

## RECYCLING BEHAVIOR OF THERMOREVERSIBLY DIELS–ALDER CROSSLINKED EPM

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### ABSTRACT

The recyclability of thermoreversibly Diels–Alder (DA) crosslinked EPM has been studied. The retro DA reaction dominates over the dehydration–aromatization process of the DA adduct. Moreover, a negative influence of air occurred as a result of a crosslinking in air flow. Nevertheless, rubber compounds prepared from EPM-g-furan and carbon black can be recycled several times without losing mechanical strength, a feature attributed to a strong antioxidant effect of the carbon black. [doi:10.5254/rct.21.79971]

### INTRODUCTION

The rubber industry has significant economic importance, with rubber polymers comprising more than 10% of the global polymer volume. Crosslinked rubbers have been known for more than 100 yr. The first example of a crosslinked rubber, that is, sulfur-vulcanized NR, was described by Charles Goodyear in 1844.<sup>1</sup> Covalent crosslinking of rubber polymers, typically in the presence of reinforcing fillers, yields unique materials with a combination of high elasticity and strength. However, the formation of a three-dimensional polymer network upon crosslinking of rubber prevents simple recycling via melt processing, a recycling process that is possible for thermoplastics. The vast number of rubber compound formulations with different rubber, plastisizer, crosslinker, and other additives provides another obstacle for recycling waste rubber to useful products. Thus, implementation of the reduce–reuse–recycle approach as one of the fundamental concepts for a future, sustainable society<sup>2</sup> is far from trivial for rubber materials. The chemical reactions that are commonly used for rubber crosslinking, such as sulfur and peroxide vulcanization,<sup>3–5</sup> but also less common reactions, such as hydrosilylation<sup>6–9</sup> and epoxide ring cleavage,<sup>10–15</sup> are not reversible. The irreversibility of these reactions yields products that are not soluble and cannot be molten, not even at elevated temperatures.

Our group has successfully applied Diels–Alder (DA) and retro DA (rDA) reactions for the thermoreversible crosslinking of a variety of polymers, including thermoreversibly crosslinked EPM.<sup>16</sup> In addition to detailed chemical evidence for the occurrence of (r)DA crosslinking, one-time recyclability of the obtained materials was demonstrated in a pragmatic way.<sup>15</sup> However, the practical aspects of the recycling of thermoreversibly crosslinked EPM require further investigation. The work described herein continues our studies and, in particular, investigates, explains, and solves possible problems in the reprocessing of thermoreversibly DA crosslinked rubbers.

### EXPERIMENTAL

#### METHODS AND MEASUREMENTS

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Mercury Plus 400 spectrometer (Varian), using CDCl<sub>3</sub> as a solvent. Fourier transform infrared spectra were recorded using a Spectrum 2000 instrument (PerkinElmer) with a diamond crystal for attenuated total reflectance measurements.

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(See Supplemental Material for the NMR and infrared spectra.) Elemental analysis for H, C, and N was performed with an Euro EA elemental analyzer. Tensile tests were performed on an Instron 5565 instrument with a clamp length of 15 mm, according to the ASTM Standard D 4-112 (Vulcanized and Thermo-elastic Tension). The calculation of Young's modulus was done in accordance with ASTM Standard E 111-17 (Standard Test Method for Young's Modulus, Tangent Modulus, and Chord Modulus).

#### MATERIALS

Distillation of toluene and dichloromethane (DCM) was done over Na and P<sub>2</sub>O<sub>5</sub>, respectively. Maleated EPM (EPM-g-MA, Keltan® 1519R, 49 wt% ethylene, 2.1 wt% maleic anhydride, number average molecular weight = 50 kg/mol, polydispersity index = 2.0) was kindly provided by ARLANXEO Performance Elastomers. Furfurylamine was purchased from Sigma-Aldrich and distilled in vacuum. ZnCl<sub>2</sub> (product no. 746355, Sigma-Aldrich) was dried at 150 °C for 1 h in vacuum (10 mmHg). Squalane, tetrahydrofuran (THF), *N*-methylmaleimide, octadecylsuccinic anhydride, hexamethyldisilazane (HMDS), 1,1'-(methylenedi-4,1-phenylene)bismaleimide (BM), and octadecyl-1-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionate (inhibitor) were purchased from TCI Europe and used without any purification. Carbon blacks (CBs) N550 and N772 were provided by Tejin Aramid.

#### PREPARATION OF EPM-G-FURAN RUBBER

EPM-g-MA (Keltan 1519R) was dried in vacuum (10 mmHg) at 175 °C for 1 h and cooled to 70–80 °C under vacuum to minimize oxidative degradation. The freshly dried rubber (18 g, 3.8 mmol of anhydride groups) was melted in a Brabender mixer ( $V_{\max} = 25$  mL) under a vigorous N<sub>2</sub> flow at 130 °C and 50 rpm for 4 min, after which furfurylamine (0.4632 g, 4.8 mmol) was added, giving a brown-colored product. The product was purified by re-precipitation from a 10 wt% solution in chloroform into a 10-fold excess (by volume) of acetone. The white or slightly yellow product was collected by filtration and dried in vacuum (10 mmHg) at 60 °C overnight. Compression molding at 175 °C and 100 bar for 30 min afforded quantitative imidization process.

#### THERMOREVERSIBLY DA CROSSLINKED EPM WITHOUT PRE-CROSSLINKING

A solution of BM (0.1862 g, 0.00052 mol) and inhibitor (1 or 0.1 wt% relative to the amount of rubber) was added to EPM-g-furan (5.00 g, 0.0010 mol of furan groups) in 50 mL of THF. The mixture was vigorously stirred with a magnetic stirrer and then poured onto a Teflon sheet. The solvent was allowed to evaporate in a fume hood. The rubbery film formed was dried overnight in vacuum at room temperature (RT). A compression molding at 160 °C and 75 bar for 30 min afforded quantitative imidization process.

#### THERMOREVERSIBLY DA CROSSLINKED EPM WITH PRE-CROSSLINKING

A solution of EPM-g-furan (5.00 g, 0.0010 mol of furan groups), BM (0.1862 g, 0.00052 mol), and inhibitor (1 or 0.1 wt%) in 50 mL of THF was refluxed for 24 h under an argon flow. Next, the mixture was poured onto a Teflon sheet. The solvent was allowed to evaporate in a fume hood, and the film was dried overnight in vacuum at RT. A compression molding at 160 °C and 75 bar for 30 min afforded quantitative imidization process.

## DA CROSSLINKING OF EPM IN PRESENCE OF AIR

A solution of EPM-g-furan (5.00 g, 0.0010 mol of furan groups), BM (0.1862 g, 0.00052 mol), and inhibitor (0.1 wt%) in 50 mL of THF was placed in a 100 mL two-neck flask, charged with an air inlet tube, and refluxed for 24 h while air was bubbled through the reaction mixture while refluxing. Next, the mixture was poured onto a Teflon sheet. The solvent was allowed to evaporate in a fume hood, and the film was dried overnight in vacuum.

SYNTHESIS OF 1-[(FURAN-2-YL)METHYL]-3-OCTADECYLPYRROLIDINE-2,5-DIONE (**2**)

The required amount of furfurylamine (0.1377 g, 1.4 mmol) was added to a solution of octadecylsuccinic anhydride (0.5000 g, 1.4 mmol) in 5 mL of dry DCM. After stirring overnight at ambient temperature (21 °C), the solvent was evaporated. The collected solid was dissolved in 5 mL of dry toluene and next anhydrous ZnCl<sub>2</sub> (0.1772 g, 1.3 mmol) and HMDS (0.2123 g, 1.3 mmol) were added. The mixture was kept at 80 °C for 5 h. The precipitate was filtered off, and the resulting solution was concentrated with a rotary evaporator. Yield was 0.3615 g, 65%.

Elemental analysis is as follows:

Found for %C 75.29; %H 10.31; %N 2.98.

Calculated for C<sub>27</sub>H<sub>45</sub>NO<sub>3</sub>: %C 75.13; %H 10.51; %N 3.24.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ, ppm: 0.88 (t, J = 6.8 Hz, 3H, CH<sub>3</sub>), 1.17 to 1.40 (m, 32H, (CH<sub>2</sub>)<sub>16</sub>CH<sub>3</sub>), 1.45 to 1.54 (m, 1H, CH<sub>2</sub>(CH<sub>2</sub>)<sub>16</sub>CH<sub>3</sub>), 1.85 to 1.96 (m, 1H, CH<sub>2</sub>(CH<sub>2</sub>)<sub>16</sub>CH<sub>3</sub>), 2.35 to 2.41 (m, 1H, COCH<sub>2</sub>CH<sub>2</sub>), 2.79 to 2.87 (m, 2H, COCH<sub>2</sub>CH), 4.66 (s, 2H, CH<sub>2</sub>N), 6.28 to 6.31 (m, 2H, furan), and 7.31 to 7.32 (m, 1H, furan).

<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>): δ, ppm: 16.77 (CH<sub>3</sub>), 25.34, 29.22, 31.92, 32.01, 32.16, 32.25, 32.29, 32.30, 32.32, 32.34, 33.91, 34.57, 36.97, 37.62, and 42.57 [(CH<sub>2</sub>)<sub>17</sub>CH<sub>3</sub>, CH<sub>2</sub>CO, CHCO], 111.05 and 113.08 (CH-furan), 145.03 (CHO), 151.41 (OC=CH), and 178.58 and 181.89 (CO).

SYNTHESIS OF DA ADDUCT (**1**) OF 1-[(FURAN-2-YL)METHYL]-3-OCTADECYLPYRROLIDINE-2,5-DIONE (**2**) WITH N-METHYLMALEIMIDE

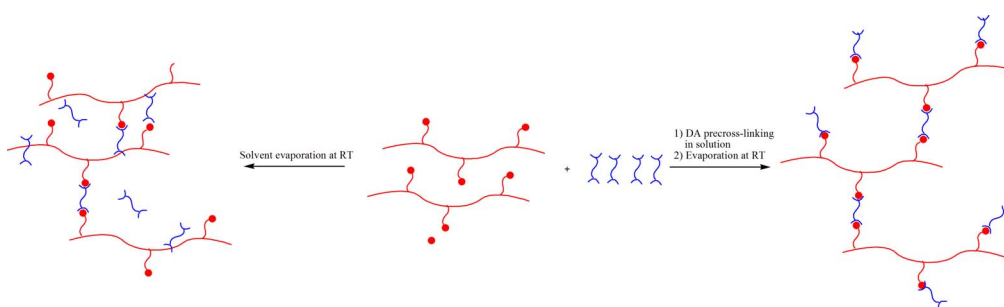
A solution of 1-[(furan-2-yl)methyl]-3-octadecylpyrrolidine-2,5-dione (**2**) (0.8633 g, 2 mmol) and *N*-methylmaleimide (0.2222 g, 2 mmol) in 5 mL of THF was refluxed for 24 h (until full conversion as shown by <sup>1</sup>H NMR). The solvent was evaporated under reduced pressure. The yellow powder obtained was dried in vacuum (10 mmHg) for 8 h at 60 °C. The product was isolated as a mixture of *exo*- and *endo*-isomers of (**1**).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ, ppm: 0.88 (t, J = 6.8 Hz, 3H, CH<sub>3</sub>), 1.17 to 1.40 (m, 32H, (CH<sub>2</sub>)<sub>16</sub>CH<sub>3</sub>), 1.45 to 1.54 (m, 1H, CH<sub>2</sub>(CH<sub>2</sub>)<sub>16</sub>CH<sub>3</sub>), 1.85 to 1.96 (m, 1H, CH<sub>2</sub>(CH<sub>2</sub>)<sub>16</sub>CH<sub>3</sub>), 2.35–2.41 (m, 1H, COCH<sub>2</sub>CH<sub>2</sub>), 2.79 to 2.87 (m, 2H, COCH<sub>2</sub>CH), 4.66 (s, 2H, CH<sub>2</sub>N), 6.28 to 6.31 (m, 2H, furan), and 7.31 to 7.32 (m, 1H, furan).

<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>): δ, ppm: 14.05 (CH<sub>3</sub>), 22.68 (N-CH<sub>3</sub>), 24.61, 25.15, 26.58, 26.99, 27.06, 29.35, 29.54, 40.23, 48.05, 48.07, 48.67, 48.72, 48.83, 48.85, and 50.43 (CH<sub>2</sub>), 78.87, 80.65, 89.15, 89.26, and 90.43 (CH-O), 134.82, 134.87, 136.61, 136.68, 137.30, 138.31, and 138.35 (C=C), and 174.40, 174.60, 174.68, 175.52, 176.39, 176.58, 179.88, 179.96, 180.60, 180.67, and 183.15 (C=O).

DECOMPOSITION OF (**1**)

For decomposition, 0.5 g of (**1**) was annealed at 175 °C for 2 h in vacuum (10 mmHg). The resulting powder was analyzed by <sup>1</sup>H NMR.



SCHEME 1. — Possible influence of refluxing step on bismaleimide crosslinker distribution in EPM-g-furan matrix.

#### PREPARATION OF RUBBER COMPOUND

EPM-g-furan rubber (52.35 g, 0.0109 mol of furan groups) was mixed with CB N550 (38.01 g, 70 phr) and N772 (38.01 g, 70 phr) reinforcing fillers and squalane (27.15 g, 50 phr) as plasticizer in an internal mixer (Brabender) at 130 °C for 4 min under vigorous N<sub>2</sub> flow. Next, the temperature was increased to 180 °C (above melting point of BM), and BM (1.95 g, 0.0055 mol) and inhibitor were added. After mixing for 3 min, the resulting black compound was retrieved. Desired samples, either dog-bone or O-rings, were produced by compression molding at 140 °C and 50 bar for 30 min.

#### RECYCLING OF NEAT EPM PRODUCTS AND EPM COMPOUNDS

Broken test pieces of gum EPM products and EPM compounds after tensile testing were cut into squares (2 mm × 2 mm). The cut fragments were then compression molded again at 160 °C and 100 bar for 30 min to produce new recycled test pieces. Rubber compounds were recycled by in the same manner as described above and then compression molded at 140 °C and 100 bar for 1 h.

#### RESULTS AND DISCUSSION

Our investigations initially compared recyclability of the DA crosslinked EPM compounds, according to the procedure described by Polgar et al.,<sup>16</sup> with those made using the new methodology in which an additional “pre-crosslinking” step was incorporated. The main difference between the two methodologies is that the material prepared without pre-crosslinking contained a crosslinker that was randomly distributed.

Previously, EPM material samples were prepared by mixing an EPM and BM solution, followed by solvent evaporation at RT and compression molding.<sup>16</sup> However, this protocol has one significant disadvantage: proper BM distribution cannot be achieved by this method. Because BM molecules in a solution distribute randomly and their position cannot be “frozen” to afford DA crosslinking, adequate BM distribution cannot be achieved after solvent evaporation. As a result, some BM groups might be located too far from furan groups of the EPM to be able to react with them during the annealing process. Herein, refluxing of the BM and EPM-g-furan solution (pre-crosslinking step) was carried out before dry-rubber film formation to improve BM distribution in the polymer matrix. Scheme 1 illustrates the differences in the crosslinking distribution.

Materials were prepared using 1,1'-(methylenedi-4,1-phenylene)bismaleimide as a crosslinker and 0.1 wt% of octadecyl-1-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionate to prevent free-

TABLE I  
RECYCLABILITY OF THERMOREVERSIBLY CROSSLINKED EPM

Sample no.	Pre-crosslinking <sup>a</sup>	Parameter <sup>b</sup>	No. of cycles			
			0	1	2	3
1	–	$\sigma$ , MPa	$1.11 \pm 0.06$	$1.23 \pm 0.05$	$0.82 \pm 0.14$	$0.65 \pm 0.02$
		$\varepsilon$ , %	$211 \pm 4$	$198 \pm 12$	$149 \pm 16$	$128 \pm 11$
		$E$ , MPa	$0.50 \pm 0.10$	$0.70 \pm 0.17$	$0.66 \pm 0.14$	$0.59 \pm 0.18$
2	+	$\sigma$ , MPa	$1.54 \pm 0.10$	$1.43 \pm 0.04$	$0.92 \pm 0.09$	$0.65 \pm 0.03$
		$\varepsilon$ , %	$282 \pm 37$	$159 \pm 11$	$120 \pm 17$	$105 \pm 10$
		$E$ , MPa	$0.58 \pm 10$	$0.98 \pm 0.14$	$0.86 \pm 0.03$	$0.62 \pm 0.06$

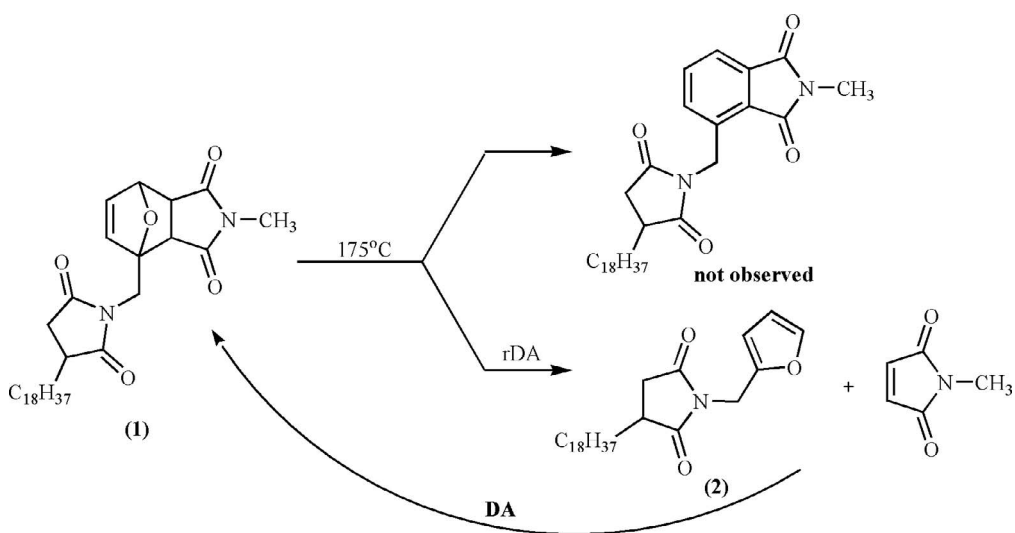
<sup>a</sup> –, without pre-crosslinking; +, with pre-crosslinking.

<sup>b</sup>  $\sigma$ , tensile strength;  $\varepsilon$ , elongation at break;  $E$ , Young's modulus.

radical side reactions and oxidative processes. The data listed in Table I (tensile strength, elongation at break, Young's modulus) highlight the advantage of including a pre-crosslinking step.

At the beginning, pre-crosslinked materials showed higher tensile strength and elongation at break. This finding might be due to efficient BM distribution and enhanced conversion. After one cycle, both materials showed similar tensile strengths. By contrast, the pre-crosslinked material became less elastic. For both materials, the tensile strength kept falling as the number of cycles progressed from two to three. The decline in tensile strength upon progressive recycling might be associated with irreversible side reactions and the oxidation process.

Previously, it was assumed that a furan-based DA compound can lose water, yielding an aromatic product.<sup>17</sup> This assumption has been experimentally checked using the model compound (1) (Scheme 2). Compound (1) was synthesized by DA reaction between furan (2) and *N*-methylmaleimide. Compound (2) was chosen for our investigations because the long hydrocarbon chain repeats the EPM backbone, and the functional moiety appears to be similar to EPM-g-furan. *N*-Methylmaleimide instead of *N*-phenylmaleimide, which would have been the exact



SCHEME 2. — Decomposition of model compound (1).

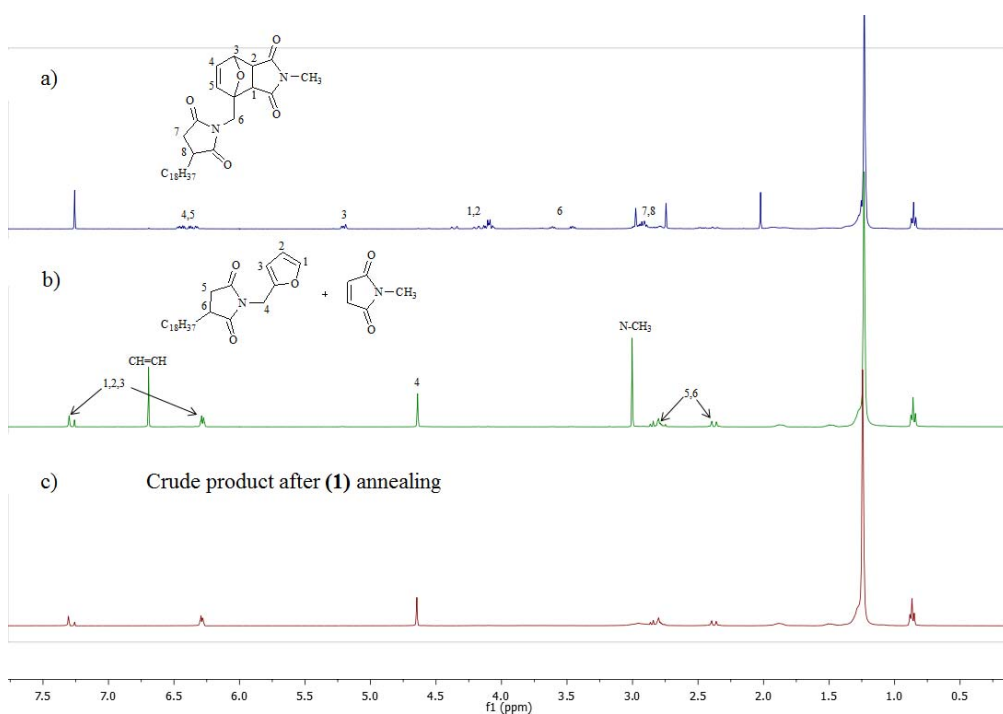


FIG. 1. —  $^1\text{H}$  NMR spectra of (a) model compound (1); (b) mixture of (2) and *N*-methylmaleimide; (c) crude product of (1) after annealing.

monofunctional analog of the BM crosslinker, was used due to its absence of aromatic groups; thus, we could make clear judgments regarding the formation of any aromatics by using NMR.



Annealing of neat (1) was performed at 175 °C under reduced pressure (10 mmHg) to avoid oxidative degradation and shift the equilibrium in favor of the production of aromatics. Ultimately, we expected a disappearance of signals at 3.5–4.5 ppm and an appearance of signals at 7.0–8.5 ppm; however, we observed a spectrum for furan (2) with a reduced amount of *N*-methylmaleimide (Figure 1).

$^1\text{H}$  NMR spectrum of the crude product contained three peaks at 7.31, 6.30, and 6.28 ppm. These chemical shifts match precisely with the signals of the furan ring in the  $^1\text{H}$  NMR spectrum of the reaction mixture before annealing. Moreover, other signals were found to match exactly with those of furan before annealing. We concluded that even if dehydration proceeds, it is much slower than that of the rDA reaction and cannot influence the reversibility of the rubber. Absence of the peaks at 6.69 and 3.00 ppm, which correspond to *N*-methylmaleimide, might be explained in terms of evaporation of this compound at 175 °C.

Pre-crosslinking in the presence of air (air was bubbled through the reaction mixture during the pre-crosslinking part) was carried out to investigate the influence of air presence on mechanical properties of the polymeric materials. Generally, when compression molding was carried out in an inert atmosphere, the resulting samples were smooth in appearance. By contrast, compression molding conducted in the presence of air produced samples exhibiting rough surfaces (Table II). This observation indicates that the sharpness of the melting process may be hindered by an additional premature, irreversible crosslinking reaction. A difference in mechanical properties also should be noted. Entrapped air may act as a flaw within the bulk of the material, leading to considerable loss in strength and less elasticity. Because increasing the concentration of crosslinks

TABLE II  
INFLUENCE OF AIR ON APPEARANCE AND MECHANICAL PROPERTIES OF CROSSLINKED EPM

Parameter <sup>a</sup>	In argon atmosphere	In presence of air
$\sigma$ , MPa	$1.54 \pm 0.10$	$0.72 \pm 0.04$
$\varepsilon$ , %	$282 \pm 37$	$69 \pm 8$
$E$ , MPa	$0.58 \pm 10$	$1.05 \pm 0.1$

<sup>a</sup>  $\sigma$ , tensile strength;  $\varepsilon$ , elongation at break;  $E$ , Young's modulus.

leads to a progressive reduction in the elongation at break of most polymers,<sup>18</sup> we conclude that the presence of air reduces tensile strength and impairs the ability of the material to be repeatedly recycled.

#### RUBBER COMPOUNDS

Recyclability of the rubber compound was investigated using dog-bone-shaped samples (Table III). The samples were prepared by compression molding at 140 °C and 50 bar for 30 min. The recycling test was carried out by cutting the samples into 2 mm × 2 mm pieces and compression molding at 140 °C and 100 bar for 1 h. Raising of time and pressure was necessary because the compound becomes harder after the first compression molding.

The materials filled with CB showed excellent amenability to recycling. Tensile strength and elongation at break stayed more or less constant, even after three cycles. Sustained integrity upon repeated recycling of the materials made of CB compared with neat rubber might be explained with a strong resistance of CB toward oxidation.<sup>19–22</sup> Moreover, when CB is added to the rubber matrix, it leads to a decrease in the polymer intake. Thus, the amount of the polymer available for oxidation is also lower than with gum rubber materials. As a result, CB-filled materials are less severely damaged by oxidative degradation.





A recyclable O-ring was made under similar conditions (compression molding at 140 °C and 100 bar for 1 h) (Figure 2). The O-rings are of much greater volume than for thin dog-bone samples. Therefore, in view of the poor thermal conductivity of our present range of materials, the molding time was increased to 1 h for the initial preparation of O-rings and then raised to 3 h for O-rings prepared from recycled material. It can be seen that the recycled sample is adequately homogeneous, indicating that the sample is not obstructed by premature crosslinking and that melting occurs somewhat freely.

#### CONCLUSIONS

The recyclability of thermoreversibly crosslinked EPM-g-furan rubber was investigated. The rDA reaction dominates over that of aromatization. Therefore, the aromatization of DA adduct cannot be considered as a reason for irreversible crosslinking. The presence of air during fabrication

TABLE III  
RECYCLABILITY OF CARBON BLACK-REINFORCED THERMOREVERSIBLY CROSSLINKED EPM

Parameter <sup>a</sup>	No. of cycles			
	0	1	2	3
$\sigma$ , MPa	2.39 ± 0.23	2.19 ± 0.41	1.94 ± 0.17	2.26 ± 0.33
$\epsilon$ , %	41 ± 5	31 ± 8	31 ± 2	36 ± 6
$E$ , MPa	5.89 ± 0.27	7.05 ± 0.54	6.15 ± 0.24	6.36 ± 0.72

<sup>a</sup>  $\sigma$ , tensile strength;  $\epsilon$ , elongation at break;  $E$ , Young's modulus.





FIG. 2. — Recycling of DA crosslinked EPM-based O-rings: (a) freshly prepared rings; (b) ring after cutting up; (c) ring after recycling.

leads to depreciation of mechanical properties and renders the material less amenable to recycling. Compression molding in the presence of air was difficult to accomplish and produced samples of poor quality. By contrast, compression molding in the absence of air improved quality and produced materials more pliable toward recycling. Addition of carbon black enhances the ease with which recycling takes place and improves surface appearance.

This work has elucidated problems that chemists and engineers are likely to encounter when confronted with a new generation of thermoreversible DA crosslinked rubber. With the current emphasis on developing sustainable materials, this work might be of interest to industrial chemists and engineers.

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