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Biobased, thermoreversibly crosslinked polyesters

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Chapter 4

Enhancing the impact properties of two Diels-Alder functionalized polymers through blending

4.1 Abstract

In order to overcome the inherent brittleness and improve the toughness of a polyester resin capable of thermoreversible crosslinking through Diels-Alder chemistry, blends are made with varying amounts of furan-functionalised rubber. In this way, the rubber can actively participate, via the furan groups, to the network formation and in principle be covalently linked to the polyester. Blank formulations were also prepared using non-functionalised rubber as reference. Blends containing up to 5% of rubber were successfully obtained. Izod impact tests show that a significant increase in toughness is obtained for the furan functionalised rubber whereas no effect is observed when incorporating the non-functionalised rubber. This indicates that inter-polymer crosslinking occurs, and plays a vital role in determining the final product properties.

4.2 Introduction

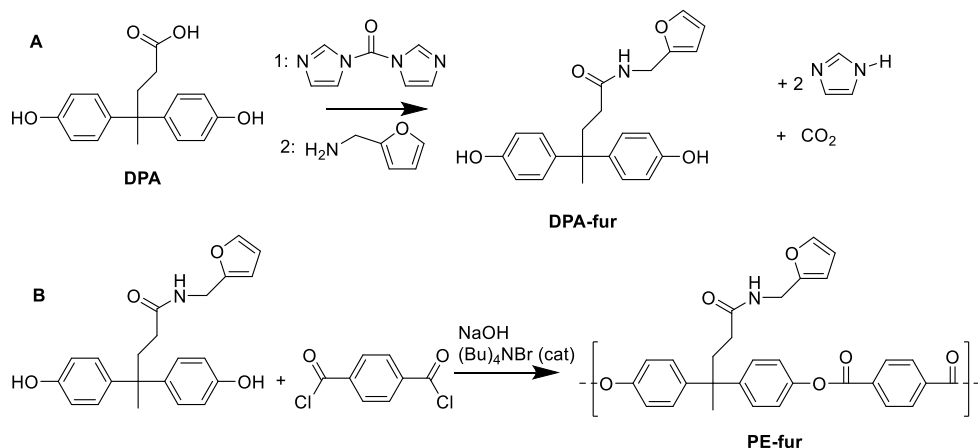
An increasing awareness regarding sustainability and the uncertain price development and availability of petroleum are encouraging academic and industrial research to develop new thermosetting resins from readily renewable carbon sources (i.e. bio-based)¹. In this context, 4,4-bis(4'-hydroxyphenyl)pentanoic acid, or diphenolic acid (DPA) has gained attention as a potential alternative to petroleum based bisphenol A (BPA), the key building block for epoxy resins and polycarbonates. DPA is a structural analogue to BPA, but may be considered to be fully renewable as it is synthesized by the condensation of levulinic acid and phenol². Levulinic acid is produced by the hydrolysis of biomass³, while phenol production from lignin-cellulose has also been described⁴. DPA and its ester derivatives, obtained by alkylation of the acidic group, have been used as diols to prepare thermosets such as high performance polybenzoxazines⁵ and epoxy resins⁶, exhibiting similar properties to the commercial ones, synthesized from BPA.

DPA based thermosets, as well as thermosetting resins in general, are (unfortunately) not designed to be recyclable according to a "cradle-to cradle" approach (i.e. by remoulding which is possible for thermoplastic materials). Thermosets and polyester based ones in particular are generally prepared via a liquid solution containing the various monomers to form a three-dimensional

covalently crosslinked structure¹. Once this reaction is complete, it is no longer possible to reshape the resulting material. Application of heat, sufficient to reshape most thermoplastic materials, would simply lead to degradation and decomposition of the thermoset. Therefore waste thermoset materials are currently reused as cheap reinforcement fillers or burned in order to recover (part of the) energy⁷. The application of reversible polymer networks represent a possible solution to this issue, since they combine the desirable mechanical properties of thermosets (high modulus, good solvent resistance, barrier properties) with the (re)processability and reworkability of thermoplastics⁸. The reversibility of these systems is based on the feasibility to break (part of) the crosslinks by applying an external stimulus (usually light or heat). The most studied covalent reversible systems are based on the Diels-Alder (DA) $[4\pi+2\pi]$ cycloaddition⁹ between a diene and dienophile moieties. In particular, the most investigated systems concern the furan/maleimide couple, mainly due to fast kinetics and high yields, as a consequence of the strong “diene” character (i.e. electron-rich) of the furan ring and the high reactivity of maleimide as a dienophile¹⁰. Notably, furan/maleimide adducts are formed at about 50 °C (crosslinking) while above 130 °C the equilibrium shifts towards the cleavage of the adducts (de-cross-linking via retro Diels Alder). Furthermore, the whole crosslinking/ de-crosslinking process can be repeated many times with negligible polymer degradation in the range of 50 °C – 150 °C¹¹.

A previous publication¹² describes the synthesis of a partly bio-based thermoset polyester from DPA, with the desired reversibility provided by Diels-Alder reactivity. The furan moiety was successfully attached to the DPA via amidation of the carboxylic group with furfurylamine (Scheme 1A). Next, the furan-modified DPA was reacted with terephthaloyl chloride, yielding a linear polyester (Scheme 1B) that could finally be crosslinked with aliphatic or aromatic bismaleimides. The resulting material displayed high recovery of mechanical properties during several heating-cooling cycles. Processability was improved by including phenol as a chain-stopper in the condensation step¹³, thus lowering the molecular weight and resulting glass-transition temperature (T_g) of the polyester.

Scheme 1: (A) Furan-modification of diphenolic acid DPA to DPA-fur and (B) polycondensation with terephthaloyl chloride

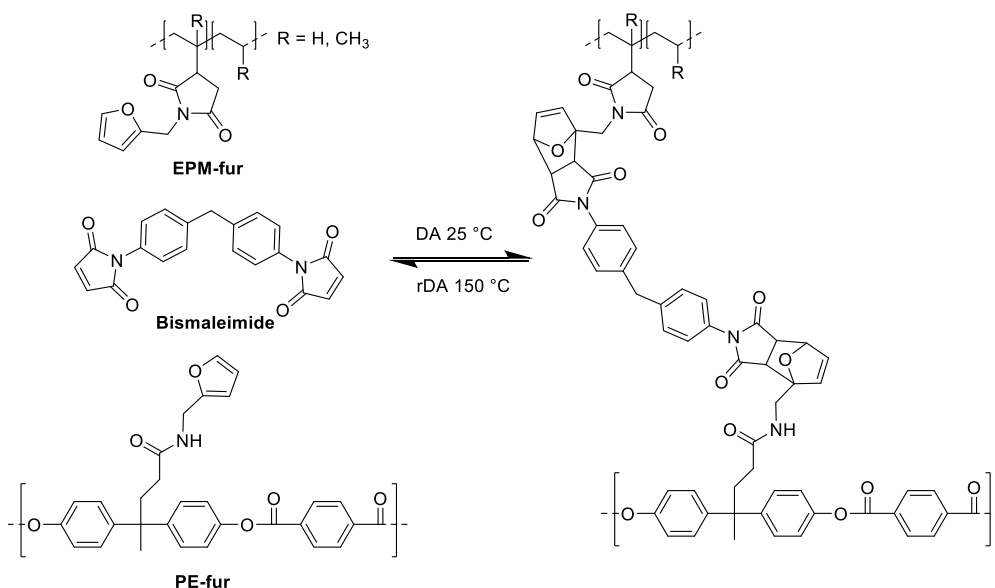


Thermosetting resins such as this one are inherently rigid and brittle. Rigidity and strength are required for many engineering applications, while brittleness or lack of crack growth resistance limits their application¹⁴. Elastomeric modification (e.g. rubber blending) is one of the most frequently used methods for improving toughness in thermosets¹⁵⁻²². Generally the applied rubber is required to have functional groups that are capable of reacting with the base thermoset resin²³ as can be observed in amine-terminated (ATBN) and carboxyl-terminated (CTBN) copolymers of butadiene and acrylonitrile, which are the most widely used toughening agents for epoxy resins^{24,25}.

Unfortunately, the application of these kind of conventional toughening agents would negate the thermoreversible crosslinking capabilities of the polyester/bismaleimide network mentioned above as these would react with the resin, effectively acting as a crosslinker. Unfortunately these crosslinks will be of an irreversible nature rendering the reversibility of the material moot. In a previous study it was shown that furan-functionalized rubbers can be used for the rubber toughening of thermoreversibly cross-linked thermosets with retention of recyclability²⁶. Therefore a furan functionalized EPM is suggested as toughening agent (Scheme 2). This chemically modified rubber has been proven, to be able to participate in thermoreversible crosslinking by use of the same DA reaction as homopolymer²⁷. It is to be expected that the furan functionality that is present in

both polymers (i.e. the EPM and the polyester) should allow for a fully reversible system based on Diels Alder chemistry in which both polymers are a part of the covalent network. The polyester imparts rigidity and the EPM acts as toughening agent, reducing the brittleness of the resulting material. This compatibility is expected to increase the miscibility and reduce the likelihood of phase separation.

Scheme 2: Crosslinking and de-crosslinking of furan-functionalized polyester PE-fur / EPM-fur rubber blends via Diels Alder (DA) and retro-Diels-Alder (r-DA) reaction with 1,1'-(methylenedi-4,1-phenylene)bismaleimide (b-Ma). The depicted reaction is expected to be the main contributor towards increased compatibility between the two components.



4.3 Experimental section

4.3.1 Materials

4,4'-Bis(hydroxyphenyl)valeric acid (DPA, Sigma-Aldrich, 95%), 2-methyltetrahydrofuran anhydrous (MeTHF, Sigma-Aldrich), N,N'-carbonyldiimidazole (CDI, Sigma-Aldrich, 97%) terephthaloyl chloride (Sigma-Aldrich, >99%), phenol (Sigma-Aldrich), tetra-n-butylammonium bromide (TBAB, Fluka), NaOH (Sigma-Aldrich, 97%), HCl (37%, Sigma-Aldrich), methanol (practical

grade, Interchema), chloroform (Lab-Scan), tetrahydrofuran (THF, Sigma-Aldrich, >99.9%) and 1,1'-(methylenedi-4,1-phenylene)bismaleimide (b-Ma) (Sigma-Aldrich, >95%) were purchased and used as received. Maleated ethylene/propylene rubber (EPM-MA, *Keltan 8550C*, 49 wt% ethylene, 49 wt% propylene, 2.1 wt% maleic anhydride, $M_n = 50$ kg/mol, PDI = 2.0) was kindly provided by ARLANXEO Netherlands. Furfurylamine (Sigma-Aldrich, >99%) was distilled prior to use. Deuterated dimethyl sulfoxide (DMSO- d_6 , Sigma Aldrich, ≥ 99.9 atom%) was used as solvent for ^1H NMR measurements.

4.3.2 Furan modification of diphenolic acid¹²

Diphenolic acid (5 g, 17.5 mmol), and *N,N'*-carbonyldiimidazole (1.2 equivalent, 3.40 g, 21.0 mmol) were weighed in a dry three-neck round bottomed flask connected to a cooler, under N_2 . MeTHF (30 mL) was added and the resulting mixture stirred under reflux conditions (90 °C) for two hours. Furfurylamine (1.2 equivalent, 1.85 ml, 21.0 mmol) was added and the reaction was allowed to proceed at 90 °C for an additional 5 h. The reaction mixture was then allowed to cool to room temperature and diluted with MeTHF (45 mL). The solution was washed with 1 M HCl (2 x 37 mL), 0.1 M NaOH (2 x 47 mL) and brine (1 x 15 mL) successively. Evaporation of the organic layer by rotary evaporation yielded a yellow oil. Final purification by recrystallization from ethanol yielded 3.26 g (51.1%) of a white solid (DPA-fur).

^1H -NMR (300 MHz, DMSO- d_6) δ 9.16 (s, 2H, OH) 8.19 (t, 1H, NH) 7.53 (s, 1H, fur-*p*) 6.93 (d, 4H, benzene-*o*) 6.62 (d, 4H, benzene-*m*) 6.35 (t, 1H, fur-*m*) 6.18 (d, 1H, fur-*o*) 4.19 (d, 2H, N- CH_2) 2.17 (t, 2H, - CH_2 -) 1.86 (t, 2H, - CH_2 -) 1.45 (s, 3H, - CH_3).

4.3.3 Polymerization of DPA-fur and terephthaloyl chloride¹³

The reaction of the DPA-fur monomer with terephthaloyl chloride results in a polyester containing pendant furan groups (PE-fur). The ratio of monomer/chain stopper added in this reaction was set at 4:2 to yield an average theoretical chain length of four monomeric repeating units, end-capped by two chain stoppers.

DPA-Fur (5.00 g, 13.7 mmol, 4 eq), TBAB (0.435 g, 8.7 %wt of DPA-Fur), phenol (0.644 g 6.84 mmol, 2 eq), NaOH (1.41 g, 34.2 mmol) and water (120 mL) were added to a 500 mL round bottomed flask. The mixture was stirred for 2 h at room temperature. Afterwards, terephthaloyl chloride (3.13 g, 15.4 mmol) dissolved in chloroform (120 mL) was added to the mixture. The reaction mixture was then

stirred overnight at room temperature. Precipitation in methanol (2 L) yielded a solid precipitate on the bottom of the beaker, as well as a suspension of small particles in the methanol phase. The methanol phase containing small solid particles was centrifuged in 50 mL cups at 4500 rpm for 15 min. Furthermore, the precipitate obtained in the centrifuge cups was filtered over a Büchner funnel and washed with water. Additionally, the solid precipitate on the bottom of the beaker was also filtered over a Büchner funnel and washed with water. Finally, all the solid products obtained were combined and dried in an oven at 70 °C for a 2 h to yield a white-yellowish solid (PE-fur, best yield achieved 74%).

¹H-NMR (300 MHz, DMSO-d₆): δ = 8.32-8.10 (m, 7H, aromatic not next to ester), 7.55 (s, 1H, fur-*p*), 7.49 (d, 1H, NH), 7.4-7.2 (m, 8H, aromatic next to ester), 6.37 (s, 1H, fur-*m*), 6.22 (s, 1H, fur-*o*), 4.23 (d, 2H, N-CH₂), 2.43 (s, 2H, -CH₂-), 1.98 (s, 2H, -CH₂-), 1.66 (s, 3H, -CH₃).

4.3.4 Furan-functionalization of EPM-MA rubber²⁷

EPM-MA was dried in a vacuum oven at 175 °C for one h to convert any diacid present into cyclic anhydride^{27,28}. Dried EPM-MA (100.0 g, 21.42 mmol MA) was dissolved in THF (≈ 10 wt % polymer) by stirring for 24 h at room temperature. Furfurylamine (6.24 g, 64.3 mmol) was slowly added to the solution. The reaction mixture was stirred in a closed system for 12 h at room temperature and then slowly poured into a tenfold amount of acetone (5 L). The polymer (EPM-fur), precipitated as yellowish flakes, was filtered and dried in an oven at 50 °C to constant weight. Amine conversion is determined by FT-IR on the basis of the decrease of the C=O asymmetric stretching band of anhydride rings at 1856 cm⁻¹ (using the methyl rocking bands at 723 cm⁻¹ as internal reference).

4.3.5 Sample preparation and crosslinking

Each blend was prepared by dissolving PE-fur and EPM-fur, combined at different weight ratios, in 100 mL THF at room temperature in a beaker. b-Ma was added in stoichiometric amounts (1:1 molar ratio between maleimide and furan groups of both polymers) and the reaction (Diels Alder cycloaddition) was allowed to proceed for 24 h at room temperature under agitation. Next, THF was partially removed by rotary evaporation (40 °C, 300 mbar). The obtained gel was dried in a vacuum oven at 50 °C for 24 h, ground and dried again in a vacuum oven at 140 °C for 1 h to yield a fine yellow powder. Reference samples, one containing PE-fur

and EPM-MA (95:5 wt% ratio) and another containing only PE-fur, were prepared and cross-linked with bismaleimide using the same procedure (Table 1). Samples have been coded by stating the type of EPM rubber and the weight ratio of rubber/polyester (in percentages).

<i>Sample</i>	<i>PE-fur</i> (g)	<i>EPM</i> (g)	<i>PE-fur/EPM</i> (w/w)	<i>b-Ma</i> (g)	<i>b-Ma</i> (mmol)
PE-fur*	10.00	-	100:0	2.68	7.50
PE-fur/EPM-fur_2.5	9.75	0.25	97.5:2.5	2.63	7.34
PE-fur/EPM-fur_5	9.50	0.50	95:5	2.57	7.18
PE-fur/EPM-MA_5*	9.50	0.50	95:5	2.55	7.13

Table 1. Amounts of PE-fur, EPM rubber (EPM-fur or EPM-MA) and b-MA used to prepare the samples and resulting wt% of rubber in each system *Reference samples

4.3.6 Characterization

¹H-NMR spectra were recorded on a Varian Mercury Plus 400 MHz apparatus using DMSO-d₆ as solvent. FT-IR spectra were recorded using a Perkin-Elmer Spectrum 2000. Films (1 mm thick) were prepared from the EPM rubbers by compression molding at 180 °C for 30 min under a pressure of 100 bar.

DSC thermograms were recorded on a TA-Instrument DSC 2920 under N₂ atmosphere. Samples were first heated from 20 °C to 180 °C and then cooled to 20 °C. Four cycles were performed at a rate of 10 °C per min.

Dynamic Mechanical Thermal Analysis (DMTA) was performed using a Rheometric scientific solid analyzer (RSA II) under air, in dual cantilever mode at an oscillation frequency of 1 Hz and a heating rate of 3 °C per min. Three cycles were performed for each specimen between room and softening temperature. DMTA specimens were on average 6 mm wide, 1.4 mm thick and 54 mm long. They were prepared by molding the cross-linked samples at 170 °C for 2 h under a pressure of 100 bar and then annealed in an oven at 50 °C for 24 h.

Izod impact strength was measured at room temperature, according to ASTM D4812 using standard unnotched specimens (12.7 mm wide, 3.3 mm thick and 64 mm long) prepared by compression molding of about 3.5 g of material at the same conditions as used for DMTA specimens and then annealed in an oven at 50 °C for 24 h. Tests were performed on a Zwick 5102 Pendulum Impact Tester equipped with a hammer. At least 10 specimens for each sample were tested. Impact strength was calculated as the ratio between the energy absorbed in the impact and the thickness of the specimen.

4.4 Results and discussion

4.4.1 Furan modification of EPM-MA

Furan-functionalized EPM rubber (EPM-fur) was obtained by reacting EPM-MA and furfurylamine in a THF solution at room temperature. The modification was studied by FT-IR transmission (see Figure 1). The most significant indication of the presence of furan groups is the appearance of the C-O-C symmetric stretching band at 1013 cm^{-1} ²⁹. Furthermore, the shift of the band at 1856 cm^{-1} to 1780 cm^{-1} (C=O asymmetric stretching) and the one from 1780 cm^{-1} to 1710 cm^{-1} (C=O stretching) in addition to the appearance of a new band at 1378 cm^{-1} (C-N symmetric stretching) confirmed the conversion of an anhydride into an imide^{28,30,31}. The areas under the peaks at 1856 cm^{-1} (C=O asymmetric stretching) and 723 cm^{-1} (methyl rocking vibration) were integrated by deconvolution analysis. From their ratio, the reaction conversion was found to be >99.9%, thus demonstrating that the chemical modification reaction is quantitative.

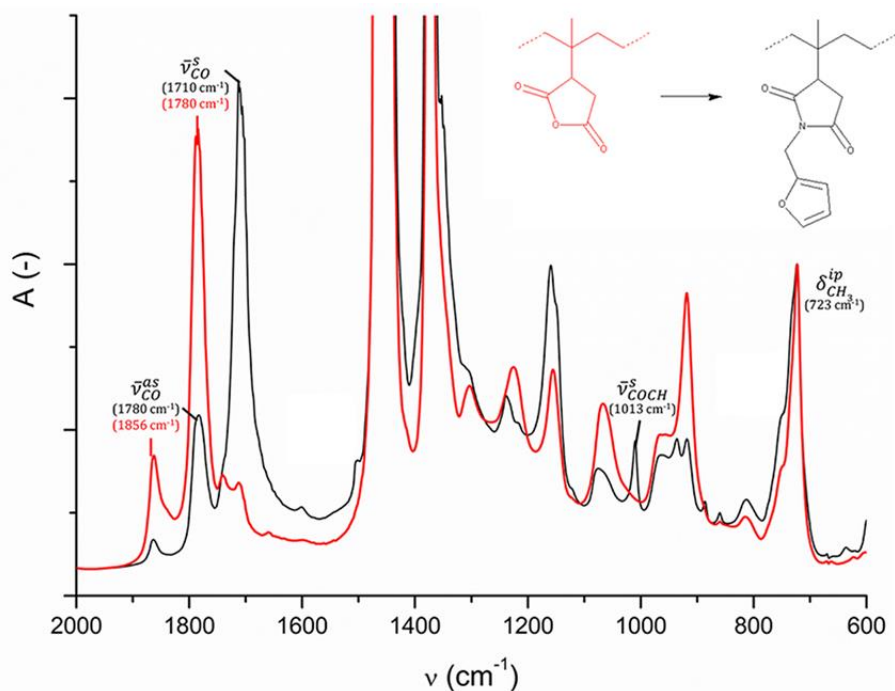


Figure 1: IR analysis of EPM rubber before (red) and after (black) functionalization with furan

4.4.2 Sample preparation and crosslinking

PE-fur/EPM-fur blends were combined and crosslinked in a THF solution at room temperature (Scheme 2, sample compositions reported in Table 1). The procedure reported^{12,13} previously for drying the pure polyester-bismaleimide networks (50 °C, 24 h in vacuum oven) did not yield sufficiently dry material when applied to the polyester/rubber blends. Coarse yellow particles were obtained which still contained a significant amount of solvent (evident from DSC). Therefore an additional drying step (140 °C, 1 h in vacuum oven) was required to achieve complete THF removal. Weighing the samples before and after drying showed the residual solvent content was about 10%. It seems that the solvent becomes trapped in the network, as it is only released once the r-DA temperature is reached. This finding is supported by DSC measurements where a large endothermic peak was observed around 140 °C.

A blend with an even higher polyester/rubber ratio (90:10) could not be prepared under these conditions, since the rubber precipitated in the form of millimeter-

scale sized particles, probably due to poor compatibility between the two polymers (i.e. the polyester is highly aromatic and polar, whereas the rubber is highly aliphatic and apolar).

All cross-linked samples were characterized by DSC in order to determine the thermal reversibility of the polyester/rubber/b-MA networks. In all thermograms, a broad endothermic transition in the range of temperature 130-180 °C, is observed for each consecutive thermal cycle (Figure 2). This transition corresponds with the retro-Diels-Alder (r-DA) reaction^{12,13,29,32,33}. The similarity in each consecutive thermal cycle demonstrates the reversible character of the crosslinked polyester alone or blended with the rubber.

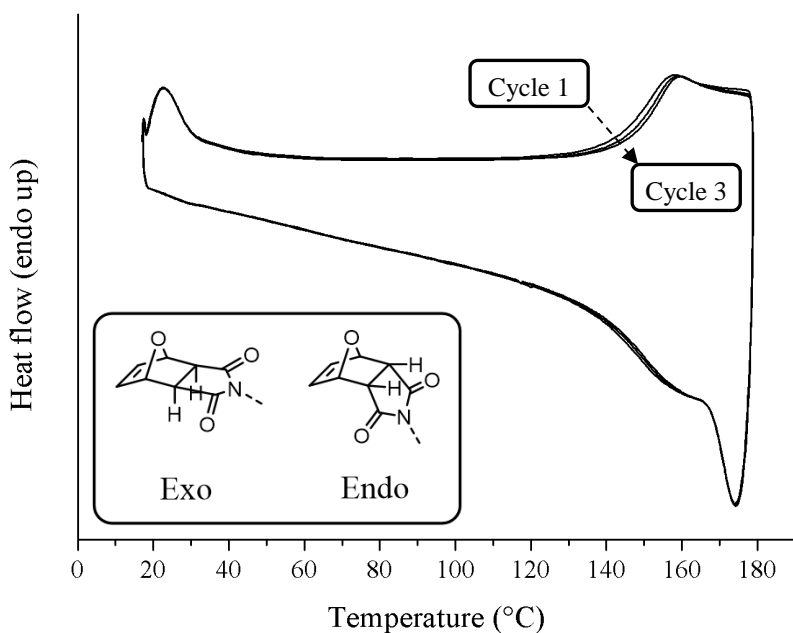


Figure 2: DSC thermal cycles of cross-linked PE-fur/EPM-fur_5 as representative example.

Inset: chemical structure of the exo and the endo stereoisomers of Diels Alder adducts.

When comparing the first with subsequent cycles, a slight shift (+ 2 °C) of the endothermic peak towards higher temperature was observed in all samples. This is consistent with previous observations reported for other thermoreversible networks based on the Diels Alder reaction with furan and maleimide^{9,34} as well as

for the b-MA crosslinked polyester^{12,13}. It may, thus, be attributed to the transition of DA adducts from the endo to the more stable exo conformation^{12,35}.

Ground samples were compression molded into homogeneous specimens (rectangular bars) suitable for DMTA (Figure 3).

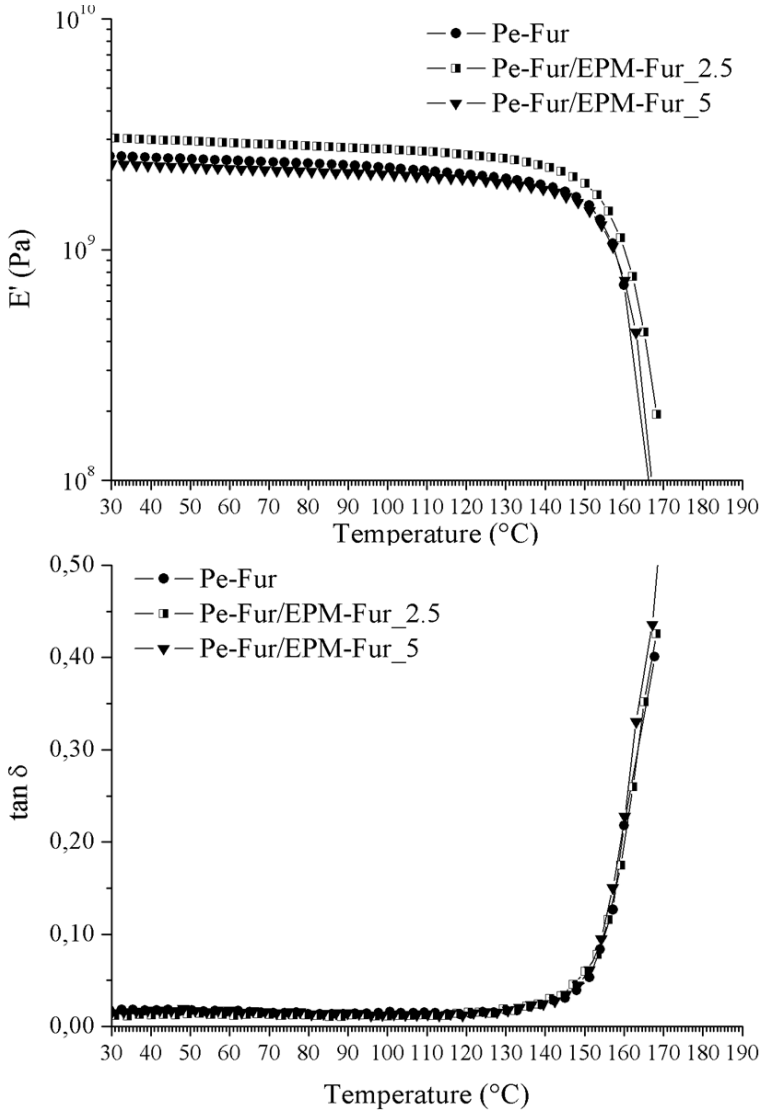


Figure 3: Storage modulus E' (top) and damping factor $\tan \delta$ (bottom) in DMTA during 1st heating stage for crosslinked PE-fur, PE-fur/EPM-fur_2.5 and PE-fur/EPM-fur_5.

For all samples the plateau in the storage modulus (E') that is characteristic for cross-linked polyesters was observed³⁶. This plateau is followed by a rapid drop at around 150 °C, implying a transition from elastic to viscous behavior. It appears that above this temperature the samples were still crosslinked, but softened due to partial cleavage of DA adducts¹⁰. Furthermore, the E' values in the plateau region appear not to be influenced by changes in the rubber content, suggesting that the rubber at these concentrations (up to 4 wt%) does not significantly affect the stiffness of the material. The softening temperature, as determined from the points of maximum decrease in E' , was found within a narrow range (168-171 °C) for all samples. After reaching the softening temperature, each sample was slowly (10 °C/min) cooled down to room temperature inside the DMTA chamber and tested again up to 3 heating cycles (Figure 4).

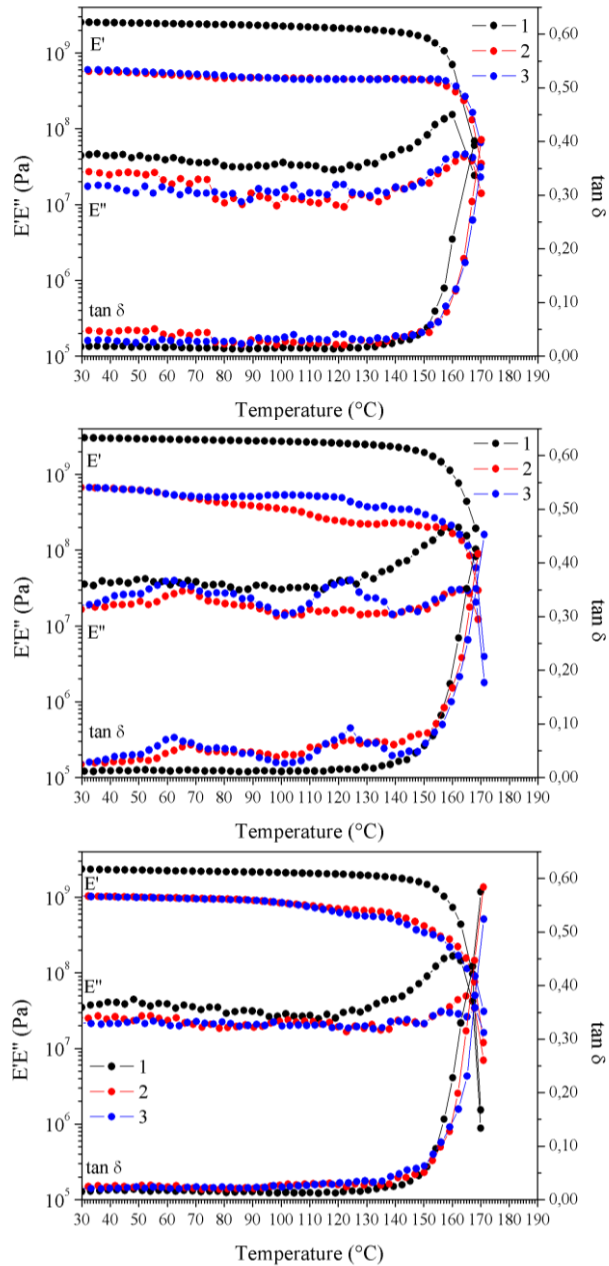


Figure 4: Storage modulus E' , loss modulus E'' and damping factor $\tan \delta$ of cross-linked samples PE-fur (top), PE-fur/EPM-fur_2.5 (middle) and PE-fur/EPM-fur_5 (bottom) for three consecutive DMTA cycles.

When comparing the first and second cycles, it is observed that storage moduli in the plateau region have slightly lower, but comparable values. This decrease was not observed when comparing the second and third cycles, suggesting that it might be due to deformation of the specimen at the end of the first heating stage. Indeed, when examining the samples after a measurement an elongation of several millimeters could be observed. This stems from the sideway force exerted on the sample by the DMTA sample holder. The slight increase in softening temperature (up to +2 °C) between subsequent cycles can be ascribed to the equilibrium between the kinetically favored *endo* and the thermodynamically more stable *exo* conformation of DA adducts^{12,37}. The constant stiffness of the material over consecutive heating cycles demonstrates the reworkability of the system, even in the presence of the rubber.

After performing thermo-mechanical tests on them, all specimens were re-ground and reshaped by compression molding (175 °C, 100 bar for 2 h) for another DMTA tests (Figure 5). In contrast to the freshly molded samples, the recycled materials exhibit lower but comparable storage and loss moduli and a slight (+1 °C) increase in the softening point, indicating full recyclability of the system. The return to similar mechanical properties after cooling down suggests that both polymers are able to re-form the DA crosslinks. Furthermore this hints towards the increased compatibility between both systems due to the shared crosslinking chemistry.

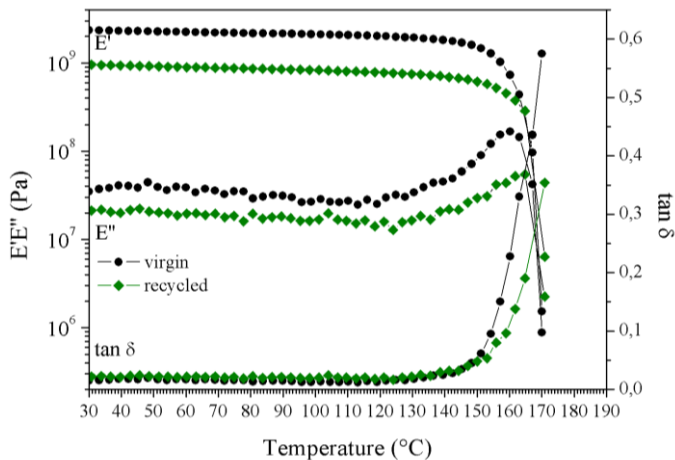


Figure 5: DMTA of cross-linked sample PE-fur/EPM-fur_5: comparison between virgin and recycled material. The recycled samples were reshaped at 170 °C and 100 bar for 2 hours

4.4.3 Impact strength

The Izod impact strength appears to monotonously increase with the amount of EPM-fur rubber (Figure 6). Ultimately, for the sample PE-fur/EPM-fur_5 (4 wt% of furan-modified rubber), a 54% increase in impact strength was observed compared to the neat crosslinked polyester. The two-tailed P value of an unpaired t test between PE-fur and PE-fur/EPM-fur_5 equals 0.0088, meaning this difference is “very statistically significant”. Meanwhile, no toughening effect was detected for the PE-fur/EPM-MA_5 (4 wt% of maleated rubber). This result indicates that, at least in this system, chemical bonding (i.e. Diels Alder cycloaddition) between the polyester matrix and the furan-modified rubber plays a crucial role in toughening, in agreement with what is generally reported for commercial rubber-toughened thermosets²³. Furthermore it serves as proof that the shared crosslinking capabilities of both polymers have successfully overcome the poor compatibility of the highly polar polyester and highly apolar EPM rubber.

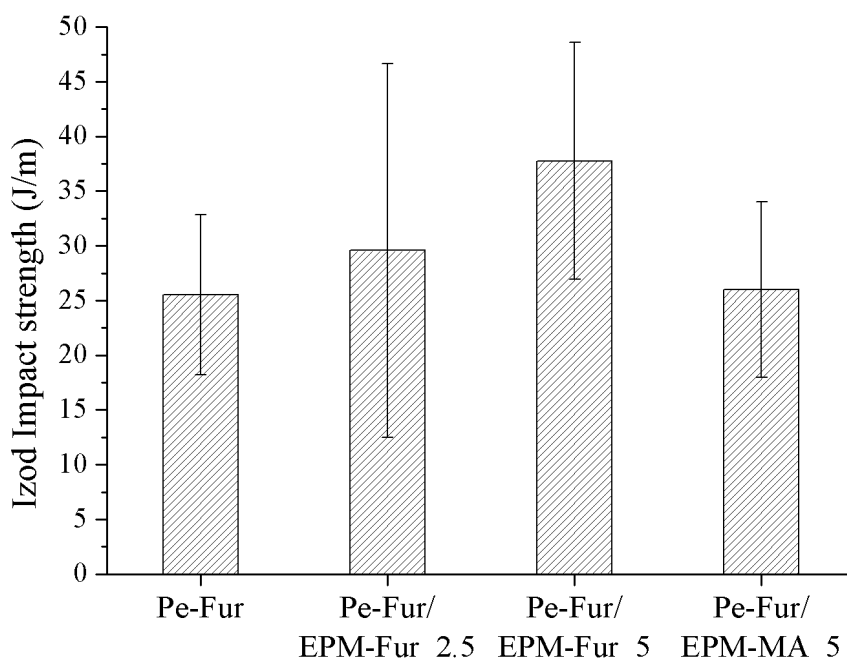


Figure 6: Izod impact strength of all b-MA samples Pe-Fur samples with and without different amounts of EPM-Fur. The error bars indicate ± 1 standard deviation.

4.5 Conclusion

Reversible, rubber toughened thermosets were prepared by mixing and cross-linking two different furan-functionalized polymers: a partially bio-based polyester, and an EPM rubber. The two polymers were successfully blended in different ratios (up to 5% in EPM) and crosslinked with an aromatic bismaleimide via the Diels Alder reaction.

Thermal reversibility was demonstrated by DSC for all prepared systems. Additionally, high recovery of mechanical properties was observed through cyclic DMTA measurements. Reworkability of the blends was demonstrated by remolding spent samples with little loss of mechanical properties.

The furan modified EPM rubber contributed to a significant enhancement (up to +54%) in toughness compared to the neat crosslinked polyester, as determined by Izod pendulum tests, without affecting mechanical properties, as determined by DMTA. While this improvement is to be expected for elastomeric modification of rigid thermosets, the fact that no significant effect was observed upon blending with non-functionalized EPM-MA indicates that the DA addition plays a crucial role. Furthermore it is a strong indication that covalent bonds are formed between both polymers, successfully overcoming the poor miscibility of the two.

4.6 Outlook

The preceding paragraphs make it abundantly clear that the toughness of a rigid polyester can be significantly improved by blending with an elastomeric component. It is clearly demonstrated that the shared capability of partaking in Diels-Alder crosslinking has a significant effect; in fact it seems required in order to see any improvement at all. The results imply an interaction between both polymers: allegedly Diels-Alder coupling occurs between the two systems. Unfortunately, no direct evidence could be obtained in order to prove this hypothesis. Therefore it would be beneficial to further analyze the system, focusing in particular on the cross-reaction between both components. Nevertheless, the results obtained are very promising and merit further investigation. A very straight-forward method of achieving greater control over the properties of the final blend would be the use of different rubbers. The

molecular weight and/or the backbone of the rubbers employed should provide ample possibilities of influencing the toughness of the final material.

4.7 References

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