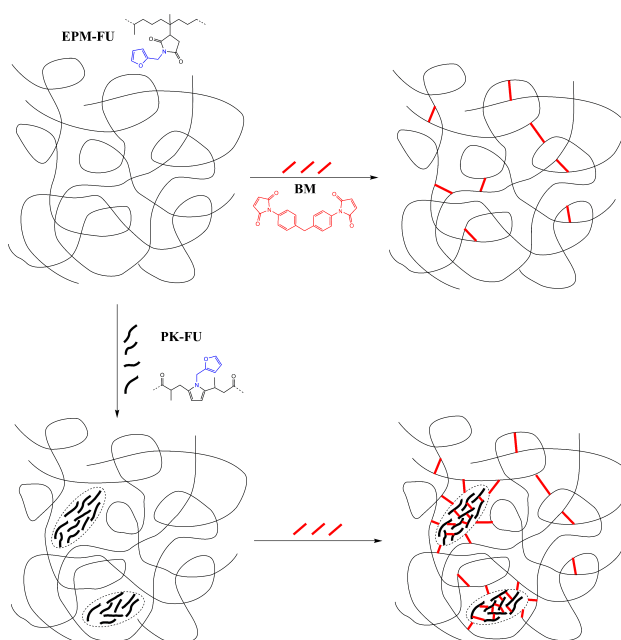
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Abstract

Furan-functionalized polyketone (PK-FU) was added to a furan-functionalized ethylene-propylene rubber (EPM-FU). The mixture was subsequently cross-linked with a bismaleimide through Diels-Alder chemistry in order to improve the mechanical properties of the rubber. Infrared spectroscopy showed the reversible interaction between both polymers and the bismaleimide cross-linker. Likewise, mechanical measurements indicated the re-workability of the mixtures with no evident differences in storage modulus and mechanical properties after several heating cycles. The cross-link density and mechanical properties, such as hardness, tensile properties and compression set, could be modulated by changing the degree of furan functionalization of PK-FU and the PK-FU loading in the blends. It is concluded that PK-FU has some characteristics of an inert filler, but mainly acts as a multi-functional cross-linking aid, enabling larger amounts of bismaleimide to cross-link EPM-FU, resulting in improved material properties with respect to the cross-linked rubber matrix.

Keywords: thermally-reversible multi-component networks, Diels-Alder, recycling, multifunctional domains

Introduction

EPM copolymers are synthetic elastomers that are obtained from the copolymerization of ethylene and propylene. EPDM rubbers contain a third monomer, i. e. a non-conjugated diene (usually 5-ethylidene-2-norbornene or dicyclopentadiene), introducing a small amount of pendant unsaturation for sulphur vulcanization. The saturated polymer backbone provides EP(D)M rubbers with inherent resistance against degradation by heat, oxygen, ozone and light, especially where compared to diene rubbers such as natural rubber and polybutadiene rubber [1, 2]. EP(D)M rubber is used in a large variety of outdoor and elevated-temperature applications, ranging from automotive to building and construction. Like other rubbers, EP(D)M rubber is compounded with (reinforcing) fillers and plasticizers, and subsequently shaped and cross-linked. Cross-linking is typically achieved via sulphur vulcanization or peroxide curing, resulting in an elastic, three-dimensional polymer network that cannot be melted or reprocessed [2, 3]. Simple mechanical grinding of waste rubber produces low quality feedstock for virgin rubber [4]. Meanwhile, pyrolysis and incineration are downcycling methods that are still associated with environmental issues. The irreversibility of the conventional cross-linking processes constitutes the major restraint in the recycling of waste rubber. Devulcanization of sulphur-vulcanized rubber, i. e. the cleavage of carbon-sulphur or sulphur-sulphur cross-links, has been widely studied [5-7] and is commercially practiced, but may cause a considerable amount of bond scission in the polymer main chain [2, 7], which is detrimental for the performance of the recycle compared to the virgin material.

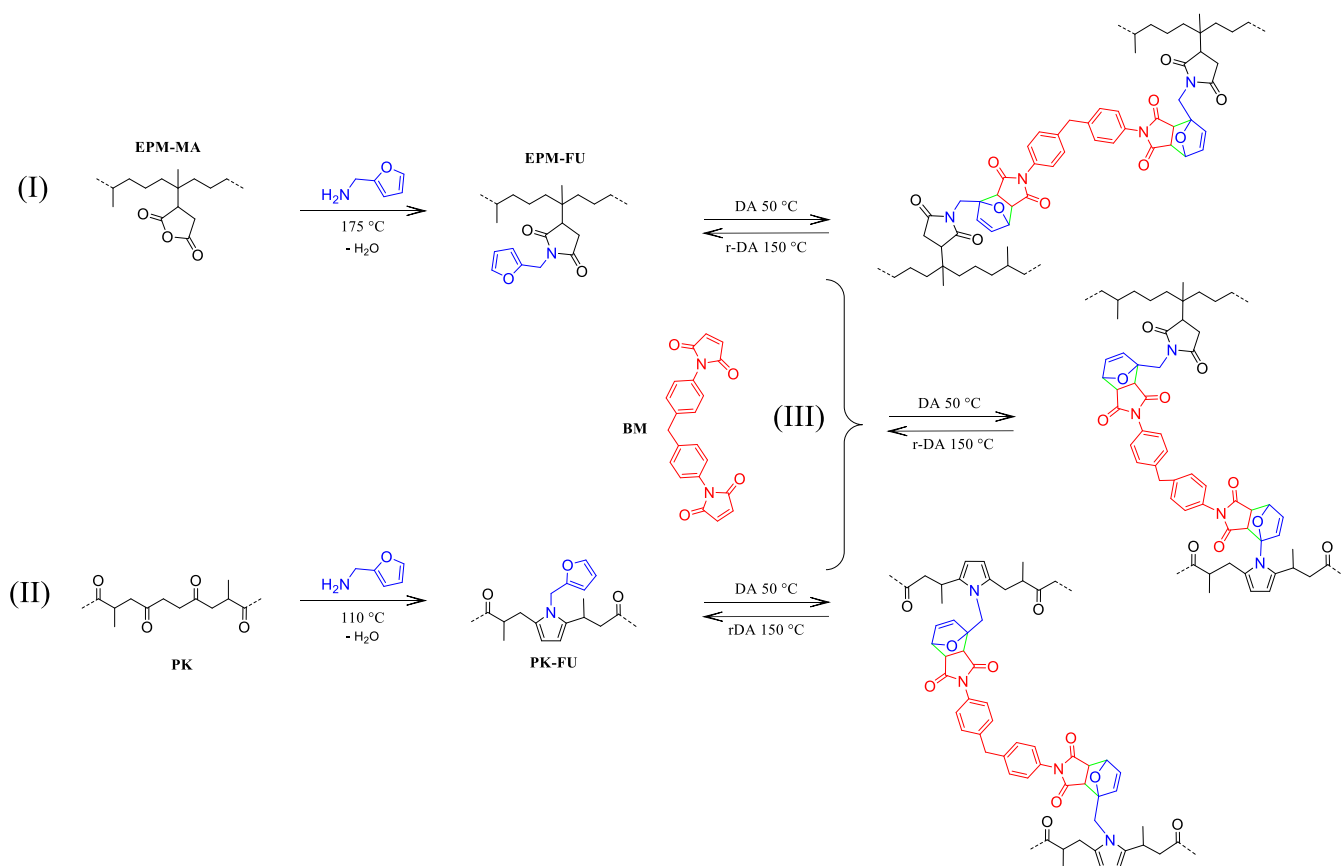
In this context, the development of iononomers, thermoplastic elastomers (TPEs) and thermoplastic vulcanizates (TPVs) [8, 9] has represented a major advancement, since these products combine the processability of thermoplastics at relatively high temperature with the elasticity of cross-linked rubbers at service temperature. The polymer backbone of TPEs, for example (hydrogenated) styrene/butadiene/styrene [S(E)BS] triblock copolymers, consists of “hard” and “soft” segments, which phase separate at low temperature, resulting in two phases with a high and a low glass transition temperature (T_g), respectively.[8, 10] Cross-linking in TPEs does not occur through chemical bonds, but because the hard domains “cross-link” the soft matrix. The hard domains soften at high

temperature, i. e. the “cross-links are broken”, and the TPE becomes melt processable [2]. The disadvantage of TPEs resides in their poor high-temperature performance, since this is factually limited by the T_g of the hard segments (e. g. around 80 °C for S(E)BS [11]).

An alternative approach for the recycling of thermoset cross-linked polymers is thermoreversible cross-linking. In particular, the Diels-Alder (DA) reaction has gained major interest for this purpose, because of the relatively fast kinetics and the mild conditions for (de)cross-linking without the need of a catalyst [12-15]. DA cross-linking proceeds via the cycloaddition of a diene to a dienophile, typically a furan and a maleimide, at relatively low temperature (e.g. 50 °C) [16-19]. De-cross-linking via the retro DA reaction is favored at high temperature (typically above 100 °C), thus allowing the material to be reshaped or recycled. In a previous study a commercial, maleated EPM (EPM-MA) was grafted with furfurylamine (FFA), yielding EPM-FU, which was then cross-linked with a bismaleimide (BM) via the DA reaction (Scheme 1:I) [20]. The resulting product showed mechanical properties similar to those of a conventionally peroxide-cured EPDM rubber with a comparable cross-link density and possessed the added value of recyclability. It was possible to recycle the material via compression molding with excellent conservation of properties.

Alternating, aliphatic polyketones (PK), obtained by copolymerization of carbon monoxide with ethylene and/or propylene, can be modified with FFA to introduce furan groups [21]. The resulting furan-functionalized polyketones (PK-FU) can be thermoreversibly cross-linked with BM (Scheme 1:II) [22]. Such products can be recycled up to 10 times with hardly any change in performance [21]. The mechanical properties can be modulated by varying the degree of furan functionalization and the furan/maleimide molar ratio [23]. The high brittleness and low impact strength of the PK-FU thermoset were overcome by the addition of a small amount of EPM-FU elastomer as a toughening-agent [24]. Upon the addition of BM, the thermoreversible reaction within and between the phase-separated EPM-FU and PK-FU in the blends (Scheme 1:III) was shown to significantly increase the impact strength [24]. Since PK is easily functionalized with controlled conversion of furan and forms reversible thermosets when cross-linked with BM [33, 35], the resulting blend of EPM-FU and PK-FU is also fully recyclable.

Scheme 1. Grafting of furan groups onto maleated EPM rubber (I) and aliphatic polyketone (II) via reaction with furfurylamine and subsequent (de)cross-linking of the EPM- FU/PK- FU blends via the (retro)Diels Alder reaction with 1,1'-(methylene di-4,1-phenylene)bismaleimide (III).



The relatively low amount of furan moieties along the EPM-FU backbone, factually limited by the chemical composition of the rubber precursor used (only 2 wt% of MA can be grafted onto EPM [20, 25, 26]), prohibits a detailed study on the effects of increasing the cross-link density and limits the mechanical properties of the cross-linked rubber. When elastomers are cured with peroxides, multi-unsaturated chemicals are usually added as coagents to increase the cross-linking efficiency [27, 28]. Typically, coagents such as trimethylolpropane trimethacrylate, triallyl (iso)cyanurate or m-phenylene bismaleimide are used. It would be useful if similar coagents could be developed for the BM cross-linking of EPM-FU.

Another way of improving the elastic and mechanical properties of EPM-FU is by formulating the gum rubber. Gum rubbers are generally compounded with reinforcing fillers, such as carbon black or silica, to enhance their mechanical properties, especially their strength. Thermoset resins, typically

phenolics, have been used as an alternative for or in combination with reinforcing fillers. These resins have excellent compatibility with the rubber and, thus, lower the melt viscosity of the rubber compound [29]. During the vulcanization stage, the phenolic resins are cured independently from the rubber, forming an interpenetrating polymer network [30-32]. Depending on the structure of the phenolic resins, covalent bonds can be formed between the two networks and, thus, phenolic resins can also be viewed as rigid cross-linking agents [33-38].

In this work, a reversed approach is applied, i. e. the mechanical properties of the DA cross-linked EPM-FU rubber are improved by incorporating small amounts of PK-FU. The PK phase could act as a rigid, multi-functional coagent domain in the EPM rubber matrix, thus factually increasing the cross-link density to industrially relevant levels (equal or above 10^{-4} mol/cm³), or as a cross-linked filler. The DA cross-linking reaction of EPM-FU with BM is slow compared to conventional cross-linking methods, such as sulphur vulcanization. The use of highly functionalized PK-FU as a multifunctional cross-linking aid may render the reaction faster. Finally, PK can be functionalized with different amounts of furan groups, allowing for a new way of tuning the cross-link density and, thus, the material properties of the thermoreversibly cross-linked EPM rubber.

The goal of this work is to blend EPM-FU and PK-FU, thermoreversibly cross-link the mixture with BM, while using PK-FU as a multifunctional aid in a way of improving the mechanical properties of EPM-FU. To the best of our knowledge, the proposed approach (and materials) constitute an absolute novelty in the field of thermo-reversible rubber cross-linking.

Experimental

Materials

Polyketone, i. e. an alternating polymer of carbon monoxide with ethylene or propylene (PK; CO, ethylene and propylene: 50, 30 and 20 mol%, respectively, M_n = 2800 g/mol and PDI = 1.7) was synthesized according to a reported procedure [8, 39]. Maleated EPM (EPM-MA; Keltan DE5005 with 49 wt% ethylene, 2.1 wt% MA, M_n = 50 kg/mol and PDI = 2.0) was kindly provided by ARLANXEO

Netherlands B.V. Furfurylamine (FFA, Sigma-Aldrich, $\geq 99\%$) was freshly distilled before use. Tetrahydrofuran (THF, $>99.9\%$), acetone ($>99.5\%$), decalin (98%), butylamine (99 %) and 1,1'-(methylenedi-4,1-phenylene)bismaleimide (BM, $>95\%$) were purchased from Sigma-Aldrich and used as received. Deuterated dimethylsulfoxide (DMSO- d_6 , Sigma Aldrich, $\geq 99.9\%$ deuteration) was used as solvent for ^1H -NMR measurements.

Furan modification of polyketone

Chemical modification of PK was performed via the Paal-Knorr reaction, using different molar ratios between the 1,4-dicarbonyl units of PK and the amines, e. g. furfurylamine or butylamine. The latter was used as a reference, which does react with PK, but the resulting modified PK (PK-BU) does not react with BM and only acts as a non-reactive filler. The reactions were performed in bulk in a 250 mL round-bottom glass reactor, equipped with a reflux condenser, a U-type anchor impeller, and an oil bath for heating. After pre-heating 60 g of PK up to $110\text{ }^\circ\text{C}$, the amine was added dropwise during 20 min. The total reaction time was 4 hr at $110\text{ }^\circ\text{C}$ with a stirring speed of 600 rpm. The resulting viscous product was frozen with liquid nitrogen, crushed to powder and washed three times with de-ionized Milli-Q water to remove any unreacted amine. After filtration and freeze drying, a light-brown powder was obtained as final product. The samples in Table 1 are coded indicating the type of amine (FU for furfurylamine and BU for butylamine) and the desired carbonyl conversion ($X_{\text{CO}} = 40, 60$ or 80%).

Table 1. Modification of polyketone (60 g).

<i>Sample</i>	<i>Amine</i>	<i>Amine</i>	X_{CO}	X_{amine}
	(g)	(mmol)	(%)	(%)
PK-BU80	26.7	365	78	98
PK-FU40	17.7	182	39	99
PK-FU60	26.6	274	58	98
PK-FU80	35.4	365	76	96

The obtained carbonyl conversion (X_{CO} in %) of PK was calculated (Eq. 1).

$$X_{CO} = \frac{2 \frac{\%N}{M_N}}{\frac{\%C}{M_C} - \frac{\%N}{M_N} n_y^C + 2 \frac{\%N}{M_N}} \cdot 100 \quad (\text{Eq. 1})$$

with %N and %C, respectively the weight of nitrogen and carbon per 100 g of final product as determined by elemental analysis, M_N and M_C the atomic weights of nitrogen and carbon, respectively (14.01 and 12.01 g/mol respectively), n_x^C the average number of carbons in the original monomer, which is $(0.3 \cdot 3) + (0.7 \cdot 4) = 3.7$ and n_y^C the average number of carbons in two neighboring modified monomers containing one pyrrole (Scheme 1), which is $(0.3 \cdot 0.3 \cdot 6) + (0.7 \cdot 0.7 \cdot 8) + (2 \cdot 0.3 \cdot 0.7 \cdot 7) + 5 = 12.4$ [20]. The amine conversion (X_{amine} in %) was calculated from the moles of amine (furfurylamine or butylamine) in the feed (mol_{amine}) (Eq. 2)

$$X_{amine} = \frac{\frac{\%N}{M_N}}{M_{amine}} \cdot 100. \quad (\text{Eq. 2})$$

Furan functionalization of EPM-MA rubber

EPM-MA was dried in a vacuum oven for one hour at 175 °C to convert any di-acid present into cyclic anhydride [20]. 100.0 g of dried EPM-MA (21.4 mmol MA) was dissolved in THF (10 wt% polymer) by stirring for 24 hr at room temperature. 6.24 g FFA (64.3 mmol) was added to the solution. The reaction mixture was stirred in a closed system for 12 hr at room temperature and then slowly dropped into 5 L of acetone under mechanical stirring. The modified rubber (EPM-FU), precipitated as yellowish strands, was filtered and dried in an oven at 50 °C up to constant weight. Finally, the intermediate amide-acid was compression molded for 15 min at 175 °C and 100 bar to ensure the complete conversion to succinimide. The conversion (X_{MA} in %) of anhydride into imide groups was calculated from FT-IR (Eq. 3)

$$X_{MA} = \left(1 - \frac{A_{1856}^{FU}/A_{723}^{FU}}{A_{1856}^{MA}/A_{723}^{MA}} \right) \cdot 100, \quad (\text{Eq. 3})$$

where A_{1856}^{FU} and A_{1856}^{MA} are the area integrals of the absorption bands at 1856 cm^{-1} (C=O asymmetric stretching of anhydride ring) for EPM-FU and EPM-MA, respectively, and A_{723}^{FU} and A_{723}^{MA} are the

respective integrals of the bands at 723 cm⁻¹ (methyl rocking), which are used as internal references [20].

Blend preparation and cross-linking via Diels-Alder addition

Blends were prepared by dissolving EPM-FU and the modified polyketones (PK-FU or PK-BU80), together at different weight ratios (95/5 or 90/10 EPM/PK, Table 2) in 50 mL THF at room temperature. BM was added to the mixture in a stoichiometric amount (1:1 molar ratio between maleimide and total furan groups of both polymers). The molar ratio of these furan units in the EPM-FU and PK-FU parts of these blends is close to unity, i. e. it ranges from 0.5 (for 10PK-FU80) to 2.0 (for 5PK-FU40). The reaction mixtures were stirred for 24 hr and the solvent was evaporated at 50 °C. All samples were compression molded into homogeneous samples for 40 min at 150 °C under a pressure of 100 bar and thermally annealed for 24 hr at 50 °C for subsequent mechanical testing. “Reprocessed” sample bars were prepared by cutting or grinding these bars into small pieces (± 50 mm³) and compression molding these pieces into new, coherent samples similar to the original bars.

Table 2. Experimental formulations of EPM-FU/(modified PK) blends with stoichiometric amounts of BM cross-linker.

<i>Sample</i>	<i>EPM-FU</i> (g)	<i>PK-FU or -BU</i> (g)	<i>EPM /PK</i> (w/w)	<i>BM</i> (mg)
EPM-FU	4.20	0.00	100/0	164
5PK-BU80	4.00	0.21	95/5	153
5PK-FU40	3.97	0.21	95/5	248
5PK-FU60	3.97	0.21	95/5	287
5PK-FU80	4.00	0.21	95/5	322
10PK-BU80	3.99	0.44	90/10	147
10PK-FU40	3.91	0.45	90/10	362
10PK-FU60	3.98	0.45	90/10	438
10PK-FU80	4.00	0.44	90/10	509

Characterization

FT-IR spectra were obtained using a Perkin-Elmer Spectrum 2000 in transmission mode or in Attenuated Total Reflection (ATR) mode with a diamond crystal. Samples for transmission FT-IR measurements were compression molded into 0.1 mm thick films for 30 min at 150 °C and 100 bar and measured in a KBr tablet holder. Ground samples and powders were measured using the ATR setup of Greasby Specac. Measurements were performed over a spectral range from 4000 to 600 cm⁻¹ at a resolution of 4 cm⁻¹, averaging 32 scans. Deconvolution was used to integrate the areas related to the anhydride peak at 1856 cm⁻¹ and the reference peak at 723 cm⁻¹. Elemental analysis was performed with an EuroVector EA. ¹H-NMR spectra were recorded on a Varian Mercury Plus 400 MHz spectrometer using DMSO-d₆ as solvent. The apparent cross-link density was assessed via equilibrium swelling tests in decalin at room temperature. About 500 mg of dried, cross-linked sample was immersed in 15 mL decalin for 72 hr in order to reach the equilibrium swelling. The sample was weighed after removing the decalin wetting the surface (W₁) and was then dried in a vacuum oven at 80 °C until a constant weight was reached (W₂). The weights of the swollen and dried samples were used to calculate the apparent cross-link density using the Flory-Rehner equation (Eq. 4) [40].

$$\frac{\ln(1 - V_R) + V_R + \chi V_R^2}{2V_S(0.5V_R - V_R^{1/3})} \text{ with } V_R = \frac{W_2}{W_2 + (W_1 - W_2) \frac{\rho_{sample}}{\rho_{decalin}}} \quad (\text{Eq. 4})$$

with ρ_{sample} the density of the blend (0.86 g/cm³ on average as the majority of each blend consists of EPM), $\rho_{decalin}$ and V_S the density and the molar volume of the decalin solvent, respectively (0.896 g/cm³ and 154.3 cm³/mol, respectively), and χ is the Flory-Huggins interaction parameter (0.121 + 0.278V_R for EPDM in decalin [28]). It is noted that the Flory-Rehner equation is only applicable for homogeneous rubber samples with difunctional cross-links, whereas the samples in this study are phase-separated mixtures of EPM with PK. Therefore, with the modified PK partly acting as a multi-functional cross-linking aid, the calculated values only represent apparent cross-link densities. Extraction experiments were performed by immersing small pieces (< 1 g) of sample in refluxing acetone for 72 hr, filtration of the mixture and drying the residue for 24 hr at 50 °C in a vacuum oven.

Small-angle X-ray scattering (SAXS) measurements were performed on an advanced Nano-Star SAXS setup, a homemade assembly of a NanoStar camera and a Microstar X-ray generator from Bruker AX-S. Optical microscopy was performed on a Nikon Eclipse E600 and images were captured with a Coolpix camera with MDC lens. Differential Scanning Calorimetry (DSC) was performed on a Perkin-Elmer DSC Pyris 1 under a nitrogen atmosphere. The samples for DSC were weighed (10-17 mg) in an aluminum pan, which was then sealed. The sample was heated from -80 to 180 °C and then cooled to -80 °C using heating and cooling rates of 10 °C/min. Four cycles were performed for each sample. Dynamic Mechanical Thermal Analysis (DMTA) was performed using a Rheometric Scientific Solid Analyzer (RSA II) in fiber film 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 to 180 °C and back with a heating and cooling rate of 0.05 °C/min. DMTA specimens were prepared by compression molding 500 mg of product into 45 mm long, 5 mm wide and 1 mm thick rectangular bars. Similar samples were used for tensile tests, which were performed on an Instron 5565 with a clamp length of 15 mm, according to the ASTM D4-112 standard. 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. Data presented are averages of the other 8 tests. Hardness Shore A was measured using a Bareiss Durometer, according to the ASTM D2240 standard. Test samples with a thickness of 2.0 ± 0.1 mm were prepared by compression molding. Average values were obtained from 10 measurements. Compression set tests were performed for 70 hr at room temperature on a homemade device, according to the ASTM D931 standard. Each measurement was performed in duplo on 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.

Results

Polymer modification

The modification of PK was performed via the Paal-Knorr reaction with FFA or butylamine at a temperature of 110 °C. The reactions proceeded to nearly full conversion of the amine (Table 1: >

96%) and, thus, the targeted carbonyl conversions are almost reached, which is in agreement with previous results for this system [20-23]. A comparison of the ^1H -NMR spectra of modified PK-FU and the original PK (Figure 1A) clearly shows the occurrence of a broad peak at ~ 5.7 ppm, which has been assigned to the hydrogen atoms of the pyrrole ring in the PK-FU backbone. The peak at 4.9 ppm has been assigned to the methylene group connecting the furan to the pyrrole, while the signals at 7.3, 6.2 and 5.9 ppm have been assigned to the hydrogen atoms of the pending furan ring [21, 23]. Figure 1 only shows these relevant peaks, which clearly increase in intensity with increasing furan concentration in the reaction mixture.

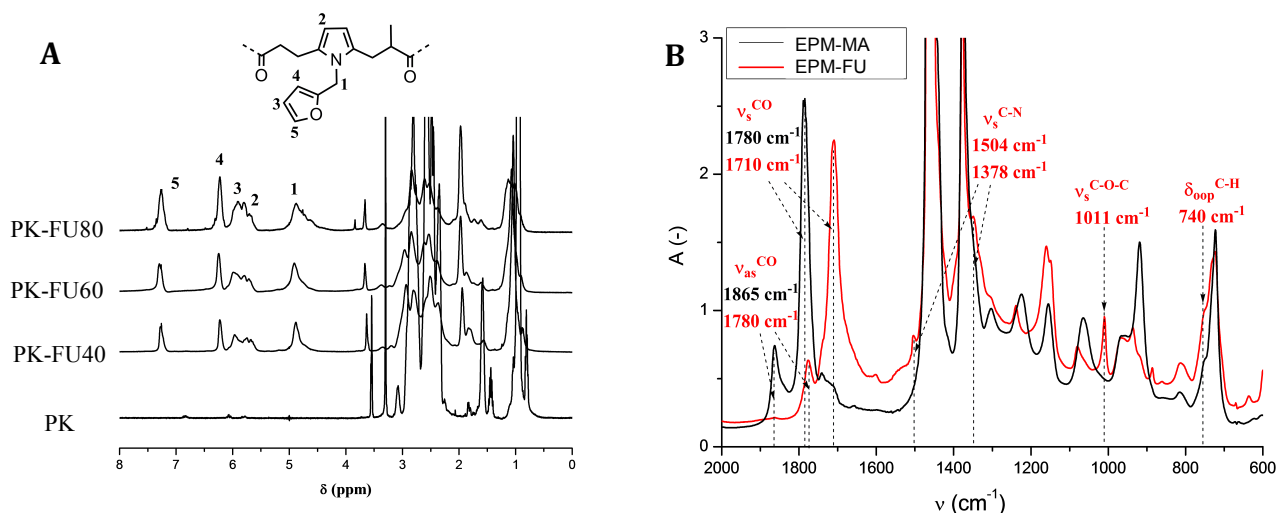


Figure 1. A: ^1H -NMR spectra of unmodified polyketone (PK) and furan-modified polyketone with different degrees of carbonyl conversion (PK-FU40, PK-FU60 and PK-FU80) and B: transmission FT-IR spectra of EPM-MA and the modified EPM-FU.

The modification of EPM-MA with FFA into EPM-FU was studied by transmission FT-IR (Figure 1B). The most indicative results for the conversion of the cyclic anhydride into the imide are the nearly complete disappearance of the C=O anhydride asymmetric stretching band at 1856 cm^{-1} and the appearance of the C=O imide stretching and the C-N imide symmetric stretching bands at 1710 cm^{-1} and 1378 cm^{-1} , respectively [23, 41]. The appearance of the symmetric C-O-C stretching band at 1013 cm^{-1} and of the out-of-plane hydrogen bending band at 740 cm^{-1} clearly indicates the presence of furan groups linked to EPM-FU [42]. The reaction conversion was calculated to be 99.9 %, which is in line with the quantitative modification achieved in our previous work [20].

Blend characterization

ATR infrared spectra of the EPM-FU/PK-FU blends with and without BM (Figure 2), clearly show the appearance of the C-O-C stretching band of the DA adduct at 1185 cm^{-1} and the disappearance of the symmetric C-O-C stretching band at 1013 cm^{-1} and of the out-of-plane hydrogen bending band at 740 cm^{-1} of the furan rings. This unambiguously proves the formation of Diels–Alder adducts in the blends [21, 23, 43, 44], whereas the C-N stretching band of the imide rings at 1378 cm^{-1} merely demonstrates the presence of BM [24]. Unfortunately, it is not clear from these spectra whether the DA adducts are formed in the EPM-FU and the PK-FU phases and/or between them.

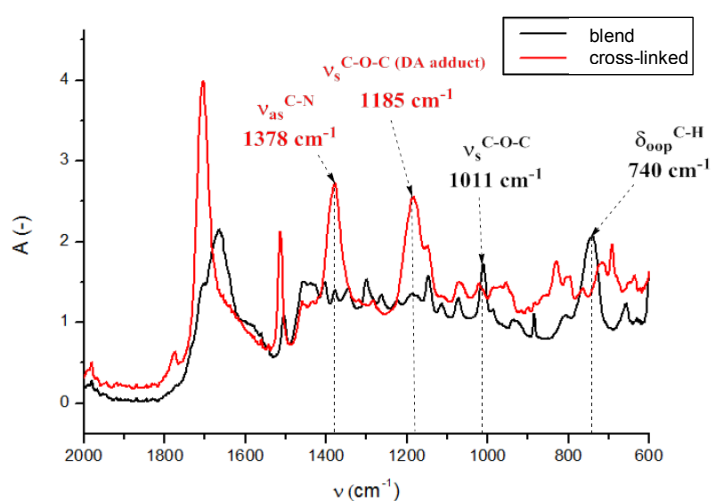


Figure 2. ATR FT-IR spectra of a PK-FU/EPM-FU blend before and after cross-linking with BM.

The occurrence of cross-linking of the PK phase of the blends was shown by extraction experiments in acetone. The cross-linked PK-FU80 could not be extracted from the 5 and 10PK-FU80 samples, whereas all PK-BU was quantitatively extracted from the 5 and 10PK-BU80 samples.

The large difference in polarity between the modified EPM and PK polymers (calculated solubility parameters are $16\text{ (J/cm}^3)^{0.5}$ for EPM-FU and 22 to 26 $\text{(J/cm}^3)^{0.5}$ for PK-FU, depending on the degree of furan functionalization [45]) suggests that EPM-FU and PK-FU are not thermodynamically miscible. In the previous study [24] EPM was dispersed in PK and formed phase-separated domains. In this study PK is the minor phase (5 to 10 wt%) and will form phase-separated domains dispersed in the rubber matrix. PK domains are indeed visible with optical microscopy on the freshly cut surface of a compression molded blend sample and seem to have a large variation in size (Figure 3A). DSC scans of

cross-linked EPM-FU/PK-FU blends show the glass transition of EPM-FU at - 60 °C (Figure 3B). The T_g of the starting PK-FU, between 5 °C and 30 °C, depending on the degree of furan functionalization [22], is increased to above 100 °C upon cross-linking with BM and is located just beneath the retro-DA endothermic peak of the cross-linked sample, giving it an asymmetric shape. This implies that PK-FU does indeed form rigid/hard domains in the soft EPM-FU matrix at room temperature. Finally, the inclined slopes of the intensity of SAXS scans (not shown for brevity) at large length scale of both the cross-linked and non-cross-linked blends also indicate that domains larger than 100 nm are present [46].

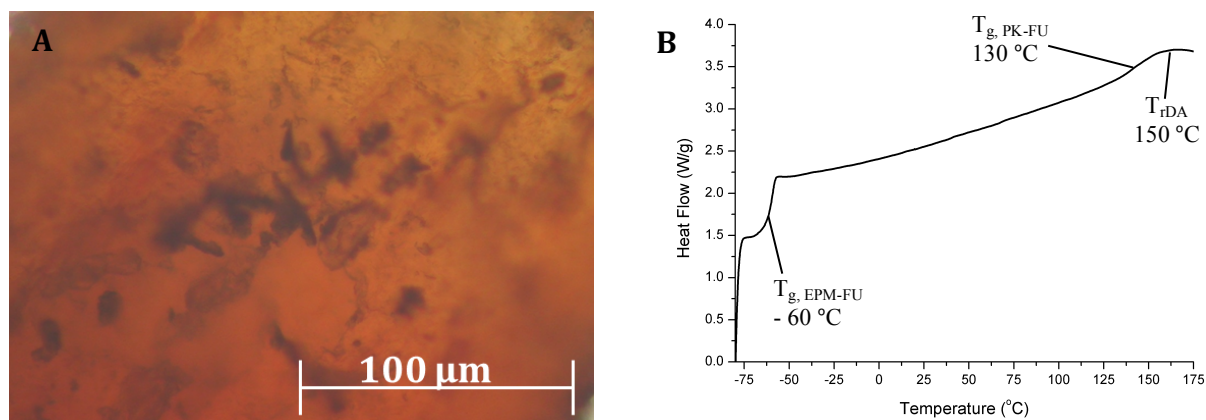


Figure 3. A: Optical micrograph of 10PK-FU60, displaying the phase-separation of 100 μm large PK domains (black spots) in the EPM matrix and B: DSC scan of 10PK-FU60 displaying two separate T_g of EPM-FU and PK-FU.

Both the furan functionalization of PK-FU and the content of the modified PK-FU affect the apparent cross-link density of the blends (Figure 4A). It is noted again that the apparent cross-link densities shown in Figure 4 are useful for relative comparisons only. The blends containing PK-FU have higher cross-link densities than the neat EPM-FU rubber, indicating that PK-FU indeed acts as a coagent for DA cross-linking with BM. For a given PK-FU product the apparent cross-link density increases with the amount of PK-FU. At constant PK-FU content the cross-link density increases with the degree of furan-functionalization of PK (and corresponding equivalent of BM). Similar behavior has been reported for rubber-based systems compounded with phenolic resins, either interpenetrating [30-32] or chemically bonded to the rubber matrix [33-38]. PK-BU is not able to form any DA adduct and, indeed, the reference blends with PK-BU show the lowest apparent cross-link densities, which are

even lower than that of the neat EPM-FU rubber. The effect of PK-BU seems to be larger than can be explained by the 5-10 wt% dilution of EPM-FU. This may be because the polar BM cross-linkers prefer the more polar PK-FU phase over the less polar EPM-FU phase.

The apparent cross-link density is also plotted versus the total BM content (Figure 4B), which corresponds with the formed amount of furan/maleimide DA adducts in the blends. The fairly linear correlation shows that the apparent cross-link density of the blends is indeed determined mainly by the BM content and thus the total furan content. When increasing the BM content in EPM-FU in the absence of PK-FU [47] on the other hand results in a decrease of the apparent cross-link density due to capping of pendant furan-groups with BM. Capping means that all furan units are linked to a single BM molecule, i. e. one maleimides function of BM is connected to only one polymer chain, while its second maleimides group is not connected. As a result, no cross-links can be formed. For the EPM-FU/PK-FU blends such an optimum is not observed as these samples always contain equimolar amounts of furan and BM, resulting in a continuously increasing apparent cross-link density.

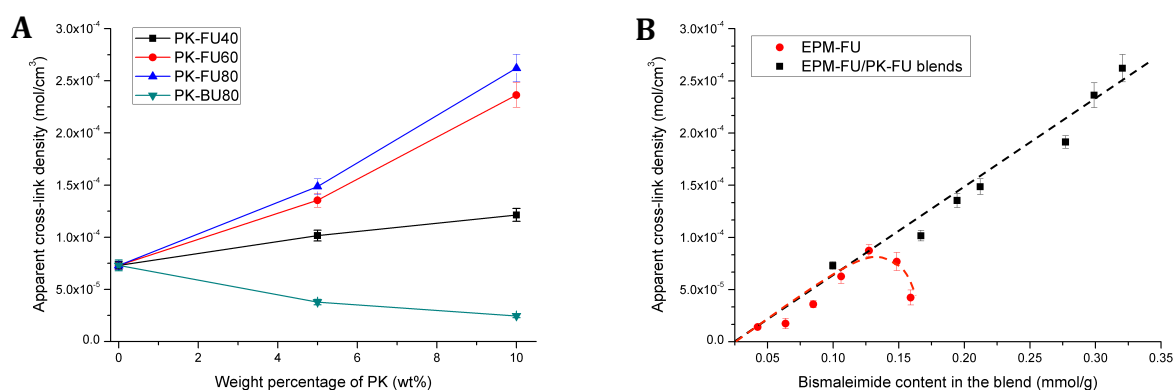


Figure 4. A: Apparent cross-link density, determined via equilibrium swelling, for cross-linked blends of EPM-FU and modified PK as a function of modified PK content and B: as a function of the total BM content in the blend (PK-BU data not included). Error bars indicate $\pm 1 \sigma$ standard deviations.

Blend properties

The temperature response of the storage modulus of the cross-linked 95/5 (w/w) EPM-FU/PK blends was studied by DMTA (Figure 5). The storage modulus shows a gradual decrease over a temperature

range from 20 to 150 °C. This plateau is followed by a steep drop above 150°C for all samples when tested. The rubber plateau is a typical feature of covalently cross-linked rubbers [1], while the drop indicates the softening of the material upon de-cross-linking via the retro-DA reaction and going into the flow regime [21]. When heated samples were cooled back to 20 °C and tested again, they display a high recovery of the storage modulus at 25 °C, notably 88 %, 94 % and 92 % for 5PK-FU40, 5PK-FU60 and 5PK-FU80, respectively. These results confirm the reversibility of cross-linking in the blends, which is in agreement with the thermoreversible behavior of the neat cross-linked rubber reported previously [20].

The samples with PK-FU display a higher storage modulus at low temperatures than the neat EPM-FU rubber as a result of increased cross-linking. The increase in storage modulus with furan functionalization of the PK-FU at the same PK loading agrees with the increased cross-link density of these samples and suggests an interaction between PK-FU and EPM-FU. The rubber plateaus of the samples with PK-FU seem to have a more negative slope compared to EPM-FU, especially at higher PK loading. This is probably due to the gradual de-cross-linking via the retro-DA reaction (both within the PK domains in the rubber matrix and between the PK domains and the rubber) and the subsequent softening of the PK domains, resulting in a loss of rubber elasticity. Finally, the addition of PK-BU to the rubber results in a decrease of the storage modulus, which decreases rapidly with the temperature approaching 150 °C. The addition of PK-BU therefore appears to disturb the elastic rubber network strongly, which was also witnessed from the apparent cross-link density. This may be because the polar BM cross-linker partly dissolves in the polar PK domains and, thus, is excluded from cross-linking the apolar EPM-FU.

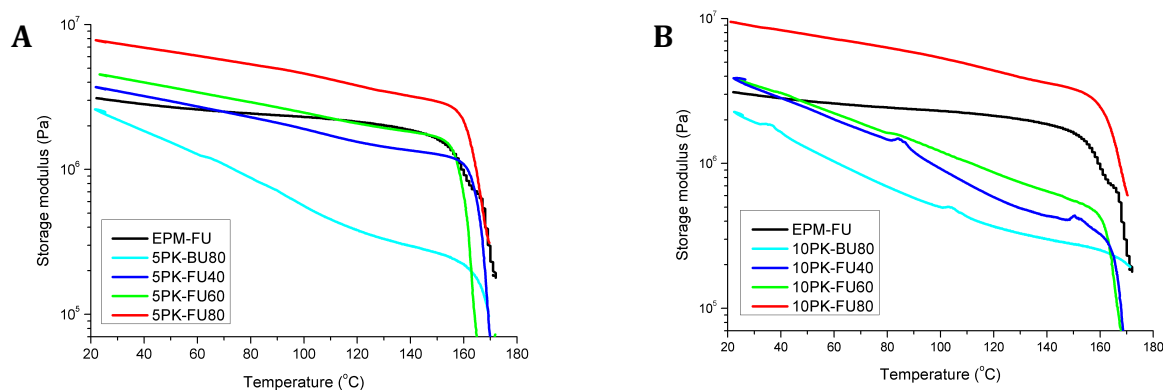


Figure 5. Storage modulus as a function of temperature for blends of EPM-FU with A: 5 wt% and B: 10 wt% of modified PK, thermo-reversibly cross-linked with BM, as measured with Dynamic Mechanical Thermal Analysis.

All blends exhibit a significantly higher hardness than the neat rubber (Figure 6A). The hardness of the mixtures with PK-FU shows the same trend as observed for the apparent cross-link density and the storage modulus. The higher hardness of the PK-BU reference sample is not consistent with the lower apparent cross-link density and suggests that the PK-BU domains are rigid. The compression set at room temperature (Figure 6B) assesses the ability of a sample to recover its original shape after deformation and, thus, provides a practical measure of the elasticity of a sample, with a low compression set representing high elasticity. The presence of PK in the blends with EPM-FU rubber has a detrimental effect on the compression set. This is particularly evident for the samples with PK-BU and with a high PK-FU content. When comparing mixtures with the same PK content, the compression set becomes lower with increasing degree of furan-functionalization.

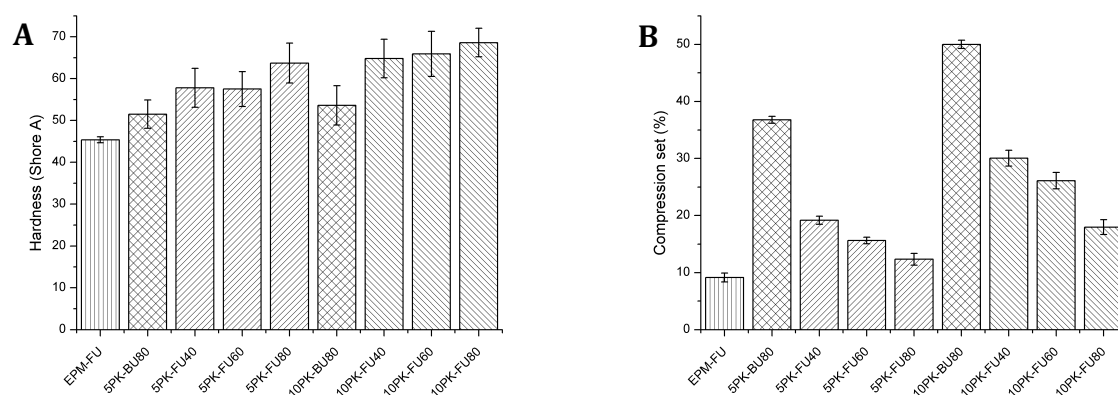


Figure 6. A: Hardness and B: compression set at room temperature of cross-linked blends of EPM-FU and PK-FU. Error bars indicate $\pm 1 \sigma$ standard deviations.

The tensile tests results (Figure 7A) show that both the Young's modulus (Figure 7B) and the tensile strength at break (Figure 7C) are significantly higher for the samples containing PK-FU compared to the neat rubber. They increase with both the PK-FU furan-functionalization and with the PK-FU content. Conversely, the elongation at break of these samples (Figure 7D) shows an opposite trend, i. e. it decreases with both PK content and degree of furan functionalization. The increased Young's modulus and the decreased elongation at break of the PK-BU reference samples imply that the observed effects should be attributed to both the addition of the non-elastic PK, as well as to the increased apparent cross-link density.

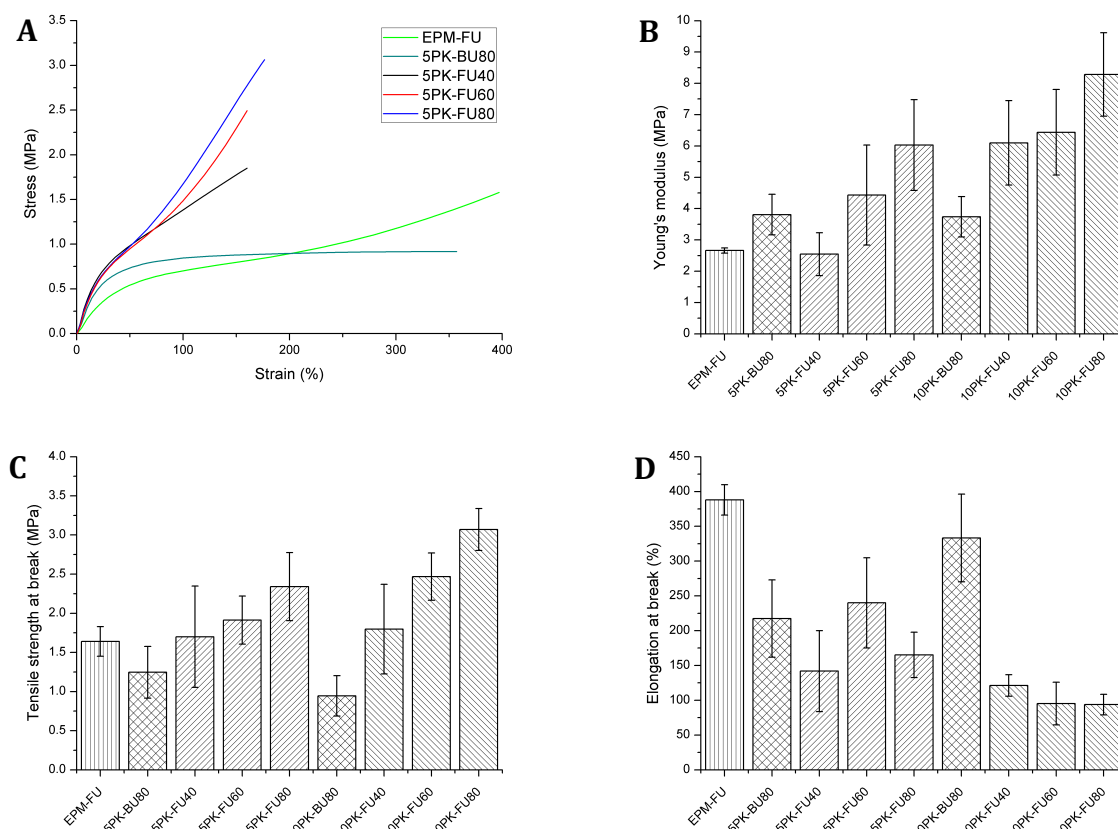


Figure 7. Median stress-strain curves (A) and average Young's modulus (B), tensile strength (C) and elongation at break (D) for cross-linked blends of EPM-FU and PK-FU. Error bars indicate $\pm 1 \sigma$ standard deviations.

A representative selection of samples with low and high PK-FU content and furan-functionalization has been reprocessed to determine the retention of the properties (reworked sample/original sample x 100%) (Figure 8). For all these samples the cross-link density and hardness are fully retained (> 95-

105 %) upon reprocessing them. The compression set and tensile properties however, are significantly influenced by reprocessing the sample bars. This influence is more evident for samples with higher PK-FU content. This may be related to the phase separation of the EPM-FU matrix and the PK-FU domains. Previous studies showed that the properties of the pure PK-FU are fully retained upon reprocessing [21, 23]. In this study the EPM-FU matrix reconnects the cut sample pieces upon reprocessing. Impoverishment of the dispersed PK-FU in the healed region may explain deterioration of the compression set and the tensile strength. Nevertheless, material properties of the reprocessed EPM-FU/PK-FU blends are still retained between 70 % and 120 % and superior to those of the starting EPM-FU.

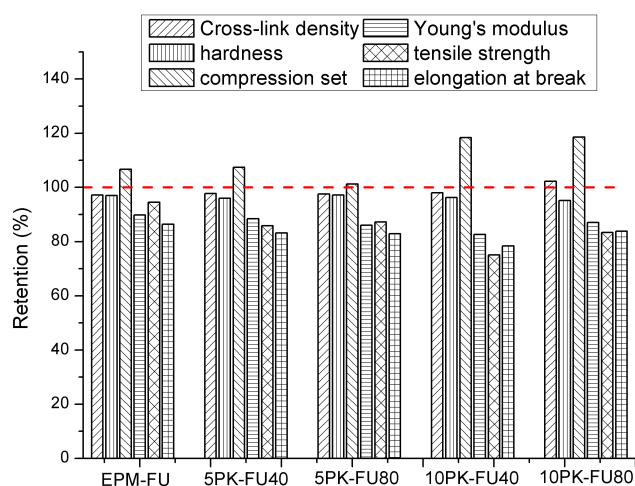


Figure 8. Retention of the cross-link density, hardness, compression set, Young's modulus, tensile strength and elongation at break for DA cross-linked EPM-FU and four characteristic EPM-FU/PK-FU blends with different PK-FU content and furan-functionalization.

Discussion

The material properties of the different EPM-FU/PK blends are compared to those of the starting EPM-FU and discussed in terms of the cross-link density. Upon addition of PK-BU80, the hardness and Young's modulus of these reference systems increases, while the cross-link density decreases. So, PK-BU interferes with cross-linking and seems to act as a filler. The tensile strength and elongation at

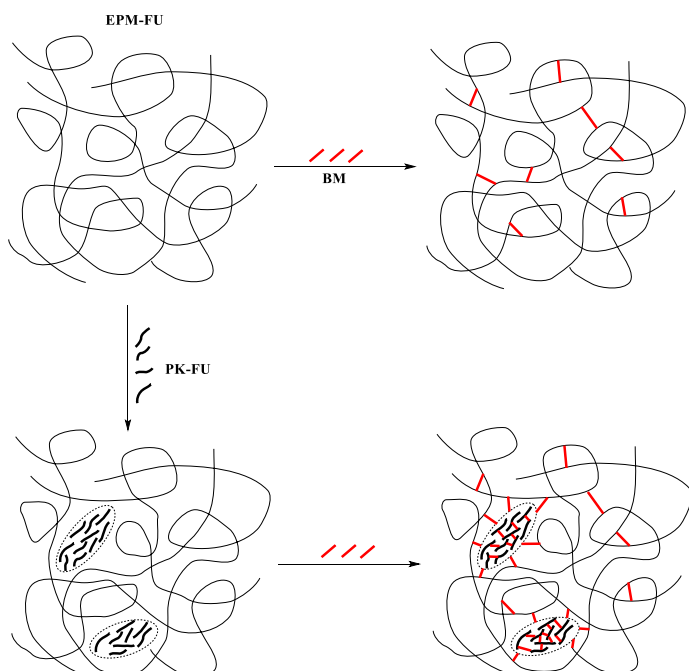
break decrease though, so PK-BU is an inert and not a reinforcing filler. Finally, the compression set strongly increases, which indicates a major loss of elasticity. This may be because the polar BM migrates from the apolar EPM-FU into the more polar PK-BU domains. In summary, PK-BU is an inert filler that disrupts cross-linking.

An increase of the furan content of the PK-FU added to EPM-FU results in an increase of the cross-link density, which correlates with the increase in hardness, Young's modulus and tensile strength and the decrease in elongation at break and compression set. These results are fully in line with the well-known trends of these properties with cross-link density for vulcanized EPDM [48] and rubber in general [49]. An increase of the amount of PK-FU also results in an increased cross-link density, which again fully explains the increase of the hardness, Young's modulus and tensile strength and the decrease of the elongation at break. However, addition of PK-FU to EPM-FU results in an increased compression set (i.e. reduced elasticity), which is not consistent with the increased cross-link density.

A series of plots of hardness, compression set, Young's modulus, tensile strength and elongation at break versus the apparent cross-link density was constructed (Figure S1). The trends discussed above are clear, but there seems to be no simple correlation, i. e. there is a lot of scatter in the data. This shows that the EPM-FU/PK-FU blends cross-linked with BM are complex systems with properties not solely determined by the cross-link density. For a part, this may be because the use of the apparent cross-link density is tricky, since it is not absolutely correct due to the heterogeneity of the EPM-FU/PK-FU-blends and the multifunctional character of PK-FU.

Overall, PK-FU behaves as a multi-functional cross-linking aid, though it also seems to have some characteristics of an inert filler. PK-FU does not act in the same way as a coagent in peroxide curing of elastomers. For peroxide resins, the addition of a coagent results in a higher cross-link density at the same peroxide content whereas the multi-functional PK-FU cross-linking aid allows for the addition of higher amounts of BM cross-linker. This results in higher cross-link densities and a corresponding improvement of the mechanical properties. The use of PK-FU as a multifunctional cross-linking aid is expected to create hard, cross-linked domains in the EPM-FU matrix, thereby increasing the apparent cross-link density (Figure 9).

Figure 9. Schematic representation of the formation of highly cross-linked PK-FU domains in EPM-FU rubbers upon addition of BM cross-linker.



The addition of PK-FU to the EPM-FU rubber allows the apparent cross-link density of the rubber compound to approach industrially relevant cross-link density levels (equal or above 10^{-4} mol/cm³) [50, 51]. On top of that, PK can easily be functionalized with different amounts of furan groups, allowing for a new way of tuning the cross-link density of the resulting rubber mixtures. Finally, the addition of PK-FU does not affect the thermoreversible nature of EPM-FU cross-linked with BM, allowing for ‘cradle-to-cradle’ production and recycling of the waste into new products with similar mechanical properties.

Conclusions

The cross-link density of thermo-reversibly cross-linked EPM rubber was increased beyond the limit imposed by its degree of maleic anhydride functionalization without affecting the thermoreversible character of the cross-links. This was achieved by mixing furan-modified EPM rubber with various amounts of a furan-functionalized PK and cross-linking the blend with an aromatic BM through Diels Alder chemistry. The addition of PK-FU to the thermoreversibly cross-linked EPM-FU system allows

for the addition of larger amounts of BM, resulting in an increase of the cross-link density. Mechanical properties, such as hardness, compression set, Young's modulus, tensile strength and elongation at break, can therefore be modulated by varying the furan functionalization and/or the amount of PK-FU. It is concluded that PK-FU acts as a multifunctional cross-linking aid, though it also has some inert filler characteristics. The resulting cross-linked polymer network exhibits excellent reversibility as proven by DMTA and the retention of properties upon reprocessing the material, allowing for the material to be recycled on a 'cradle-to-cradle' basis.

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