

University of Groningen

## Practical application of thermoreversibly Cross-linked rubber products

Polgar, L. M.; Picchioni, F.; De Ruiter, E.; Van Duin, M.

*Published in:*  
IOP Conference Series: Materials Science and Engineering

*DOI:*  
[10.1088/1757-899X/223/1/012004](https://doi.org/10.1088/1757-899X/223/1/012004)

**IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.**

*Document Version*  
Publisher's PDF, also known as Version of record

*Publication date:*  
2017

[Link to publication in University of Groningen/UMCG research database](#)

*Citation for published version (APA):*  
Polgar, L. M., Picchioni, F., De Ruiter, E., & Van Duin, M. (2017). Practical application of thermoreversibly Cross-linked rubber products. *IOP Conference Series: Materials Science and Engineering*, 223(1), 1-10. [012004]. <https://doi.org/10.1088/1757-899X/223/1/012004>

### Copyright

Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

The publication may also be distributed here under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license. More information can be found on the University of Groningen website: <https://www.rug.nl/library/open-access/self-archiving-pure/taverne-amendment>.

### Take-down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

*Downloaded from the University of Groningen/UMCG research database (Pure): <http://www.rug.nl/research/portal>. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.*

PAPER • OPEN ACCESS

## Practical application of thermoreversibly Cross-linked rubber products

To cite this article: L M Polgar *et al* 2017 *IOP Conf. Ser.: Mater. Sci. Eng.* **223** 012004

View the [article online](#) for updates and enhancements.

### Related content

- [Determination of thermophysical characteristics of vulcanizable rubber products by the mathematical modeling method](#)  
S G Tikhomirov, Y V Pyatakov, O V Karmanova et al.
- [Recycling of waste rubber as fillers: A review](#)  
M Nuzaimah, S M Sapuan, R Nadlene et al.
- [Cross-Linked Poled Polymer: Poling and Thermal Stability](#)  
Shinji Aramaki, Yuko Okamoto and Tetsuo Murayama

## Practical application of thermoreversibly Cross-linked rubber products

**L M Polgar**<sup>1,2</sup>, **F Picchioni**<sup>1,2</sup>, **E de Ruiter**<sup>1</sup> and **M van Duin**<sup>1,3</sup>

<sup>1</sup>University of Groningen, Departement of Chemical Engineering, Nijenborgh 4, 9747 AG Groningen, The Netherlands

<sup>2</sup>Dutch Polymer Institute (DPI), P.O. Box 902, 5600 AX Eindhoven, The Netherlands

<sup>3</sup>ARLANXEO Netherlands, Keltan R&D, P.O. Box 1130, 6160 BC Geleen, The Netherlands

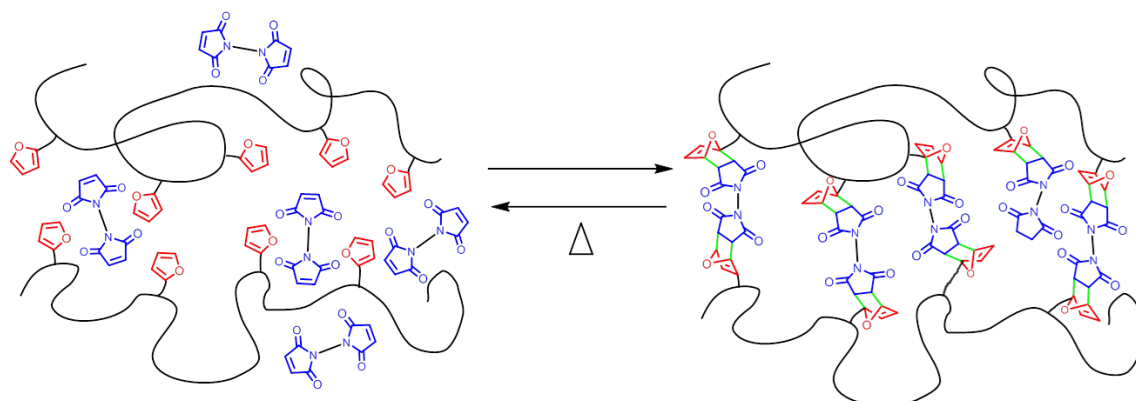
E-mail: [l.m.polgar@rug.nl](mailto:l.m.polgar@rug.nl)

**Abstract.** Currently, rubber products cannot simply be reprocessed after their product life, due to the irreversible cross-linking methods traditionally applied. The purpose of this work is to investigate how thermoreversible cross-linking of rubbers via Diels Alder chemistry can be used for the development of recyclable rubber products. Unfortunately, the applicability of the thermoreversible EPM-g-furan/BM system appears to be limited to room temperature applications, because of the rapid deterioration of the compression set at elevated temperatures compared to irreversibly cross-linked EPM. However, the use of EPM rubber modified with thiophene or cyclopentadiene moieties may extend the temperature application range and results in rubber products with acceptable properties. Finally, rubber products generally comprise fillers such as silica, carbon black or fibers. In this context, the reinforcing effect of short cut aramid fibers on the material properties of the newly developed thermoreversibly cross-linked EPM rubbers was also studied. The material properties of the resulting products were found to be comparable to those of a fiber reinforced, peroxide cured reference sample.

### 1. Introduction

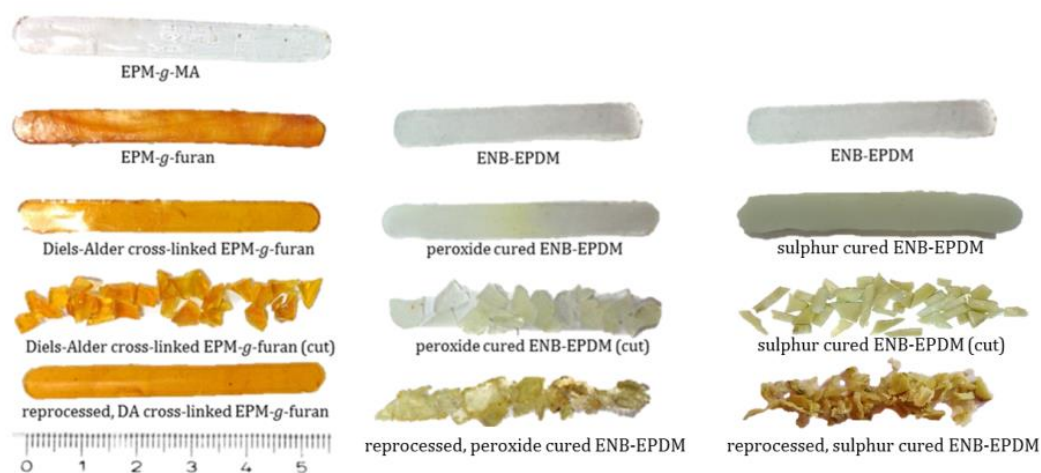
Rubber products have become an integral and essential part of our daily lives over the last 150 years since the invention of sulphur vulcanization by Charles Goodyear. Cross-linking is crucial as it provides good elasticity and high strength to rubber products. Unfortunately, cross-linking also prevents melt processability, making it difficult to recycle cross-linked rubber products, at least in a cradle-to-cradle context. Devulcanization allows for the cleavage of cross-links, but also causes bond scission in the polymer main chain, which is detrimental for the performance of the rubber recycle compared to the virgin rubber material [1,2]. An alternative to devulcanization of rubbers is found in thermoreversible cross-linking with Diels-Alder (DA) chemistry being particularly useful [3]. Thermoreversibly cross-linking is applied to obtain materials that combine the elastic properties of a permanently cross-linked rubber at service conditions with the melt (re)processability of a non-cross-linked rubber or thermoplastic. In our previous studies a commercial ethylene-propylene rubber (EPM) grafted with maleic anhydride has first been modified with furfurylamine to introduce furan groups along the rubber backbone. Next, these pendant furan groups were cross-linked with a bismaleimide (BM) via a DA coupling reaction (Figure 1).





**Figure 1.** Diels-Alder Cross-Linking and Retro-Diels-Alder De-Cross-Linking of Furan-Functionalized Elastomers with Bismaleimide Cross-Linkers.

The thermoreversibly cross-linked products can be compression moulded into samples that display material properties similar to peroxide cured and sulphur vulcanized EPDM reference samples. Furthermore, upon cutting and re-moulding samples with similar properties as the original samples were obtained (Figure 2). This demonstrates the thermoreversibility of the DA reaction and the recyclability of DA cross-linked rubber.



**Figure 2.** Reprocessing of Bismaleimide Cross-Linked, Peroxide Cured and Sulphur Vulcanized EP(D)M Rubbers [3]

The goal of this study is to investigate the conditions at which these newly developed thermoreversibly DA cross-linked rubber products can be applied with a focus on the effects of compression and relaxation times and temperature on elasticity. Some alternative DA diene-dienophile couples are studied and suggested for further research in order to overcome any shortcomings of the original EPM-*g*-furan/BM combination. Some rubber products are compounded with strong fibers, such as aramid fibers, for reinforcement [4,5]. It will be explored whether benefits of applying

thermoreversibly cross-linking in the presence of aramid fibers can be found, for example in the recovery of the fibers by de-cross-linking the rubber matrix, the ability to homogeneously redistribute the fibers by reprocessing the product and/or the possibility of inducing (thermoreversible) interactions between the fibers and the rubber matrix.

## 2. Experimental

### 2.1. Materials

Non-cross-linked, peroxide cured and sulphur vulcanized EPDM reference samples with a medium ethylidene (ENB-EPDM, *Keltan 8550C*, 53 wt% ethylene, 5.5 wt% ENB) and non-cross-linked, maleated EPM (EPM-g-MA, *Keltan DE5005*, 49 wt% ethylene, 2.1 wt% MA,  $M_n = 50$  kg/mol, PDI = 2.0) were kindly provided by ARLANXEO Netherlands B.V. Prior to the reaction, EPM-g-MA was dried in a vacuum oven for one hour at 175 °C to convert present diacids into anhydride. Short cut aramid fibers (3 mm) were kindly provided by Teijin Aramid. Furfurylamine (FFA, Sigma-Aldrich,  $\geq 99\%$ ) and 2-thiophenemethylamine (2-TMA, Sigma-Aldrich, 97%) were freshly distilled before use. 3-Chloropropylamine (APCl,  $> 99\%$ ), lithium cyclopentadiene (LiCp,  $> 99\%$ ), 1,1-(Methylenedi-4,1-phenylene)bismaleimide (BM, 95%), Bis(t-butylperoxy-i-propyl) benzene (*Perkadox14-40*, AkzoNobel), Octadecyl-1-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate (99%), tetrahydrofuran (THF,  $>99.9\%$ ), decalin (98%) and acetone ( $>99.5\%$ ) were all bought from Sigma-Aldrich.

### 2.2. Methods

#### 2.2.1. Furan-functionalization and BM Cross-linking of EPM-g-MA

The EPM-g-MA precursor was converted into EPM-g-furan according to a reported procedure [6]. 40.0 g of EPM-g-furan (8.6 mmol furan content) and 40 mg anti-oxidant were dissolved in 500 mL THF. 0.5 eq. (based on furan content of EPM-g-furan as determined from characterization by infrared spectroscopy and elemental analysis) of the BM was dissolved in THF and added to the 10 wt% rubber solution under stirring. 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 and thermally annealed in an oven at 50 °C for 7 days. Compression molding was performed on a Taunus Ton Technik V8UP150A press, equipped with a temperature controller.

#### 2.2.2. Cyclopentadiene Modification and Cross-linking

The method for the functionalization of EPM-g-MA with furfurylamine was slightly modified to facilitate grafting of thiophene and cyclopentadiene moieties to the EPM backbone. Cyclopentadiene

was grafted onto the EPM by first grafting 3-Chloropropylamine and using the halide as a leaving group for lithium cyclopentadiene according to a reported procedure [7,8]. 45.0 g EPM-g-MA rubber (9.6 mmol MA) was dissolved in 500 mL THF at room temperature. 4.5 g of APCI (28.9 mmol; 3.0 eq. based on MA content in EPM-g-MA) was then added to the 10 wt% rubber solution. The reaction mixture was stirred for 5 h in a closed system at room temperature and then precipitated by pouring it slowly into a tenfold amount of acetone (5 L) under mechanical stirring, yielding the polymer product as white threads. The product (EPM-g-Cl) was dried to constant weight in an oven at 35 °C. Subsequently, the product was briefly compression molded at 175 °C and 100 bar to ensure the conversion of all intermediate maleimide acid products to imide products. 40.0 g of the resulting EPM-g-Cl (8.6 mmol pendant Cl groups as determined from characterization by infrared spectroscopy and elemental analysis) and 40 mg anti-oxidant were dissolved in 500 mL THF under N<sub>2</sub>. An equimolar amount of LiCp was added under stirring and left to react at 30 °C for 18 h. Afterwards, the reaction mixture was precipitated in a 20:1 molar excess of demi-water under mechanical stirring, yielding the polymer product as white threads. The product (EPM-g-Cp) was dried in a vacuum oven at 150°C overnight to remove any traces of water and unreacted LiCp. The resulting product was compression molded at 150 °C and 100 bar for 1 h and thermally annealed in an oven at 90 °C for 3 days.

### 2.2.3. Thiophene-functionalization and BM Cross-linking of EPM-g-MA

45.0 g EPM-g-MA rubber (9.6 mmol MA) was dissolved in 500 mL THF at room temperature. 3.2 g of freshly distilled 2-TMA (28.9 mmol; 3.0 eq. based on MA content in EPM-g-MA) was then added to the 10 wt% rubber solution. The reaction mixture was stirred for 5 h in a closed system at room temperature and then precipitated by pouring it slowly into a tenfold amount of acetone (5 L) under mechanical stirring, yielding the polymer product as white threads. The product (EPM-g-thiophene) was dried to constant weight in an oven at 35 °C. Subsequently, the product was briefly compression molded at 175 °C and 100 bar to ensure the conversion of all intermediate maleimide acid products to imide products. 40.0 g of the resulting EPM-g-thiophene (8.6 mmol thiophene content as determined from characterization by infrared spectroscopy and elemental analysis) and 40 mg anti-oxidant were dissolved in 500 mL THF. 0.5 eq. (based on thiophene content of EPM-g-thiophene) of the BM was dissolved in THF and added to the 10 wt% rubber solution under stirring. 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 and thermally annealed in an oven at 90 °C for 3 days.

#### 2.2.4. Preparation of fiber-filled, BM Cross-linked EPM-g-furan Rubber Compounds

18 g of EPM-g-furan was fed to an internal mixer (70% fill factor) and homogenized at 50 rpm and 130 °C for 4 min. Then, 1, 3 or 5 phr of short cut aramid fibers was added. When the torque was stable (after typically 2-3 min), the BM cross-linker was added (0.2 to 1.5 molar eq. based on furan content). Mixing was continued for 2 min before the compound was removed from the mixer. Sample bars of the obtained products were obtained by pre-heating the materials in a mold at 140 °C for 5 min and compression molding them at 140 °C and 100 bars for 15 min. The resulting sample bars were thermally annealed in an oven at 50°C for a minimum of 72 h to ensure complete cross-linking.

#### 2.2.5. Preparation of fiber-filled, Peroxide Cured ENB-EPDM Rubber Compounds

18 g of ENB-EPDM was fed to an internal mixer (70% fill factor) and homogenized at 50 rpm and 70 °C for 4 min. Then, 1, 3 or 5 phr of short cut aramid fibers was added. When the torque was stable (after typically 2-3 min), 0.5, 1 or 2 phr of pure peroxide was added slowly to the mixture. The rubber compound was mixed for 4 more min until it was removed from the mixer. This rubber compound was then vulcanized by pre-heating in a mold at 160 °C for 5 min and compression molding at 160 °C and 50 bars for 35 min.

### 2.3 Characterization

The conversion of EPM-g-MA to EPM-g-furan, EPM-g-thiophene and EPM-g-Cl was followed by Fourier Transform Infrared spectroscopy (FT-IR) and elemental analysis (EA). FT-IR spectra were recorded on a Perkin-Elmer Spectrum 2000. Rubber films with a thickness of 0.1 mm were compression molded at 150 °C and 100 bar for 30 min, thermally annealed to ensure maximum DA cross-linking and measured in a KBr tablet holder. Measurements were performed over a spectral range from 4000 to 600  $\text{cm}^{-1}$  at a resolution of 4  $\text{cm}^{-1}$ , co-averaging 32 scans. Deconvolution was used to quantify the areas under the individual FT-IR peaks ( $R^2 > 0.95$ ). The differences in relative peak areas were used to calculate the reaction conversions. The methyl rocking vibration peak at 723  $\text{cm}^{-1}$  was used as an internal reference, as it originates from the EPM backbone and is not affected by chemical modification. The decrease of the absorbance of the C=O symmetrical stretch vibration of the anhydride groups at 1856  $\text{cm}^{-1}$  was used to calculate the conversion of the reaction from EPM-g-MA to EPM-g-furan, according to a reported procedure [6]. EA for the elements N, C and H was performed on a Euro EA elemental analyzer. The nitrogen content was related to the anhydride conversion according to a reported procedure [3].

Tensile tests were performed on an Instron 5565 with a clamp length of 15 mm, according to the ASTM D4-112 standard. A strain rate of  $500 \pm 50$  mm/min was applied. Test samples of 45 mm long, 5 mm wide and 1 mm thick were prepared by compression molding. For each measurement 10 samples were tested and the two outliers with the highest and the lowest values were excluded. Data presented are averages of the other 8 tests. The median stress-strain curves in the figures were selected to represent the entire series of a sample. The compression set test is used to measure the elasticity as it is affected by the time and temperature of compression and/or relaxation. Compression set tests were generally performed according to the ASTM D931 standard, using a home-made device and cylindrical samples with a thickness of  $6.0 \pm 0.1$  mm and a diameter of  $13.0 \pm 0.1$  mm, which were prepared by compression molding. The samples were compressed to 75% of their original thickness for 70 h at room temperature and relaxed for 30 min at 50 °C. Another series of compression set experiments was performed in which the samples were compressed to 75% of their original thickness for 70 h at 25, 60, 100 and 140 °C and relaxed for 30 min at room temperature.

### 3. Results

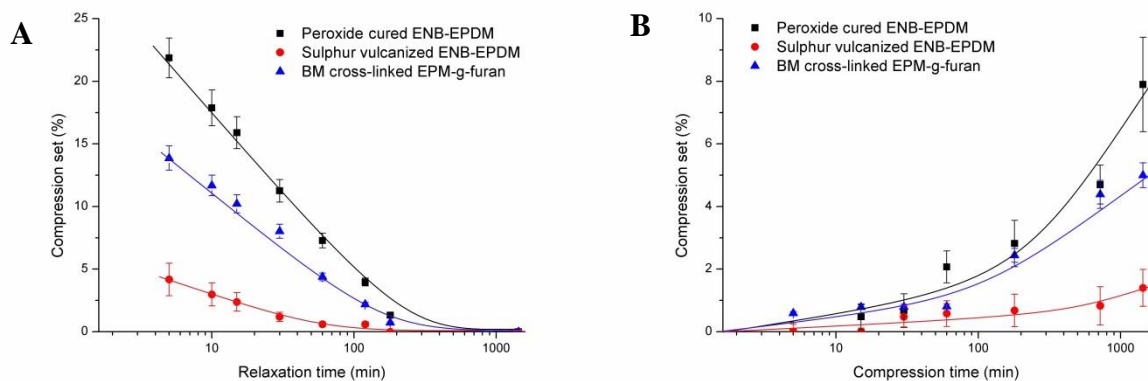
#### 3.1. Application Window

The furan-functionalization of EPM-g-MA and subsequent BM cross-linking was successfully performed according to the reported procedure [6]. The cross-link density of this thermoreversibly cross-linked rubber was found to be  $2.07 \cdot 10^{-4} \pm 0.21 \cdot 10^{-4}$  mol/cm<sup>3</sup>, which is similar to that of the irreversibly peroxide cured and sulphur vulcanized EPDM reference samples ( $1.98 \cdot 10^{-4} \pm 0.18 \cdot 10^{-4}$  and  $1.85 \cdot 10^{-4} \pm 0.16 \cdot 10^{-4}$  mol/cm<sup>3</sup>, respectively). Compression set experiments were performed on these samples under different conditions to probe the effects of the dynamics of the thermoreversibly cross-linked rubber with the thermoset rubber references (Figure 3). The compression set was studied as a function of relaxation time at room temperature for the 3 mentioned rubber products after 70 h of compression at room temperature (Figure 1A) and as a function of the compression time at room temperature followed by 30 min relaxation at room temperature (Figure 1B).

The compression set of the BM cross-linked EPM-g-furan, the sulfur vulcanized and peroxide cured EPDM reference samples decreases with the time after the imposed compression. It appears that the decay in compression set is linear up to 50 min after the measurement at which the initial compression set value seems to have halved for all three samples. Similarly, longer compression times result in higher compression set values for all three samples. Meanwhile, the compression set differs significantly between the different samples despite their similar cross-link densities. The results suggest that the dynamic character of the thermoreversible cross-links does not have a significant

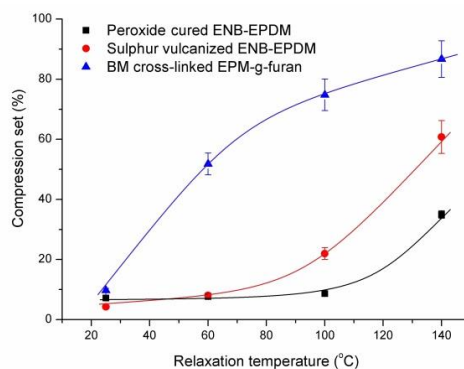


effect on the elastic properties of the reprocessable rubbers at room temperature and that the DA cross-links act as covalent cross-links at room temperature.



**Figure 3.** Compression set of BM cross-linked EPM-g-furan samples and of peroxide cured and sulphur vulcanized EPDM reference samples with similar cross-link densities applying A: relaxation for different times at room temperature after 70 h of compression at room temperature and B: 30 min relaxation at room temperature after compression for different times at room temperature. Lines are guides to the eye. Error bars indicate  $\pm 1\%$  standard deviation.

The compression set of BM cross-linked EPM-g-furan and the peroxide cured and sulphur vulcanized EPDM references have also been studied for different compression temperatures (Figure 4).



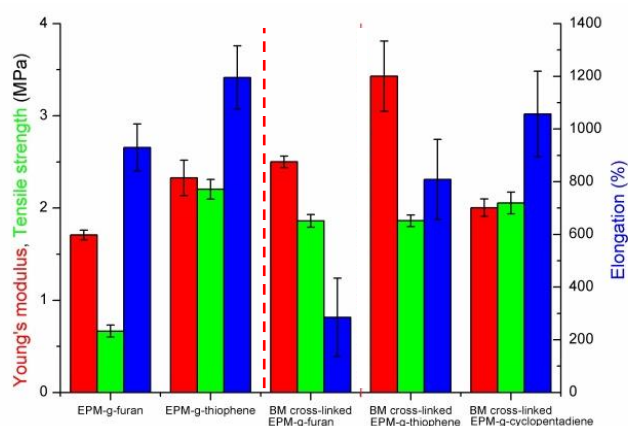
**Figure 4.** Compression set at different temperatures of BM cross-linked EPM-g-furan samples and of peroxide cured and sulphur vulcanized EPDM reference samples with similar cross-link densities. The lines are guides to the eye. The error bars indicate  $\pm 1\%$  standard deviation, taken here as relative error on the measured data.

Although the room temperature compression set is similar for the 3 rubber samples, it appears that a slight increase in compression temperature has a strongly detrimental effect on the compression set of the thermoreversibly cross-linked EPM-g-furan sample compared to the irreversibly cross-linked reference samples. This is probably due to a shift of the DA reaction equilibrium towards the retro-DA reaction at elevated temperatures. The dynamic equilibrium allows for a rearrangement of the cross-links and, thus accommodating the sample to the imposed compression. This means that the use of the

thermoreversibly cross-linked EPM-g-furan is strictly limited to (below) room temperature applications, such as wire and cable insulation or sealant applications. Away to overcome this can be found in using a different diene-dienophile couple for the DA cross-linking reaction.

### 3.2 Alternatives Yielding Improved High Temperature Performance

Other diene-dienophile couples can be used to thermoreversibly cross-link modified elastomers with bismaleimide via DA chemistry [9]. An example is the modification of EPM-g-MA with 2-thiophenemethylamine and the thermoreversible BM cross-linking of the resulting EPM-g-thiophene. The product was found to be cross-linked based on its insolubility (cross-linked polymers are non-soluble with respect to their non-cross-linked precursors) and the high Young's modulus and low elongation at break with respect to its non-cross-linked precursor (Figure 5).



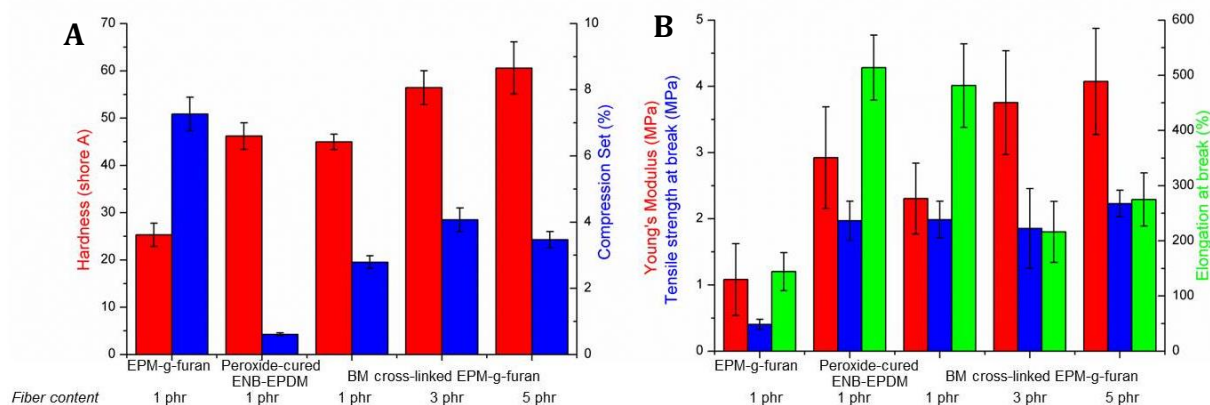
**Figure 5.** Tensile Test Results of Non-Cross-Linked EPM-G-Furan and EPM-G-Thiophene, Their BM Cross-Linked Products and A BM Cross-Linked EPM-G-Cyclopentadiene rubber. Error Bars Indicate  $\pm 1$  Standard Deviation.

Cyclopentadiene also seems to be a good alternative for furan as the temperature at which the retro-DA reaction is known to start occurring is higher (150-215°C for cyclopentadiene [10,11] versus 110-170 °C for furan [12-14]). Some preliminary experiments were performed in which EPM-g-MA was functionalized with 3-chloropropylamine and the resulting pendant chloride group was reacted with lithium cyclopentadiene [7]. Although this approach was successful for the highly functionalized polyketones used in a previously reported study [7], the application to EPM-g-MA elastomers with a low degree of functionalization was less successful. The high reactivity of the cyclopentadiene groups is responsible for a number of side-reactions [15], resulting in a low conversion. More importantly, the formation of cross-links between the pendant cyclopentadiene groups upon reaction with bismaleimide was found to proceed much slower compared to the furan/bismaleimide couple. This is probably

because the DA reaction kinetics for cyclopentadiene requires higher temperatures, but may also be related to the lower concentration of functional groups, but is also likely to be a result of the low mobility of the polymer backbones that make it hard for the functional groups to recombine. The relatively small, bifunctional BM cross-linking agents were found to have a relatively high mobility in the rubber matrix, allowing for a faster recombination of diene and dienophile. As a result, the cyclopentadiene cross-linked EPM has a lower Young's modulus and higher elongation at break with than the BM cross-linked EPM-g-furan (Figure 5). It is clear that further optimization of this system is actually required before being able to draw any conclusion on its applicability.

### 3.3. Aramid Fiber Reinforced Rubber Composites

Finally, rubber products are usually reinforced with fillers such as aramid fibers. For the BM cross-linked EPM-g-furan, the Hardness and Young's modulus increase and the elongation at break of the rubber compounds decreases upon compounding with larger amounts of short cut aramid fiber (Figure 6). No significant changes were observed in the tensile strength and the compression set. With the exception of the compression set, the effect of fiber loading of the thermoreversibly cross-linked rubbers on the material properties was the same as for fiber-loaded, peroxide cured ENB-EPDM rubbers with the same cross-link density ( $2.45 \cdot 10^{-4} \pm 0.28 \cdot 10^{-4}$  and  $2.63 \cdot 10^{-4} \pm 0.27 \cdot 10^{-4}$ , respectively). The inferior compression set of the thermoreversibly cross-linked rubbers with respect to that of the peroxide cured reference sample might be a result of the rearrangement of cross-links under compression. Nevertheless, fiber filled rubber products may prove to be a suitable application for thermoreversibly cross-linked rubber as the addition of aramid fibers significantly increases the hardness and Young's modulus.



**Figure 6.** A: Hardness and Compression Set at Room Temperature and B: Young's Modulus, Tensile Strength and Elongation at Break of Non-Cross-Linked EPM-G-Furan and Peroxide Cured ENB EPDM with 1 phr of Short-Cut Aramid Fibers and BM Cross-Linked EPM-G-Furan with Different Fiber Loading. Error Bars Indicate  $\pm 1$  Standard Deviation.

#### 4. Conclusions

The applicability of a newly developed, reprocessable EPM rubber modified with furan groups and cross-linked with bismaleimide was studied by determining the material properties under different conditions. The dynamic character of the thermoreversible Diels-Alder cross-linking chemistry does not have a significant effect on the elastic properties of the reprocessable rubber at room temperature. However, the application of this thermoreversibly cross-linked elastomer remains limited to room temperature applications, because of the rapid deterioration of the elasticity upon an increase in temperature compared to irreversibly cross-linked rubbers. Alternative diene-dienophile couples, such as bismaleimide cross-linking of EPM modified with thiophene or direct cross-linking with cyclopentadiene are proposed to overcome these issues regarding the temperature stability. Using such components should increase the threshold temperature for the retro-DA de-cross-linking reaction. Finally, the BM cross-linked EPM-g-furan rubber was used for the preparation of aramid fiber reinforced rubbers. The material properties of the resulting products are comparable to those of a fiber reinforced, peroxide cured reference sample and improve with the fiber loading.

#### Acknowledgements

This research forms part of the research program of the Dutch Polymer Institute, project #749.

#### References

- [1] Sutanto P *et al* 2006 *Int. Polym. Proc.***21** 211.
- [2] Sutanto P *et al* 2006 *J. Appl. Polym. Sci.* **102** 5028.
- [3] Polgar LM *et al* 2015 *Macromol.***48** 7096.
- [4] Hintze C *et al* 2014 *Polym. Eng. Sci.***54** 2958.
- [5] Hintze C *et al* 2013 *Rubber Chem. Technol.***86** 579.
- [6] Polgar LM *et al* 2016 *J. Vis. Exp.***e54496**.
- [7] Toncelli C *et al* 2016 *J. Appl. Polym. Sci.***133** 42924.
- [8] Patet RE *et al* 2015 *Acs Catalysis* **5** 2367.
- [9] Toncelli C *et al* 2011 Thermoreversibility in Polymeric Systems *Self-Healing at the Nanoscale* ed Amendol V and Meneghetti M (Boca Raton: CRC Press) 197-247.
- [10] Peterson AM, Palmese GR 2009 *Click Chemistry for Biotechnology and Materials Science* (Hoboken: John Wiley & Sons, Ltd).
- [11] Stille J, Plummer L 1961 *J. Org. Chem.* **26** 4026.
- [12] Chen XX *et al* 2002 *Science* **295** 1698.
- [13] Teramoto N *et al* 2006 *Carbohydr. Polym.***64** 78.
- [14] Gandini A *et al* 2008 *Eur. Polym. J.***44** 4029.
- [15] Kobuke Y *et al* 1970 *J. Am. Chem. Soc.***92** 6548.