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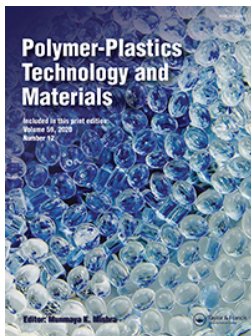
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Sustainable EPM rubber compounds

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ABSTRACT

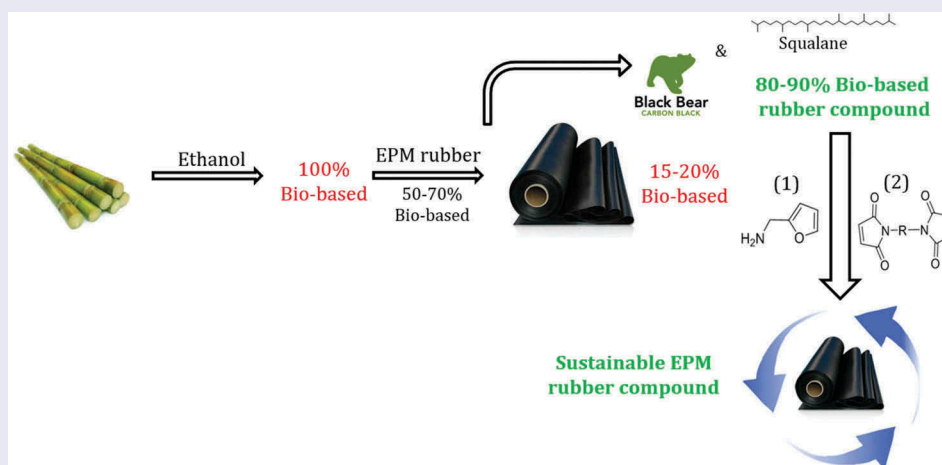
Two important aspects that should be considered when designing new, sustainable rubber products are the bio-based character of the rubber compound ingredients and the recyclability of the vulcanized rubber product. In this work, both are addressed by compounding a thermoreversible cross-linked EPM rubber with pyrolysis carbon black and squalane as sustainable filler and plasticizer, respectively. The resulting rubber product is fully reprocessable in the melt and it displays material properties comparable to those of compounds with conventional additives with high retention of the material properties upon reprocessing.

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1. Introduction

Sustainability has become a very important and unavoidable topic when designing new (chemical) materials or products. Sustainable products can broadly be defined as products that can be produced and re-used indefinitely without affecting the natural eco-system equilibrium. The carbon footprint, the carbon dioxide greenhouse gas emission, and the recycle potential of the material after the product life have become key issues that should be taken into consideration in the development of new, sustainable materials.

Obviously, natural rubber is fully bio-based and has found widespread application because of its high strength and abrasion resistance. Synthetic rubbers have been especially developed to meet higher demanding requirements, particularly with respect to resistance against heat, oxygen,

ozone and/or polar media. Currently, thermoset, synthetic rubber products are fossil-fuel-based and not recyclable via simple melt processing. In principle, these synthetic rubber products can be produced from bio-based monomer analogues. A good example is the recently developed, partly bio-based Keltan® Eco EPDM rubber^[1], which contains ethylene that is produced from sugar cane. The resulting EPDM rubber polymers have a bio-based ethylene content ranging from 50 to 70 wt% and provide the same material properties as their synthetic analogues.^[2] EPDM products may contain up to 400 parts per hundred rubber (phr) of compounding ingredients such as (reinforcing) fillers and plasticizers.^[3] Sustainable alternatives for (reinforcing) fillers and traditional plasticizer oils are required as traditional carbon black (CB) is typically produced through the incomplete combustion of hydrocarbons with natural gas, while traditional oil plasticizers are typically refinery fractions of

crude oil. Recycled CB produced by the pyrolysis of waste rubber tires appears to be a suitable, sustainable alternative for N550 medium reinforcing CB fillers.^[4] These pyrolysis CBs are considered sustainable because rubber waste is viewed as a major environmental issue and pyrolysis seems to be one of the preferred recycling technologies with respect to the relatively low CO₂ emission. 2,6,10,15,19,23-Hexamethyltetracosane, i.e. squalane, is a fully saturated, apolar liquid, originally collected from shark livers, but today produced via fermentation of biomass.^[5,6] It is considered as a bio-based alternative for mineral oil plasticizers for apolar rubbers, such as EPDM. Combining partly bio-based EPDM with pyrolysis CB and squalane has resulted in EPDM compounds for automotive sealing applications with a sustainable content of up to 90% and a technical performance similar to that of traditional EPDM compounds.^[7]

Even if rubbers and compounding ingredients would be completely “green,” the resulting rubber products are not fully sustainable, as they will still result in the accumulation of rubber waste. Unfortunately, the chemical reactions typically used to cross-link elastomers, such as sulfur vulcanization and peroxide curing, are irreversible and, thus, prohibit the re-use of rubber scrap via simple melt reprocessing. This problem is particularly evident for rubber tires, which is often still dumped in landfills, placing a burden on the environment.^[8] In the last decades, considerable efforts have been devoted to the de-vulcanization of a variety of sulfur vulcanized rubbers.^[9–14] For some isoprene-based rubbers, such as NR and IIR, reclaiming processes are commercially practiced for decades and devulcanization in high shear/temperature processes using devulcanizing agents is now a common technology.^[15,16] It appears to be more difficult to apply the devulcanization technology to hydrocarbon elastomers with a saturated main chain, such as EPDM.^[17,18] An appealing, alternative approach that allows for *cradle-to-cradle* reprocessing of rubber products was found in thermoreversible cross-linking^[19–23], which yields rubber materials that combine the material properties

of permanently cross-linked rubbers with the recyclability of non-cross-linked thermoplastics. Thermoreversible cross-linking of maleated EPM rubber modified with furfurylamine (FFA) has successfully been performed using the thermoreversible furan/maleimide Diels-Alder (DA) reaction (Figure 1).^[20,24] These DA cross-linked rubbers show material properties similar to those of conventionally cross-linked EP(D)M rubbers and can be reprocessed with high retention of the material properties.^[20,24] Furthermore, practical EPM rubber compounds with carbon black fillers and oil plasticizer can also be recycled.^[25]

The goal of this work is to combine both aspects of sustainability described above by compounding a thermoreversibly cross-linked EPM rubber for recycling with pyrolysis CB and squalane as sustainable filler and plasticizer, respectively.

2. Experimental

2.1. Materials

An EPDM with a medium 5-ethylidene-2-norbornene content (ENB-EPDM, *Keltan*[®] 8550 C, 48 wt% ethylene, 5.5 wt% ENB, $M_n = 80$ kg/mol, PDI = 4.0), maleated EPM (EPM-g-MA, *Keltan*[®] 1519 R, 49 wt% ethylene, 2.1 wt% MA, $M_n = 50$ kg/mol, PDI = 2.0) and Sunpar 2280 oil were kindly provided by ARLANXEO Performance Elastomers. Carbon black (CB) N550 and N772 were kindly provided by Teijin Aramid. Recycle carbon black BBC500 was kindly provided by Black Bear. Furfurylamine (FFA, Aldrich, ≥99%) was freshly distilled. Squalane (Amyris), octadecyl-1-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate (Sigma-Aldrich, 99%), bis(tert-butylperoxy-*i*-propyl)-benzene (*Perkadox14-40*, AkzoNobel), 1,1-(methylenedi-4,1-phenylene)bismaleimide (Sigma-Aldrich, BM, 95%) and decahydronaphthalene (decalin, mixture of *cis* and *trans*, Sigma-Aldrich, >98%) were used as received as bio-based oil, phenolic antioxidant, peroxide curative, thermoreversible cross-linker and swelling solvent, respectively.

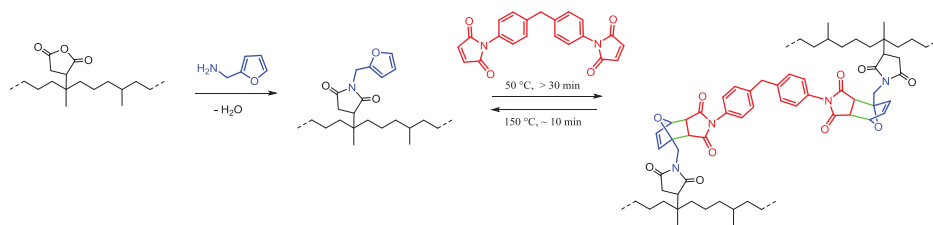


Figure 1. Furan-functionalization of maleated EPM rubber and subsequent thermoreversible cross-linking with bismaleimide via (retro-) Diels-Alder chemistry.

2.2. Methods

2.2.1. Compounding and peroxide curing of ENB-EPDM rubber

First, a filler/oil pre-mixture of 70 phr N550 and 70 phr N772 CB with 50 phr Sunpar 2280 oil was prepared. Alternatively, a sustainable filler/oil pre-mixture of 140 phr of carbon black BBC500 with 50 phr squalane was prepared. Ten grams of ENB-EPDM was homogenized in a 50 mL Brabender internal mixer. Then, 19 g of the dry (sustainable) filler/oil mixture was added at 50 rpm and 70°C for 4 min. After 3 min, 2.5 phr of peroxide was added slowly to the mixture and the rubber compound was mixed for 4 more min. Finally, this rubber compound was vulcanized by pre-heating in a mold at 160°C for 5 min and compression molding at 160°C and 50 bar for 35 min.

2.2.2. Functionalization, compounding, and BM cross-linking of EPM-g-MA

First 10 g of EPM-g-MA was functionalized with 0.57 g of FFA (1.25 molar eq.) in an internal mixer at 130°C and 50 rpm for 3 min. Next, the temperature of the mixer was increased to 180°C to ensure the complete conversion of the amide-acid intermediate to the imide, the full evaporation of unreacted FFA and the further compounding with oil/filler and the BM cross-linker ($T_m = 176^\circ\text{C}$). After homogenizing the EPM-g-furan product at 180°C for 3 min, 19 g of a dry (sustainable) filler/oil mixture (see above) was added. After 3 min, 0.80 g BM cross-linker (1 molar eq. based on MA content) was added and 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 samples in a mold at 140°C for 5 min and compression molding them at 140°C and 100 bar for 15 min. The resulting sample bars were thermally annealed in an oven at 50°C for 72 h to ensure complete cross-linking.

2.2.3. Reprocessing of BM cross-linked EPM-g-furan rubber compounds

Thermally annealed sample bars of BM cross-linked EPM-g-furan rubber compound were cut in small pieces (~10-50 mm³), fed into the internal mixer, and mixed at 130°C and 50 rpm for 3 min, when a stable torque indicated that a homogeneous mixture was obtained. The reprocessed material obtained from the internal mixer was compression molded and yielded coherent samples. The resulting, new sample bars were thermally annealed in an oven at 50°C for 72 h to ensure complete re-cross-linking.

2.3. Characterization

Equilibrium swelling experiments were performed in decalin. The rubber sample (approximately 500 mg) was weighed in 20 mL vials (W_0) and immersed in 15 mL solvent until equilibrium swelling was reached (3 days). The sample was weighed after removing the solvent on the surface with a tissue (W_1) and was then dried in a vacuum oven at 110°C until a constant weight was reached (W_2). Next, W_0 , W_1 , and W_2 were corrected for the presence of CB and W_0 was also corrected for the presence of plasticizer to enable the calculation of the rubber gel content (Eq. 1). The overall cross-link density $[XLD]_0$ was calculated from W_1 and W_2 applying the Flory-Rehner equation (Eq. 2).^[26] Next, a correction for the adsorption of decalin by CB was performed via the Kraus equation (Eq. 3), yielding the value for the corrected cross-link density $[XLD]_c$.^[27] Three samples were measured for each vulcanizate to determine an average $[XLD]_c$.

$$\text{rubber gel content} = \frac{W_2 - W_0 f_{CB}}{W_0(1 - f_{oil} - f_{CB})} \cdot 100\% \quad (1)$$

f_{CB} Weight fraction of CB in original compound (140/290 = 0.483)

f_{oil} Weight fraction of oil in original compound (70/290 = 0.241)

$$\begin{aligned} [XLD]_0 &= \frac{\ln(1 - V_R) + V_R + \chi V_R^2}{2V_S(0.5V_R - V_R^{1/3})} \text{ with } V_R \\ &= \frac{W_2}{W_2 + (W_1 - W_2) \cdot \frac{\rho_r}{\rho_{\text{decalin}}}} \quad (2) \end{aligned}$$

V_R Volume fraction of rubber in swollen sample

V_S Molar volume of solvent (decalin: 154 mL/mol at room temperature)

χ Flory-Huggins interaction parameter (decalin-EPDM: $0.121 + 0.278V_R$)^[28]

ρ Density ($\rho_r = 0.860$ g/mL for EPDM and EPM-g-furan, $\rho_{\text{decalin}} = 0.896$ g/mL for decalin)

$$[XLD]_c = \frac{[XLD]_0}{1 + K \cdot \phi} \text{ with } \phi = \frac{f_{cb2} \cdot \rho_{res} \cdot W_r}{\rho_{cb} \cdot W_1} \quad (3)$$

K Kraus correction factor for the given filler (roughly 2.3 for both CBs used)^[29,30]

f_{cb2} Weight fraction of CB in dried residue

W_r Weight of rubber present in dried residue (g)

ρ_{res} Density of dried residue (1.4 g/mL as a weighted average)

ρ_{cb} Density of CB (~1.8 g/mL for both BBC500^[30] and a N550/N770 50/50 mixture^[31])

Table 1. The sustainable content, gel content, and (Krauss corrected) cross-link density of various EP(D)M samples.

Compound	Sustainable content (%)	Gel content (%)	[XLD] ₀ (10 ⁻⁴ mol/mL)	[XLD] _c (10 ⁻⁵ mol/mL)
(1) Conventional peroxide-cured EPDM compound	0	100	3.0 ± 0.1	8.6 ± 0.3
(2) Sustainable peroxide-cured EPDM compound	65.3	100	3.9 ± 0.1	8.7 ± 0.4
(3) BM cross-linked EPM-g-furan gum rubber ^{[20]*}	0	78	1.1 ± 0.1	11.2 ± 0.7
(4) Reprocessed (3)	0	73	0.9 ± 0.1	8.9 ± 0.6
(5) Conventional BM cross-linked EPM-g-furan compound	0	79	3.7 ± 0.2	9.3 ± 0.1
(6) Reprocessed (5)	0	77	3.6 ± 0.4	9.0 ± 0.2
(7) Sustainable BM cross-linked EPM-g-furan compound	65.1	77	3.5 ± 0.1	7.9 ± 0.4
(8) Reprocessed (7)	65.1	74	3.2 ± 0.2	6.7 ± 0.6

*Gum rubber is defined as the polymer without any additives and a Krauss correction is not required for the calculation of their cross-link density.

Square samples (5 x 5 cm and a thickness of 2 mm) for hardness measurements and dumbbell test samples (45 mm long, 5 mm wide and 1 mm thick) for tensile testing were prepared by compression molding. Discs with a diameter of 13.0 ± 0.1 mm were cut out of the latter samples for compression set (CS) testing. Hardness (Hs) was measured using a Bareiss Durometer, according to the ASTM D2240 standard. Average values were obtained from 10 measurements. 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 ± 50 mm/min was applied. For each measurement, 10 samples were tested and the two outliers were excluded for calculating the averages. The median stress-strain curves are shown in the figures. CS tests were performed according to the ASTM D931 standard, using a home-made device and the cylindrical sample discs. The samples were compressed to 75% of their original thickness at room temperature for 70 h and then relaxed at 50°C for 30 min.

3. Results and discussion

The calculated, sustainable content of the peroxide-cured reference compound is obviously 0% (Table 1). The sustainable content of the sustainable peroxide-cured EPDM compound and the BM crosslinked EPM compound is 65%. The sustainable content could be further increased to 82.5% if the EPDM and maleated EPM would be bio-ethylene based as in Keltan® Eco.

While the non-cross-linked starting EPDM rubber is fully soluble in decalin at 23°C, the reference samples of peroxide-cured EPDM gum^[25] and compound have a gel content of 100% (Table 1), indicating that they are fully cross-linked. The situation is similar for the fully soluble EPM-g-furan precursors as the BM cross-linked EPM-g-furan gums and compounds display rubber gel contents of >75%. This indicates a high level of DA cross-linking. The presence of a considerable amount of sol fraction in the BM cross-linked EPM-g-furan gum and compound samples may be the result of the reversible character of

the DA cross-links, which are in a dynamic equilibrium and may allow part of the polymer to dissolve over time during the swelling experiment. The soluble fraction of the conventional and sustainable rubber compounds is rather similar, assuming that Sunpar 2280 oil and squalane are both fully soluble and that all CB types used are completely insoluble.

The cross-link density of the various rubber gum and compound samples [XLD]₀ was determined by equilibrium swelling. The Krauss correction of [XLD]₀ to [XLD]_c for the presence of filler results in a decrease by roughly a factor 5 for all rubber compounds (Table 1). The relatively small standard deviation (approximately 1-5% for all samples) demonstrates that the obtained values for the cross-link density are highly reproducible. The cross-link densities of the gel fractions of all rubber compounds were found to be 7–9.10⁻⁵ mol./mL after the Krauss correction. These values are rather similar to that of the BM cross-linked EPM-g-furan gum rubber 11.10⁻⁵ mol./mL, indicating that the compounding with (sustainable) plasticizer and filler hardly affects the crosslink density and, thus, the conversion of the DA crosslinking reaction.

DA chemistry was used to thermoreversibly cross-link the maleated EPM rubber in such a way that the products will combine the material properties of a permanently cross-linked rubber with the recyclability of a non-cross-linked thermoplastic. Compression molding of cut samples is a practical method to assess the effects of cross-linking and de-cross-linking.^[20] After cross-linking, gum rubber and rubber compounds are generally no longer melt processable. This was evident for the samples of the peroxide-cured EPDM compounds that simply turned into crumbs after heating and shearing them in an internal mixer. In contrast, the samples of BM cross-linked EPM-g-furan compound turned into a homogeneous batch in the mixer that allowed for the compression molding of new, coherent samples, demonstrating the thermoreversibility of the DA cross-linking (Figure 2).

The recovery of the cross-link density upon reprocessing of both the conventional and the sustainable, BM cross-linked EPM-g-furan compounds (85% and 95%,

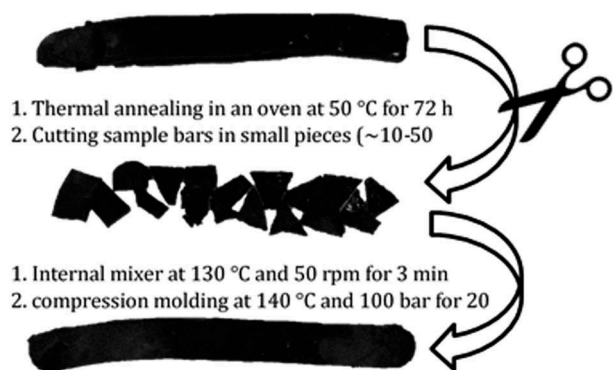


Figure 2. Sample bars of the same compound before and after reprocessing.

respectively) is larger than that of the BM cross-linked EPM-g-furan gum rubber (80%). This somewhat better recovery may be the result of a reversible interaction between the rubber-pendant furan groups and the carbon black filler^[25] and indicates that the compounding with the (sustainable) plasticizer and filler does also not affect the thermoreversibility of the BM cross-links.

The cross-link density is one of the main characteristics affecting the material properties of cross-linked rubbers.^[32] Thus, the similar cross-link density of the various samples (cf. Table 1) allows for a fair comparison of the material properties of these samples mutually, but also with the peroxide-cured EPDM samples (Figure 3).

The tensile strength (TS) of both peroxide-cured compounds is relatively low with respect to values found in the literature (12 MPa).^[33] This may be because the use of 1 phr peroxide in the absence of coagents is simply too small^[33], but may also be related to the use of a different type of EPDM or formulation recipe. The hardness (Hs), Young's modulus (MY) and TS of the sustainable, peroxide-cured EPDM compound are smaller than those of the conventional peroxide compound and the compression set (CS) is somewhat larger. This was also observed in sulfur-vulcanized EPDM compounds^[7] and is attributed to the somewhat lower surface area and surface structure of the pyrolysis black compared to N550.^[7] This is not the case though for the BM cross-linked EPM-g-furan compounds, as the sustainable compound displays slightly larger Hs, TS, and elongation at break (EAB) compared to the conventional BM compound. This may be related to the way the rubber-pendant furan groups interact with the filler.^[25] MY and CS are similar for both compounds.

The smaller Hs, MY, and TS of both BM cross-linked compounds with respect to the peroxide-cured compounds may be related to the larger number-average molecular weight of the ENB-EPDM (80 kg/mol) compared to that

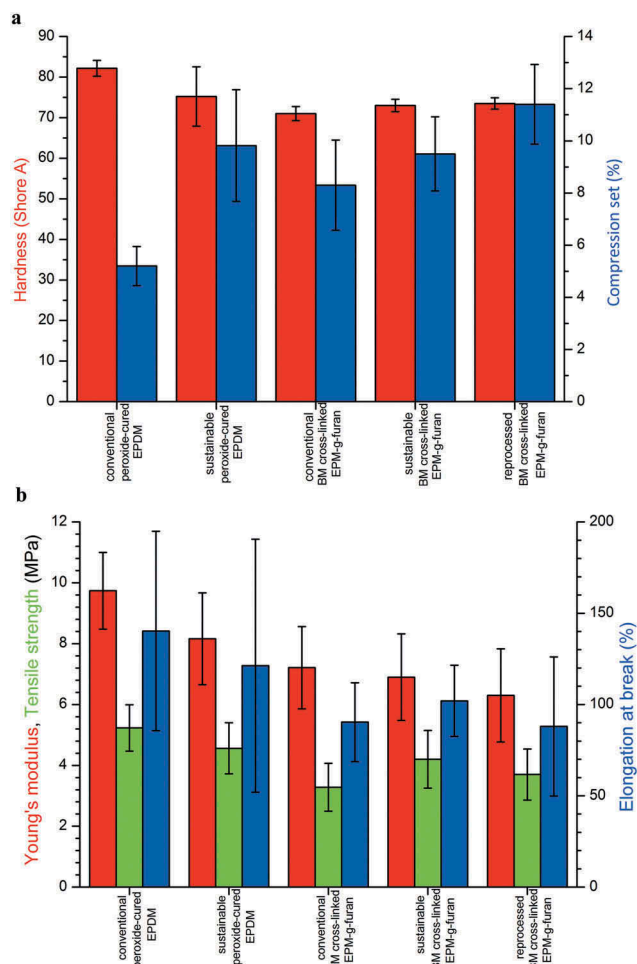


Figure 3. Hardness and compression set (top) and Young's modulus, tensile strength and elongation at break (bottom) of conventional and sustainable compounds of peroxide-cured EPDM and BM cross-linked EPM-g-furan. The error bars indicate ± 1 standard deviation.

of EPM-g-MA (50 kg/mol). Ways to overcome this are, for example, using other BM cross-linkers^[34], the addition of multi-functional cross-linking aids^[35], increasing the ethylene content^[23] and, thereby, increasing the crystallinity (and also the bio-based content) and/or simply using a higher molecular weight starting, maleated EPM. Finally, reprocessing appears not to significantly influence the material properties of the sustainable, BM cross-linked EPM-g-furan product. This means that the investigated pyrolysis CB and squalane are indeed sustainable alternatives for conventional filler and oil, respectively, and, thus, allow the development of "green" cradle-to-cradle rubber compounds without affecting the recyclability of the rubber products.

4. Conclusions

Two important aspects that should be considered when designing new, sustainable rubber products are the bio-

based character of the rubber compound ingredients and its recyclability. In this work, both aspects are addressed by compounding a thermoreversibly cross-linked EPM rubber with sustainable components, viz. pyrolysis carbon black and squalane as sustainable filler and plasticizer, respectively. The resulting product is fully reprocessable in the melt and it displays material properties comparable to those of products with conventional additives with high retention of material properties upon reprocessing. The material properties as such are somewhat inferior when compared to those of the peroxide-cured EPDM reference compound though, which is probably related to the lower molecular weight of the starting EPM-g-furan rubber. The overall conclusion is that pyrolysis black and squalane can be considered technical alternatives for medium reinforcing furnace black and processing oil, respectively. In combination with thermoreversible DA cross-linking, they can significantly contribute to the development of new, sustainable rubber products.

Acknowledgments

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Notes on contributors

L. M. Polgar is Test Engineering manager of the Vehicle Network Transceivers segment in NXP Semiconductors. His background is in Chemical Engineering with his Cum Laude PhD research on recyclable rubber for the Dutch Polymer Institute exemplifying his expertise in polymers and rubber structure/property relationships. Laurens remains connected to the world of polymers through package innovation projects, Disrubb B.V. and supervising students.

N. Migliore received his Master degree (2017) in Industrial Chemistry at the University of Pisa (Italy), however he spent the last year of his master as research student at University of Groningen (Netherlands) where he had the opportunity to work on conductive and smart materials. The same year, he joined the University of Groningen as PhD student in the Chemical Product Engineering group under the supervision of the assistant prof. Patrizio Raffa and prof. Francesco Picchioni, working on the synthesis and the studies of new amphiphilic copolymers. He spent the last year and a half as visiting PhD student, first at University of Florida (USA), then at CSIRO (Australia), where he had the opportunity to deepen his knowledge on controlled photo-polymerization synthesis.

F. Picchioni (born in Italy in 1971) received his Master (1996) and PhD (2000) degrees in Polymer Chemistry at the University of Pisa (Italy). After 3 years postdoc (2000-2002) at the Technical University of Eindhoven, he joined the University of Groningen (2003) first as assistant (until 2008), then associate (until 2013) and currently as full

professor in the Chemical Product Engineering group, which he chairs at the moment. He is (co)author of over 130 peer reviewed papers and book chapters as well as (co) inventor in 6 patent applications (5 more underway). He is frequently invited for keynote and plenary lectures at international conferences (at least twice a year). He has been nominated several times as Teacher of the Year for the Faculty of Science and Engineering.

M. Van Duin is Principle Scientist at Innovation in ARLANXEO Performance Elastomers, the global leader of synthetic rubbers. Structure - reactivity - performance relationships are the main theme in his professional and scientific career. Main areas of expertise are rubber crosslinking, polymer modification, reactive extrusion, thermoplastic vulcanisates and rubber structure/properties relationships. He holds a position as part-time professor on Rubber Products at the RijksUniversiteit Groningen.

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