Video Article

The Preparation and Properties of Thermo-reversibly Cross-linked Rubber Via Diels-Alder Chemistry

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Abstract

A method for using Diels Alder thermo-reversible chemistry as cross-linking tool for rubber products is demonstrated. In this work, a commercial ethylene-propylene rubber, grafted with maleic anhydride, is thermo-reversibly cross-linked in two steps. The pending anhydride moieties are first modified with furfurylamine to graft furan groups to the rubber backbone. These pendant furan groups are then cross-linked with a bis-maleimide via a Diels-Alder coupling reaction. Both reactions can be performed under a broad range of experimental conditions and can easily be applied on a large scale. The material properties of the resulting Diels-Alder cross-linked rubbers are similar to a peroxide-cured ethylene/propylene/diene rubber (EPDM) reference. The 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, solubility tests and mechanical properties. Recyclability of the material 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 mechanical properties, which is not possible for conventionally cross-linked rubbers.

Video Link

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Introduction

Sulfur vulcanization and peroxide curing are currently the main industrial cross-linking techniques in the rubber industry, yielding irreversible chemical cross-links that prevent melt reprocessing.[1, 2] A 'cradle to cradle' approach to recycle cross-linked rubbers requires a material that behaves similar to permanently cross-linked rubbers at service conditions, while having the processability and complete recyclability of a thermoplastic at high temperatures. An approach to achieve such recyclability uses rubbery networks with reversible cross-links that respond to an external stimulus, such as temperature (most feasible from the viewpoint of future industrial applications).[3-5] The formation of these cross-links at relatively low service temperatures is required for good mechanical behavior of the rubber, while their cleavage at high temperatures (similar to processing temperature of original non-cross-linked compound) allows for recycling of the material.

Some specific materials can be reversibly cross-linked by making use of so-called dynamic covalent networks via polycondensation reactions[6] or by so-called reversible network topology freezing via transesterification reactions.[7-9] The disadvantage of these approaches is the necessity of designing and synthesizing new polymers rather than modifying existing, commercial rubbers that already have the desired properties. Techniques to thermo-reversibly cross-link rubbers involve hydrogen bonding, ionic interactions and covalent bonding such as via thermo-activated disulfide rearrangements.[10-13] Recently, thermo-reversible cross-linking via Diels-Alder (DA) chemistry was developed.[14-21] 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.[17, 22-24] Their low coupling and high decoupling temperatures make furan and maleimide excellent candidates for reversible polymer cross-linking.[18-20, 25-28]

The aim of the present work is to provide a method for the use of DA chemistry as a thermo-reversible cross-linking tool for an industrial rubber product (**Figure 1**).[5] First, 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).[29-34] Secondly, a furan group can be grafted onto such a maleated EPM rubber by inserting furfurylamine (FFA) into the pendant anhydride to form an imide.[35, 36] Finally, the furan moieties that are thus attached to the rubber backbone can then participate in thermo-reversible DA chemistry as an electron-rich diene.[25, 37] The electron-poor bis-maleimide (BM) is a suitable dienophile for this cross-linking reaction.[19, 26, 38]

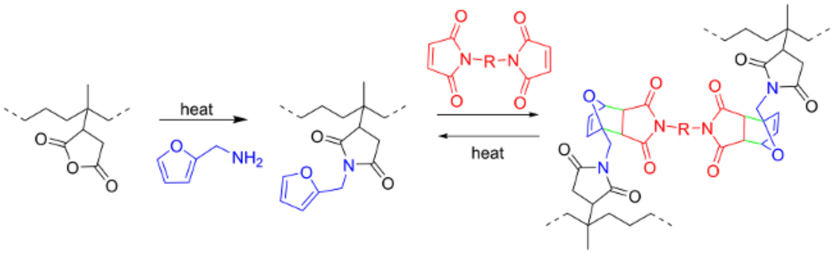

Figure 1. Reaction scheme. Furan grafting and bismaleimide cross-linking of EPM-g-MA rubber (reprinted with permission from [5]). Please click here to view a larger version of this figure.

Protocol

1. Rubber Modification

1. Prepare the maleated EPM (EPM-g-MA, 49 wt% ethylene, 2.1 wt% MA, Mn = 50 kg/mol, PDI = 2.0) rubber and furfurylamine (FFA) before starting the experiment as indicated in steps 1.1.1-1.1.4.[5]
    1. Dry the EPM-g-MA rubber in a vacuum oven for one hour at 175 °C to convert present di-acid into anhydride.[11]
    2. Compression mold a 0.1 mm thick rubber film in a hot press for 10 min at 150 °C and 100 bar.
    3. Record a transmission infrared spectrum of the resulting film after placing it in a KBr tablet holder.
    NOTE: The conversion of the hydrolyzed di-acid into anhydride is complete if the typical carboxylic acid peak ($\bar{\nu}^{s}_{CO}$ = 1,710 cm^{-1}) is absent and the characteristic cyclic anhydride peak ($\bar{\nu}^{as}_{CO}$ = 1,856 cm^{-1}) is present.[5]
    4. Using standard distillation glassware, distill 2.8 g FFA (boiling point = 145 °C, 28.9 mmol; 3.0 eq. based on MA content in EPM-g-MA) under atmospheric pressure.

2. Prepare a 10 wt% rubber solution by weighing 45.0 g of EPM-g-MA rubber (9.6 mmol MA) and dissolving it in 500 ml tetrahydrofuran (THF) at 23 °C in a closed beaker under vigorous stirring.
3. Add the 2.8 g freshly distilled FFA to the 10 wt% rubber solution.
4. Stir the reaction mixture in a closed system at 23 °C for at least 1 hr.
5. Precipitate the reaction mixture by pouring it slowly into a tenfold (5 L) of acetone under mechanical stirring, yielding the polymer product as white threads that are easily fished out of the beaker using large tweezers.
6. Dry the collected product (EPM-g-furan) to constant weight in a vacuum oven at 35 °C (this takes approximately 1 day).
7. Compression mold the resulting, slightly yellowish product in a mold between two metal plates in a hot press for 10 min at 175 °C and 100 bar to convert the intermediate maleamic acid product into the imide product.
8. Cut the resulting plaque of rubber in small pieces (0.05 g) with scissors and wash them thoroughly by immersing them in acetone to remove any unreacted FFA.
9. Record a transmission infrared spectrum of the product in a KBr tablet holder after compression molding it into a 0.1 mm thick film.[5]
NOTE: The absence of any remaining amide-acid can be deduced from the absence of a peak at 1,530 cm^{-1}.[39, 40] The most illustrative indication for the successful modification are the nearly complete disappearance of $\bar{\nu}^{as}_{CO}$ at 1,856 cm^{-1} of the anhydride and the appearance of $\bar{\nu}^{s}_{CO}$ at 1,710 cm^{-1} and the C-N stretching vibration ($\bar{\nu}^{s}_{CN}$ = 1,378 cm^{-1}) of the maleimide.
10. Determine the reaction conversion of EPM-g-MA to EPM-g-furan from the decrease in absorbance of the C=O symmetrical stretch vibration of the anhydride groups ($\bar{\nu}^{as}_{CO}$ = 1,856 cm^{-1}) by integrating the areas under the individual infrared (FT-IR) peaks after deconvolution (R^2 > 0.95).[5]
NOTE: The methyl rocking vibration ($\rho^{ip}_{CH_3}$ = 723 cm^{-1}), originating from the EPM backbone, remains unchanged upon modification and can be used as an internal reference.
11. Determine the modification conversions by performing Elemental Analysis (EA) for N, C and H on the washed and dried rubber samples.[5]
NOTE: The molar contents can be derived from the measured mass percentages. The molar nitrogen content in EPM-g-furan is equal to that of the grafted furan groups. The conversion can be calculated by comparing the molar ratio of MA-grafted monomer to the non-grafted EPM monomers in the EPM-g-MA precursor (7.69×10^{-3}) with the molar ratio N:EPM of the EPM-g-furan sample.
12. Measure the Shore A Hardness of the compression molded samples at least 10 times pressing a durometer onto a rubber sample, covering the entire cylindrical surface of the Durometer.[5]
NOTE: Samples with a thickness of 2 ± 0.1 mm should be used for these tests.
13. Measure the elongation (at break) and the ultimate tensile strength by performing tensile tests on samples of approximately 1 mm thick and 5 mm wide using a clamp length of 15 mm and a strain rate of 500 ± 50 mm/min. Determine the Young's modulus from the initial slope of the resulting stress-strain curves.
NOTE: For each measurement, test 10 samples and exclude two outliers with the highest and the lowest values.
14. Determine the compression set at 23 °C by compressing cylindrical samples with a thickness of 6 ± 0.1 mm (t_0) and a diameter of 13 ± 0.1 mm between to metal plates to 3/4th of their initial thickness (t_n) for 70 hr, let them relax at 50 °C for ½ hr and measure the thickness (t_i).
NOTE: The compression set value can be determined from $(t_0-t_i)/(t_0-t_n)$.

2. Diels-Alder Cross-linking and Reprocessing

1. Before the experiment, synthesize the aliphatic bismaleimide (BM) from didodecylamine and maleic anhydride (MA) according to a reported procedure.[41]

2. Weigh 40.0 g of EPM-g-furan rubber (8.6 mmol furan content) and 0.04 g phenolic anti-oxidant (octadecyl-1-[3,5-di-tert-butyl-4-hydroxyphenyl]propionate) and dissolve them in a large, closed beaker with 500 ml THF at 23 °C.
3. Add 1.48 g of the aliphatic bismaleimide (4.3 mmol, 0.5 eq. based on furan content in EPM-g-furan) to beaker with the 10 wt% solution.
4. Stir the reaction mixture for at least 1 hr at 50 °C in the closed beaker, then remove the cap to open the system to evaporate the solvent. Evaporation of the THF can also be performed using a rotary evaporator.
5. Dry the collected product to constant weight in a vacuum oven at 35 °C.
6. Compression mold the product for 30 min at 175 °C and 100 bar.
7. Anneal the resulting product by storing it in an oven at 50 °C for at least three days.
8. Cut the resulting plaque of rubber in small pieces (0.05 g) using scissors and wash them thoroughly by immersing them in acetone to remove any unreacted components and compression mold it into a 0.1 mm thick film.
9. Record an transmission infrared spectrum of the resulting film in a KBr tablet holder, using the same set-up as described for 1.9.1.[5]
10. Determine the cross-linking conversion from relative decrease in the C-O-C symmetric stretch vibration of the furan rings ($\bar{\nu}^{s}_{COC}$ = 1,013 cm^{-1}) as described in 1.10.[5]
11. Determine the cross-linking conversion by performing EA for N, C and H on the washed and dried rubber samples.[5]
12. Determine the Shore A hardness, Young's modulus, the elongation at break, the ultimate tensile strength and compression set at 23 °C in the same way as described in 1.12-14.
13. Reprocess the samples after testing by cutting them into small pieces using scissors (± 50 mm^3) and compression molding these under the same conditions into new, homogeneous samples with the same dimensions.

3. Peroxide and Sulfur Curing of ENB-EPDM

1. Heat an internal batch mixer to 70 °C and let it rotate at 50 rpm.
   NOTE: An initial conditioning step by flushing the chamber with nitrogen gives better control of the cross-linking processes.
2. Feed 18.1 g of ENB-EPDM (48 wt% ethylene, 5.5 wt% ENB) to the internal batch mixer to reach a 70% fill factor and mix for 2 min to yield a homogeneous melt.
3. Feed 1.25 phr of peroxide di(tert-butylperoxy-isopropyl) benzene) or 1.88 phr of a 80% pure, standard, semi-efficient sulfur vulcanization system and mix it with the rubber for 3 min at 70 °C.
4. Compression mold the resulting compound in a hot press for 30 min at 175 °C and 100 bar to cure it.
5. Determine the Shore A hardness, Young's modulus, the elongation at break and the ultimate tensile strength compression set in the same way as described in 1.12-14.

4. Cross-link Density Determination

1. Cut a piece of compression molded, cross-linked rubber of approximately 50 mg using scissors.
   1. Determine the initial weight of the rubber sample precisely by weighing it in a 20 ml glass vial (W_0).
   2. Immerse the weighed rubber in 15 ml of decalin.

2. Let the rubber swell in the decalin until its weight does not increase anymore and equilibrium swelling is reached (approximately 3 days).
3. Carefully take the swollen sample out of the vial and carefully dab the surface with a paper tissue to remove any solvent from the surface without squeezing it.
4. Weigh the swollen rubber sample in a new sample vial (W_1).
5. Dry the swollen sample in a vacuum oven at 80 °C until a constant weight is reached and determine the sample's dry weight (W_2).
6. Obtain the gel content from W_2/W_0 x 100%
7. Determine the cross-link density ([XLD] in mol/cm^3) using the Flory-Rehner equation [42, 43], $[XLD]= (\ln(1-V_R)+V_R +\chi V_R^2)/(2V_S(0.5V_R-V_R^{1/3}))$ with V_S the molar volume of the solvent (decalin: 154 ml/mol at 23 °C), χ the interaction parameter (decalin-EPDM: $0.121 + 0.278V_R$[44]) and V_R the volume fraction of rubber in swollen sample that can be determined from $W_2/(W_2+(W_1-W_2)\cdot\rho_{EPM\text{-}g\text{-}furan}/\rho_{decalin})$ with the densities (ρ) being 860 kg/m^3 for EPM-g-furan and 896 kg/m^3 for decalin, respectively.

Representative Results

The successful modification of EPM-g-MA into EPM-g-furan and the cross-linking with the bismaleimide is shown by Fourier transform infrared spectrometry (FTIR) (**Figure 2**). The presence of furan groups in the EPM-g-furan product can be deduced from the splitting of the CC aliphatic stretching peak ($\bar{\nu}^{s}_{CC}$ = 1,050 cm^{-1}) into two furan peaks ($\bar{\nu}^{as}_{COC}$ = 1,073 cm^{-1} and $\bar{\nu}^{s}_{COC}$ = 1,013 cm^{-1}), the appearance of the C=C furan stretching vibration ($\bar{\nu}^{s}_{CC}$ = 1,504 cm^{-1}) and of the deformation vibration at 599 cm^{-1}.[15, 37, 37] The furan ring stretching peaks at 1,436 and 1,345 cm^{-1} cannot not be observed as they are hidden by the large overlapping CH_2-vibrations of the rubber backbone at 1,450 cm^{-1} and 1,350 cm^{-1}.[15] The incorporation of the BM can be deduced from the appearance of δ^{ip}_{DAring} at 1,190 cm^{-1} and of the characteristic succinimide bands ($\bar{\nu}^{s}_{CNC}$ = 1,385 cm^{-1}, δ^{ip}_{HNC} = 1,311 cm^{-1} and δ^{asoop}_{OCN} = 620 cm^{-1}).[45, 46] The furan-related absorption ($\bar{\nu}^{s}_{COC}$) decreases upon cross-linking and the $\bar{\nu}^{s}_{CO}$ carbonyl band increases as a result of a second absorption around 1,770 cm^{-1} that is attributed to the succinimide ring resulting from the cycloaddition.[25]

FTIR and elemental analysis were used to determine the modification and cross-linking conversions (**Table 1**). The FT-IR and EA conversions were used to determine the cross-link density of the DA cross-linked EPM-g-furan, which was found to be $1.8 \times 10^{-4} \pm 3 \times 10^{-5}$ mol/cm^3. According to swell tests (protocol 4), the gel content of all cross-linked samples was approximately 100% and the cross-link density of the DA cross-linked EPM-g-furan was $2.1 \times 10^{-4} \pm 2 \times 10^{-5}$ mol/cm^3. The cross-link densities of the sulfur- and peroxide-cured EPDM reference systems were found to be respectively $1.7 \times 10^{-4} \pm 6 \times 10^{-6}$ and $1.8 \times 10^{-4} \pm 8 \times 10^{-6}$ mol/cm^3, respectively.

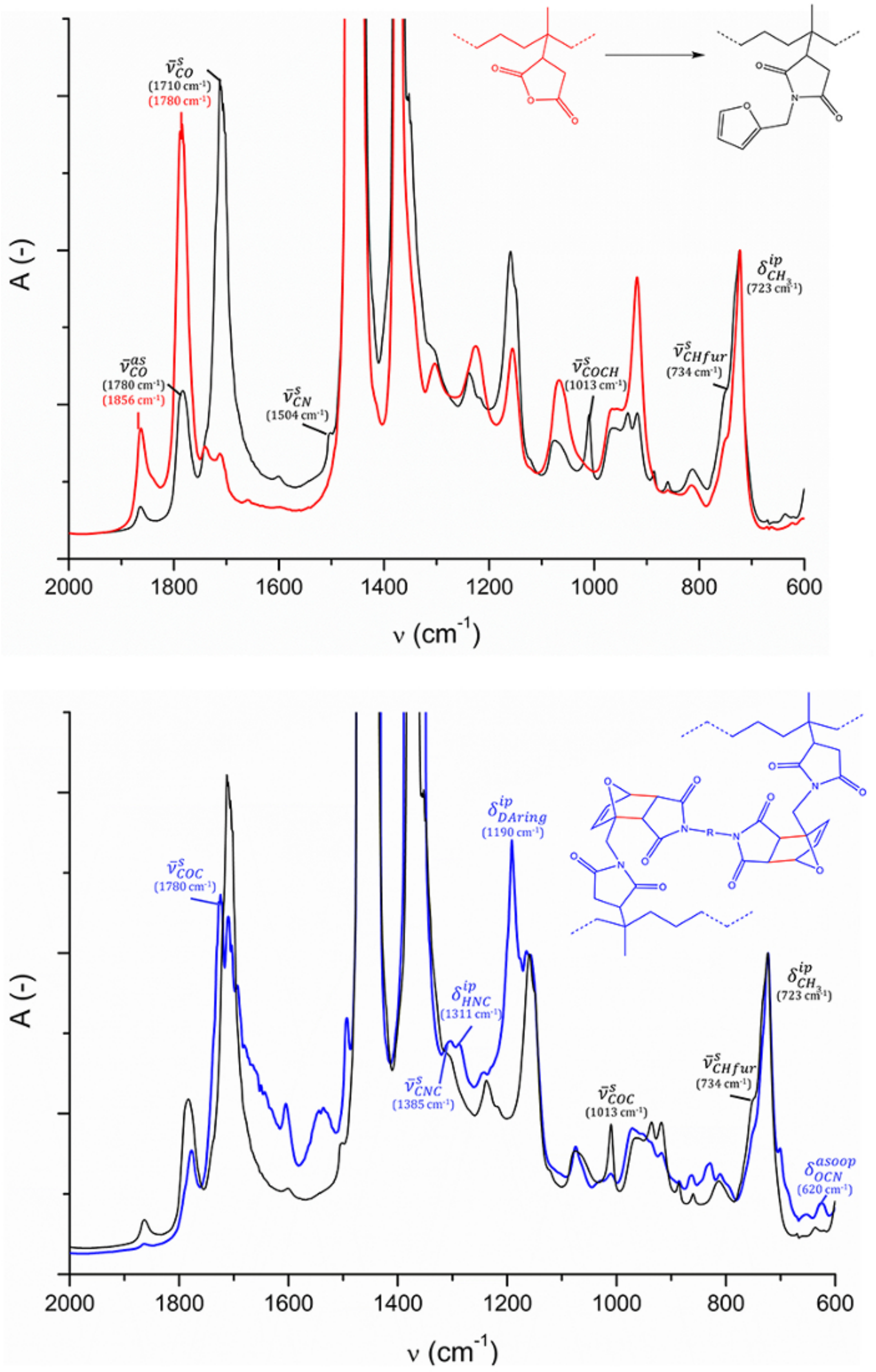

Figure 2. FT-IR absorption spectra. Spectra of left: EPM-g-MA (red) and modified EPM-g-furan (black) and right: of the non-cross-linked EPM-g-furan (black) and the Diels-Alder cross-linked EPM-g-furan (blue) (reprinted with permission from [5]). Please click here to view a larger version of this figure.

	wt% N	wt% C	wt% H	FT-IR conversion (%)	EA conversion (%)
EPM-g-MA	< 0.01	84.7	14.3		-
EPM-g-furan	0.3	84.8	14.2	96	93
DA cross-linked EPM-g-furan	0.4	84.2	14	72	80

Table 1. Reaction conversions. Results from Elemental Analysis and FT-IR (adapted with permission from [5]).

The de-cross-linking of the DA cross-linked EPM-g-furan product was followed by transmission FT-IR (**Figure 3**). Some characteristic furan peaks such as and at respectively 1,504 and 1,013 cm^{-1} decrease upon thermal annealing at 50 °C and increases after compression molding at 175 °C. This indicates that cross-linking and de-cross-linking takes place via a reversible DA reaction between the grafted furan groups and the added BM cross-linking agents.[47] Solubility tests are a more practical method to observe the effects of cross-linking and de-cross-linking. EPM-g-furan is soluble in decalin (5 wt%) at 23 °C. The same material cross-linked with BM is clearly insoluble under the same conditions. Thermo-reversibility of the cross-linking reaction was shown by dissolving the product during 1 hour of heating to 175 °C. Finally, a practical way of testing the material's reworkability is by grinding or cutting the cross-linked rubber and compression molding it at 160 °C and 100 bar for 30 minutes. The resulting reprocessed material was found to have a cross-link density of 2.0 x 10^{-4} ± 2 x 10^{-5} mol/cm^3. When an EPDM rubber is irreversibly cross-linked with peroxide, remolding the cut pieces under the same conditions does not yield a coherent sample (**Figure 4**).

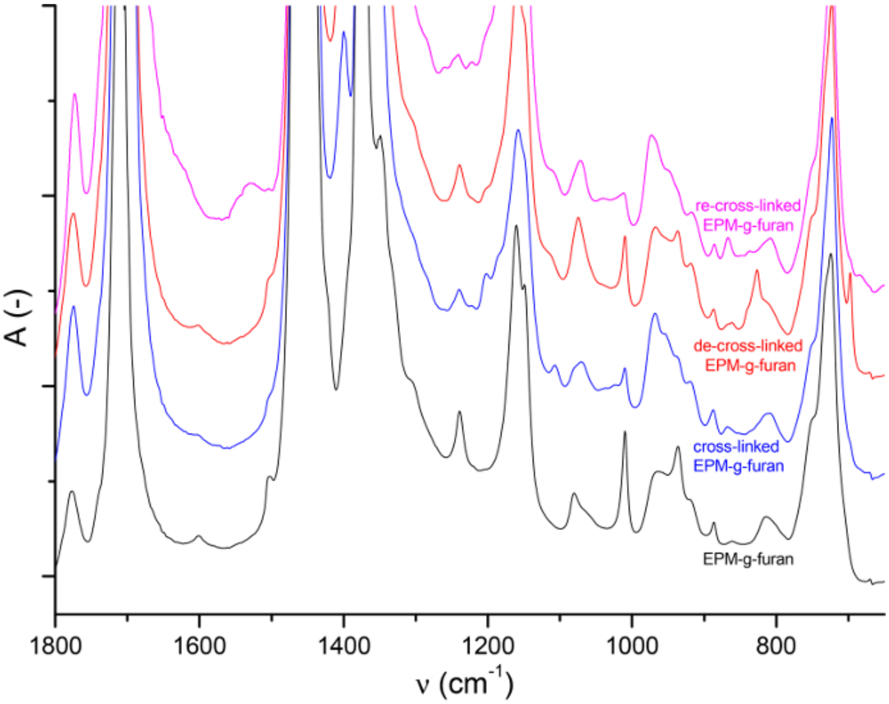

Figure 3. FT-IR absorption spectra. Spectra of EPM-g-furan and DA (de/re-)cross-linked EPM-g-furan (reprinted with permission from [5]). Please click here to view a larger version of this figure.

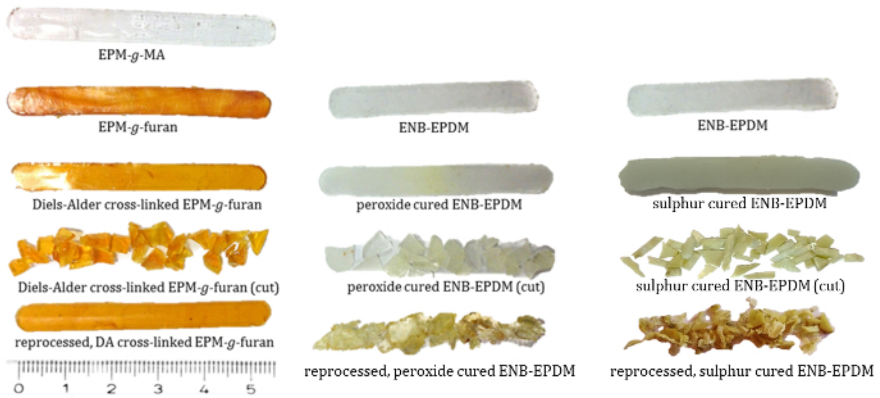

Figure 4. Reprocessing rubber samples. Sample bars of thermoreversibly cross-linked and sulphur- and peroxide-cured rubbers that are all reprocessed under the same conditions. Please click here to view a larger version of this figure.

The hardness increases and the compression set decreases when going from the non-cross-linked EPM-g-MA and EPM-g-furan precursors to the DA cross-linked EPM-g-furan (**Figure 5**). This clearly indicates the conversion of the 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 DA 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, their compression set is slightly inferior to the DA cross-linked samples.

The elongation at break decreases when going from the non-cross-linked EPM-g-MA to the modified EPM-g-furan (**Figure 6**). This difference could be explained by synergetic effects of the pending, conjugated furan groups.[48] 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. The cross-linked EPM-g-furan samples show significantly higher tensile moduli and lower elongation at break values compared to their non-cross-linked precursors. These high tensile moduli and low elongation are indicative for cross-linked rubbers.[49, 50] It also appears that the recycled cross-linked rubbers retain these characteristic properties of cross-linked rubbers, indicating that these cross-linked rubbers can be reshaped or reworked, regardless of their high modulus and low elongation. The median stress-strain curves also show that the thermo-reversibly, DA 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. This distinction is illustrative for the different behavior of cross-linked and non-cross-linked rubbers as is illustrated by the peroxide and sulfur cured EPDM samples.[51, 52] These peroxide and sulfur cured reference samples appear to have slightly higher Young's moduli than the DA cross-linked rubbers even though they were measured to have similar cross-link densities. The tensile strength and elongation at break of the DA cross-linked samples however, are at least as good as those of the peroxide and sulfur cured samples.

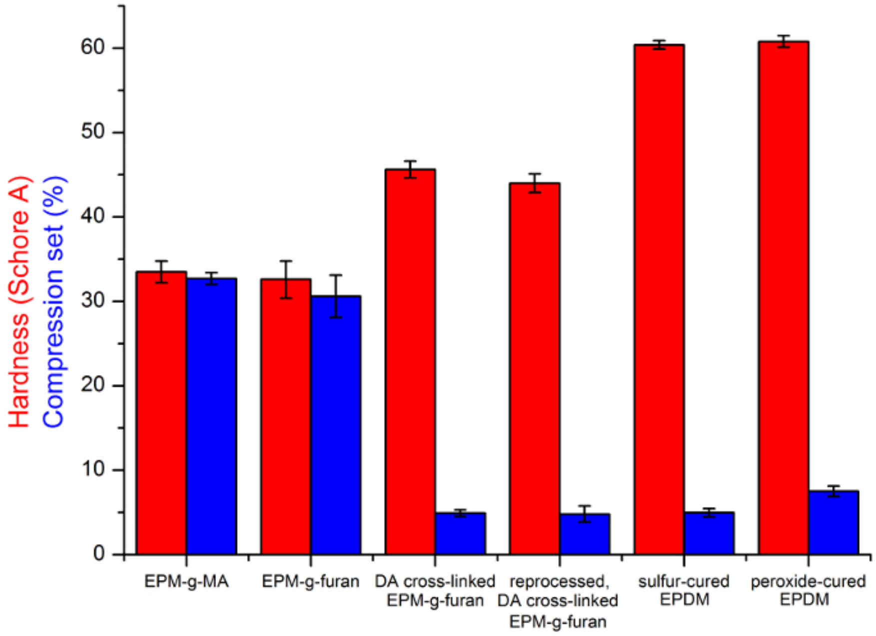

Figure 5. Hardness and compression set. Results for non-cross-linked EPM-g-MA and EPM-g-furan, DA cross-linked EPM-g-furan and irreversibly sulfur- and peroxide-cured EPDM rubbers. Error bars represent the standard deviations (reprinted with permission from [5]). Please click here to view a larger version of this figure.

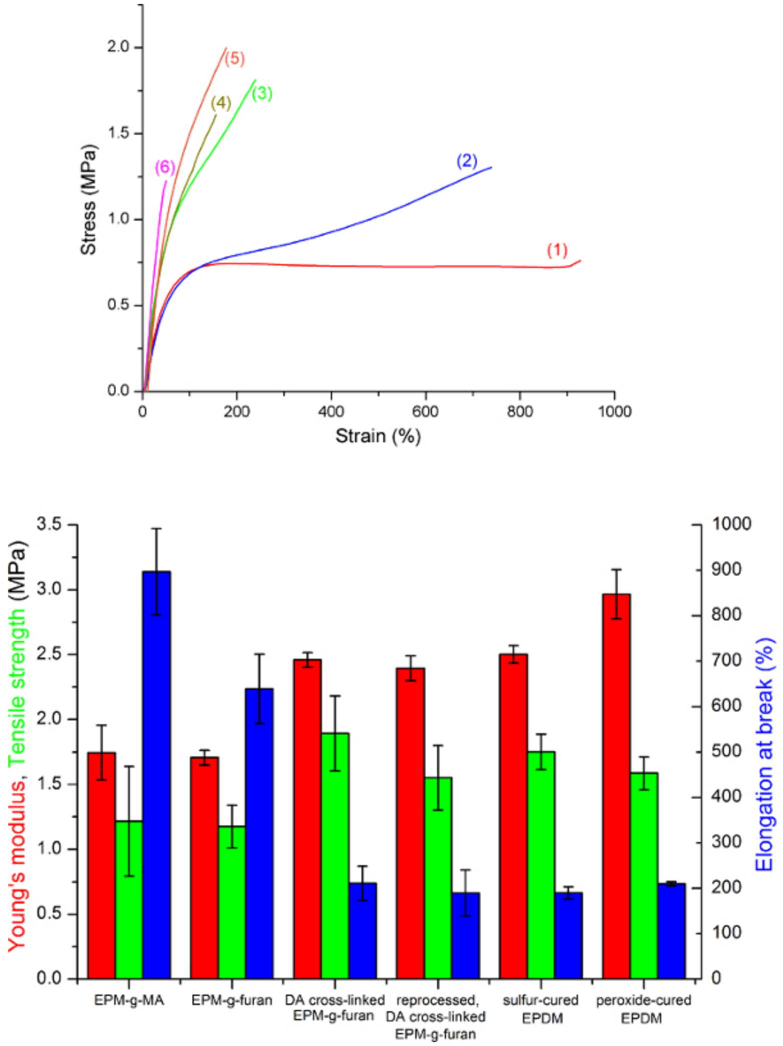

Figure 6. Tensile test. Results for EPM-g-MA (1), EPM-g-furan (2), DA cross-linked EPM-g-furan (3) and reprocessed, DA cross-linked EPM-g-furan (4) together with sulfur- (5) and peroxide- (6) cured EPDM. Median stress-strain graphs (left) and the corresponding Young's modulus, tensile strength and elongation at break (right). Error bars represent the standard deviations. (Reprinted with permission from [5]) Please click here to view a larger version of this figure.

Discussion

A commercial EPM-g-MA rubber was thermo-reversibly cross-linked in a simple two-step approach. The maleated rubber was first modified with FFA to graft furan groups onto the rubber backbone. The resulting pending furans show reactivity as Diels-Alder dienes. An aliphatic BM was used as cross-linking agent, resulting in a thermo-reversible bridge between two furan moieties. Both reactions were successful with good conversions (> 80%) according to infrared spectroscopy, elemental analysis. Cross-linking was shown by swelling and solubility tests, yielding a gel content of 100%.

For the successful execution of the protocol described, it is critical that the individual components are carefully prepared. Unfortunately, the preparation of reworkable rubbers by making use of the method described here does not allow for easy upscaling to larger quantities. Although no other methods of preparing this reworkable rubber product have been described in the open literature, an analogy with the well-known free-radical grafting of maleic anhydride onto EPM rubber can be drawn in this respect.[32] Melt modification of the rubber is a promising alternative that does not require a solvent, intermediate purification or drying steps and can be executed on commercial equipment such as melt mixers or extruders. The production of such a reworkable rubber would be much more time and cost efficient if it were to be executed via melt processing. On the other hand, the method described allows for more control of the reaction and a more well-defined end-product.

On a more general level of comparison between the current approach towards reworkable rubbers and other recycling approaches (*e.g.,* devulcanization), it must be noted that the materials have to be modified prior to cross-linking and that the formed cross-links fail at relatively low temperatures (> 180%). Nevertheless, this approach does allow for the production of a "cradle-to-cradle" recyclable rubber product whereas the recyclability of devulcanized rubbers is severely limited up to the reuse of few percentages in combination with virgin components.[54, 55]

The cross-link densities of the DA cross-linked EPM-g-furan as determined from FT-IR and EA correspond to those determined from swell tests. The resulting values are characteristic for loosely cross-linked, rubbery networks and correspond to the typical cross-link densities of sulfur and peroxide cured EPDM gums (1-5 x 10^{-4} mol/cm^3) reported in literature.[53, 54] The cross-link density of the DA cross-linked samples is comparable to those of sulfur- and peroxide-cured EPDM references, allowing for a comparison of properties.

Finally, the Shore A hardness, Young´s modulus, elongation at break, ultimate tensile strength and compression set all indicate the transformation of a viscous polymer into an elastic rubber network upon the addition of BM. These mechanical properties correspond to those of sulphur- and peroxide-cured references samples and they were retained after reprocessing the thermo-reversibly cross-linked rubber. Reprocessing of the material was performed for up to 5 times without any significant loss of properties.

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.

Disclosures

The author Martin van Duin is an employee of LANXESS Elastomers B.V. that produces EPM-g-MA rubbers used in this Article.

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