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

Publication date:
2016

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

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A R T I C L E   I N F O

A B S T R A C T

In this work we present a reversible and toughened thermoset system based on the covalent incorporation of a furane functionalized ethylene–propylene rubber (EPM-Fu) into a thermoset furane functionalized polyketone (PK-Fu) via Diels–Alder (DA) reversible cross-linking with bismaleimide (b-MA). FT-IR and DSC analyses proved the reversible interaction between PK-Fu and EPM-Fu with b-Ma via DA and r-DA sequence. Likewise, thermo-mechanical experiments (DMTA) indicated the re-workability of the material with no evident differences in elastic and loss modulus after several heating cycles and recycling procedures. Moreover, a considerable increase in the softening point (tangent δ) was also found for the higher toughened system containing 12 wt% of EPM-Fu (neat thermoset $T = 137\ °C$ whereas toughened thermoset $T = 155\ °C$). A two-fold increase in IZOD impact strength compared to the neat thermoset (up to 27 J/m) was also recorded by the toughened system. Overall, this approach clearly indicates that fully thermally reversible and toughened thermosets can be realized starting from mixtures of furan functionalized polyketone and EPM rubber, cross-linked via reversible Diels–Alder chemistry.

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1. Introduction

Thermosetting resins are polymers that upon heat or light radiation convert into infusible and insoluble polymer networks being cross-linked by covalent chemical bonds. Due to this network, thermosets offer many superior properties compared to thermoplastics such as mechanical strength, dimensional stability at elevated temperature and solvent resistance [1]. These features confer them the ability to be widely used as composites, adhesives and coatings. Unlike thermoplastics, thermoset cannot be re-melted or re-shaped, since they degrade or decompose upon heating. These features limit their recyclability [2] so that at the end of their life service, they are simply grinded to produce cheap reinforcement fillers or are thermally processed (pyrolysis, incineration) to recover the fiber content or just energy [3–5]. A more sustainable strategy is to re-design thermosets by replacing classical chemical cross-links with reversible covalent bonds [2] that can be repeatedly broken and re-connected by heating. These thermoreversible networks combine many mechanical properties of thermosets with the processability of thermoplastics [6] but with the added value of intrinsic self-healing properties [7]. Among several

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reversible reactions, the Diels–Alder (DA) [$4\pi + 2\pi$] cycloaddition between furan and maleimide moieties is one of the most exploited in thermoreversible cross-linking [8] for several reasons. First, DA is an equilibrium reaction influenced by temperature: covalent furan/maleimide adducts are formed at about 50 °C (cross-linking) and broken (de-cross-linking via retro Diels Alder) at about 120 °C. Furthermore, the whole cross-linking–de-cross-linking process can be repeated many times with negligible degradation [9] in the range of 50–150 °C. Finally, the strong dienic character of the furan ring and the high reactivity of the maleimide as a dienophile, ensure fast kinetics and high yields [10]. Most of the studied thermoreversible networks are based on DA reaction of polymers bearing pendant furan and/or maleimide groups, but their syntheses are often too expensive or complex to permit an industrial scale up. In contrast, a system based on aliphatic polyketones with pending furan groups and cross-linked with 1,1′-(methylenedi-4,1-phenylene) bismaleimide was proposed as a promising low cost and efficient alternative [11]. Alternating aliphatic polyketones, obtained by copolymerization of carbon monoxide, ethylene and propylene were modified through the Paal–Knorr reaction in order to introduce furan groups directly attached to the backbone chain. The modification reaction proceeded in bulk with high yields and fast kinetics, producing water as only byproduct. The thermoset obtained upon cross-linking with bismaleimide was re-healed up to seven times, displaying quantitatively retained mechanical properties [11]. Furthermore, thermal and mechanical properties could be modulated as a function of the degree of furan functionalization and the furan/maleimide molar ratio [12].

Besides the poor recyclability of thermosets currently offered on the open market, they generally show a high brittleness compared to thermoplastic, due to their inadequacy in dissipating energy under mechanical stress. This causes poor resistance to crack formations as well as low fracture toughness and impact strength [1]. This point constitutes a major limit in the application of thermosets, so that many systems were developed aimed at enhancing toughness in epoxy resins, being these materials widely used for structural applications. Those systems are essentially based on the incorporation of either rigid or soft toughening agents in the epoxy matrix as a separate phase [13]. These modifiers can be inorganic fillers as silica, glass beads [14,15], engineered thermoplastics as polyphenylene oxide [16,17], rubbery core–shell particles [18–20] or liquid reactive rubbers such as carboxyl-terminated (CTBN) and amine-terminated butadiene–acrylonitrile copolymers (ATBN) [21–23]. CTBN and ATBN are the most investigated and widely used on commercial scale since they improve toughness of the epoxy matrix without significantly affecting its bulk properties such modulus or T_g [1]. As a common procedure, the liquid rubber is initially miscible with the uncured epoxy resin, while during the curing stage it irreversibly reacts with the epoxy through the functional groups (e.g. carboxylic or amino) and, as the molecular weight increases, it precipitates forming a second phase [24].

Herein, we report an innovative procedure aimed at introducing rubber toughening to the polyketone/bismaleimide system mentioned above, without interfering in the reversible character of the thermoset polymer. The rubber, an EPM grafted with furan groups, was chosen as a second cross-linked toughening phase as it can be easily prepared from commercial maleated EPM and reversibly cross-linked with bismaleimide, as recently reported [25]. The furan-modified polyketone and EPM were blended in solution, at different weight ratios, and cross-linked with bismaleimide. Systems morphology was investigated by means of electronic and optical microscopy whereas polymer toughness was determined in terms of Izod impact strength. Thermal reversibility was tested by FT-IR and DSC measurements while thermomechanical properties, re-workability and recyclability were evaluated by DMTA analysis.

2. Experimental

2.1. Materials

Alternating polyketone, a terpolymer of ethylene, propylene and carbon monoxide (PK30, M_w = 2687 g/mol) was synthesized according to a reported procedure [26,27]. The olefinic part of the polyketone is constituted of 30 mol% ethylene and 70 mol% propylene. Maleated ethylene/propylene rubber (EPM-MA, 49 wt% ethylene, 49 wt% propylene, 2.1 wt% maleic anhydride, M_n = 50 kg/mol, PDI = 2.0) was kindly provided by LANXESS elastomers and dried in a vacuum oven at 175 °C for one hour, in order to convert hydrolyzed diacids into anhydrides. Furfurylamine (Sigma–Aldrich, ⩾99%) was freshly distilled before use. Tetrahydrofuran (THF, Sigma–Aldrich, >99.9%), acetone (Sigma–Aldrich, >99.5%) and 1,1′-(methylenedi-4,1-phenylene)bismaleimide (Sigma–Aldrich, >95%) were purchased and used as received. Deuterated dimethylsulfoxide (DMSO-d$_6$, Sigma Aldrich, ⩾99.9 atom%) was used as solvent for ^{1}H NMR measurements.

2.2. Furan-derivatization of PK30 via Paal–Knorr reaction

The reaction between PK and furfurylamine was carried out in bulk according to the Paal–Knorr reaction (Fig. 1).

In a typical experiment, about 60 g of PK30 were weighed into a sealed 250 ml round bottom glass reactor equipped with a U-type anchor impeller, a reflux condenser and an oil bath for heating. The reactor was heated to 110 °C and 35.4 g (0.365 mol) of furfurylamine, based on the targeted carbonyl conversion of 80% (i.e. the di-carbonyl unit of polyketone modified into pyrrole ring, Fig. 1), were added dropwise during the first 20 min. The reaction was allowed to proceed for 4 h. The light brown product (PK-Fu) was cooled with liquid nitrogen, crushed and ground into small particles. The particles were washed three times with Milli-Q water to remove the unreacted furfurylamine, if any, filtered and freeze-dried for 24 h.

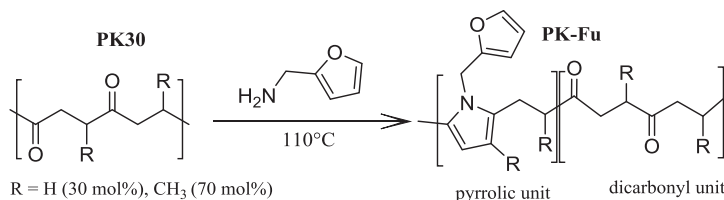The carbonyl conversion (C_{CO}) of PK was calculated according as follows:

Fig. 1. Modification of the aliphatic polyketone in bulk via Paal–Knorr reaction.

$$C_{CO} = \frac{y}{x+y} \cdot 100 \qquad (1)$$

being x the moles of dicarbonyl unit and y the moles of pyrrolic unit (Fig. 1) after conversion. y was calculated according to the formula:

$$y = \frac{N}{M_N} \qquad (2)$$

where N is the weight of nitrogen in the final product, as determined by elemental analysis and M_N is the atomic weight of nitrogen. x was calculated as follows:

$$x = \frac{\frac{C}{M_C} - y \cdot \overline{n_y^C}}{\overline{n_x^C}} \qquad (3)$$

where C is the weight of carbon in the final product as determined by elemental analysis, M_C is the atomic weight of carbon, $\overline{n_y^C}$ and $\overline{n_x^C}$ are the average number of carbons in the pyrrolic and in the dicarbonyl unit, respectively. Conversion efficiency (η) was calculated as follows:

$$\eta = \frac{y}{mol_{Fa}} \cdot 100 \qquad (4)$$

being mol_{Fa} the moles of furfurylamine in the feed.

2.3. Furan-derivatization of EPM-MA

Typically 100.0 g of EPM-MA (21.42 mmol MA) were dissolved in 900 g THF by stirring for 24 h at room temperature in a closed flask. 6.24 g of furfurylamine (3 equivalents based on the molar content of maleic anhydride) were added to the solution and agitation was maintained for 12 h. After reaction, the product (EPM-Fu) was purified by mixing the polymer with 5 l of acetone under mechanical stirring. Once the polymer precipitates as yellowish flakes, it is collected and dried in an oven at 50 °C up to constant weight. Conversion (C) of MA groups was calculated from FT-IR spectra according to a reported method [25], by using the following formula:

$$C = \left(1 - \frac{A_{1856}^{Fu}/A_{723}^{Fu}}{A_{1856}^{MA}/A_{723}^{MA}} \right) \cdot 100 \qquad (5)$$

where A_{1856}^{Fu} and A_{1856}^{MA} are the integrals of the absorption bands at 1856 cm^{-1} (C=O asymmetric stretching of anhydride rings) for EPM-Fu and EPM-MA respectively; A_{723}^{Fu} and A_{723}^{MA} are the integrals of the bands at 723 cm^{-1} (methyl rocking), used as internal reference.

2.4. Samples preparation and cross-linking

PK-Fu and EPM-Fu (set at different weight ratios) were dissolved in a nine-fold amount of THF, in a round bottom flask equipped with a magnetic stirrer, an oil bath and a reflux condenser. The mixture was heated at 50 °C for 24 h. A stoichiometric amount of 1,1′-(methylenedi-4,1-phenylene)bismaleimide (considering a 1:1 molar ratio between maleimide and the total amount of furan groups) was added to the mixture and the reaction (Diels–Alder cycloaddition) was allowed to proceed for 24 h under agitation at 50 °C. After reaction, the cross-linked gels were placed in a vacuum oven during 24 h at 50 °C to evaporate the solvent. Reference samples, one containing PK-Fu and EPM-MA (80:20 wt% ratio) and another containing only PK-Fu, were prepared and cross-linked with bismaleimide using the same procedure. An overview of all prepared systems is reported in Table 1. Samples have been coded by stating the type of EPM rubber and the percentage weight ratio rubber/polyketone.

Table 1
Amounts of polyketone (PK-Fu), EPM rubber (EPM-Fu or EPM-MA) and 1,1′-(methylenedi-4,1-phenylene)bismaleimide used to prepare the samples and resulting wt% of rubber in each system.

Sample code	PK-Fu (g)	EPM (g)	PK-Fu/EPM (w/w)	Bismaleimide (g)	Rubber (wt%)[a]
PK-Fu[a]	6.00	–	100:0	4.77 (13.3 mmol)	–
PK-Fu/EPM-Fu_10	5.41	0.60	90:10	4.31 (12.0 mmol)	6
PK-Fu/EPM-Fu_15	5.09	0.90	85:15	4.09 (11.4 mmol)	9
PK-Fu/EPM-Fu_20	4.80	1.20	80:20	3.86 (10.8 mmol)	12
PK-Fu/EPM-MA_20[a]	4.81	1.20	80:20	3.81 (10.6 mmol)	12

[a] Reference systems.

2.5. Characterization

Elemental analysis was performed with an EuroVector EA apparatus. ^{1}H NMR spectra were recorded on a Varian Mercury Plus 400 MHz apparatus using DMSO-d_6 as solvent. FT-IR spectra were obtained using a Perkin–Elmer Spectrum 2000. KBr pellets with 1.5 wt% content of polymer were prepared from powders of the polyketone/rubber samples. Films (1 mm thick) were prepared from the EPM rubbers by compression molding at 180 °C for 30 min under a pressure of 100 bars. DSC thermograms were recorded on a TA-Instrument DSC 2920 under N$_2$ atmosphere. Samples were first heated from 0 °C to 180 °C and then cooled to 0 °C. Four cycles were performed at a rate of 10 °C per minute. Dynamic Mechanical Thermal Analysis (DMTA) was performed using a Rheometric scientific solid analyzer (RSA II) under air environment, in dual cantilever mode at an oscillation frequency of 1 Hz and a heating rate of 3 °C per minute. Three cycles were performed for each sample, between room and softening temperature. DMTA specimens were 6 mm wide, 1.4 mm thick and 54 mm long. They were prepared by molding the cross-linked samples at 150 °C for 30 min under a pressure of 40 bars 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 in the same conditions used for DMTA specimens. Tests were performed on a Zwick 5102 Pendulum Impact Tester equipped with a hammer. At least 6 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. The morphological study of the systems was performed using a Philips XL30 Field-Emission Environmental Scanning Electron Microscopy SEM-FEG on fresh-fractured surfaces coated with gold nanoparticles (10 nm size). A simple observation on fracture toughness was registered using an optical microscope on samples prepared with the polymerography technique [28,29].

3. Results and discussion

3.1. Synthesis of furan-functionalized polyketone

Furan-functionalized polyketone (PK-Fu) was synthesized by reacting PK30 with furfurylamine in bulk at 110 °C for 4 h (Fig. 1). A high quantitative carbonyl conversion of 76% (80% targeted) and a conversion efficiency of 96% were obtained, confirming the Paal–Knorr reaction as a simple and efficient route to modify polyketones, as previously reported [11,12,30]. ^{1}H NMR spectra of PK30 and PK-Fu are shown in Fig. 2.

The resonance signals at 7.5, 6.3 and 6.1 ppm were assigned to protons on the furan ring connected to the polymer backbone, the resonance peak at 5.6 ppm was assigned to the protons of the pyrrole ring whereas the peak at 4.9 ppm was ascribed to the CH$_2$ group connecting the furan and the pyrrole ring [11,12].

3.2. Synthesis of furan-functionalized EPM rubber

A pre-thermal treatment was done on the EPM-MA rubber in vacuum at 175 °C in order to turn the hydrolyzed diacids moieties into maleic anhydrides [25,31]. Subsequently, furan-functionalized EPM rubber (EPM-Fu) was synthesized by reacting EPM-MA and furfurylamine in a THF solution at room temperature. The resulting EPM-Fu rubber was then studied by FT-IR transmission (Fig. 3). The appearance of the C—O—C symmetric stretching band at 1013 cm^{-1} clearly proved the presence of furan groups in the product [32]. Furthermore, the shift of the band at 1856–1780 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) demonstrated the conversion of anhydride rings into imide derivatives [12,31,33].

A deconvolution analysis was used to integrate the areas related to the peaks at 1856 cm^{-1} (C=O asymmetric stretching) and 723 cm^{-1} (methyl rocking vibration). From their ratio, the reaction conversion was determined and was found to be >99.9%, thus demonstrating quantitatively the chemical modification process.

3.3. Cross-linking of polyketone/rubber blends via Diels–Alder cycloaddition

PK-Fu/EPM-Fu blends were cross-linked with 1,1′-(methylenedi-4,1-phenylene) bismaleimide in THF solutions at 50 °C for 24 h (see table for experimental conditions). A scheme of one of the possible Diels–Alder (DA) adducts is reported in
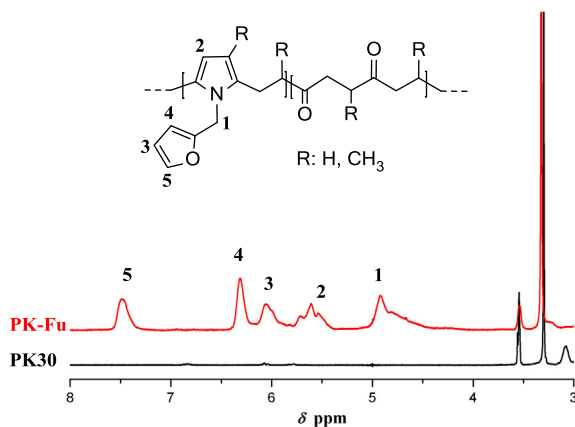
Fig. 2. ^{1}H NMR spectra of unmodified polyketone (PK30, black curve) and furan modified polyketone (PK-Fu, red curve). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 4. The FT-IR spectra of the sample PK-Fu/EPM-Fu_20 were recorded before and after the reaction with the bismaleimide (Fig. 5).

Fig. 5 clearly displays the appearance of the band at 1185 cm^{-1} (C—N—C stretching in succinimide ring of DA adduct) and the disappearing of the bands at 740 cm^{-1} (out-of-plane proton bending) and 1011 cm^{-1} (V_s C—O—C) of unreacted furans. Notably, this result substantially proves the formation of Diels–Alder adducts [11,12,34,35] while the band at 1378 cm^{-1} (C—N stretching in maleimide rings) demonstrates the presence of the bismaleimide.

3.4. Differential scanning calorimetry

All cross-linked samples were characterized by Differential Scanning Calorimetry (DSC) in order to determine the thermal history, reversibility and the exo/endo-thermal process related to the DA and r-DA sequence, respectively. All thermograms displayed a broad endothermic transition in the range of temperature 120–150 °C for each consecutive thermal cycle (Fig. 6). The similarity in each consecutive thermal cycle demonstrates the reversible character of the cross-linked PK-Fu, even when blended with the rubber.

The endothermic transition corresponds to the r-DA process, so that the maximum of the curve corresponds to the temperature at which all DA adducts are broken ($T_{rDA\ peak}$). The area under the curve associated to this peak, is therefore related to the energy absorbed during the cleavage of the DA adducts [7,12]. Notably, it can be noticed that the energy absorbed
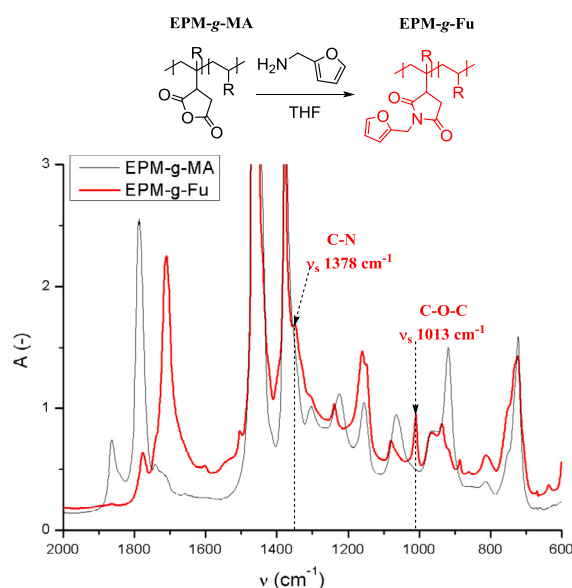

Fig. 3. FT-IR spectra of EPM-MA and the modified EPM-Fu: the reaction sequence is displayed in the inset.
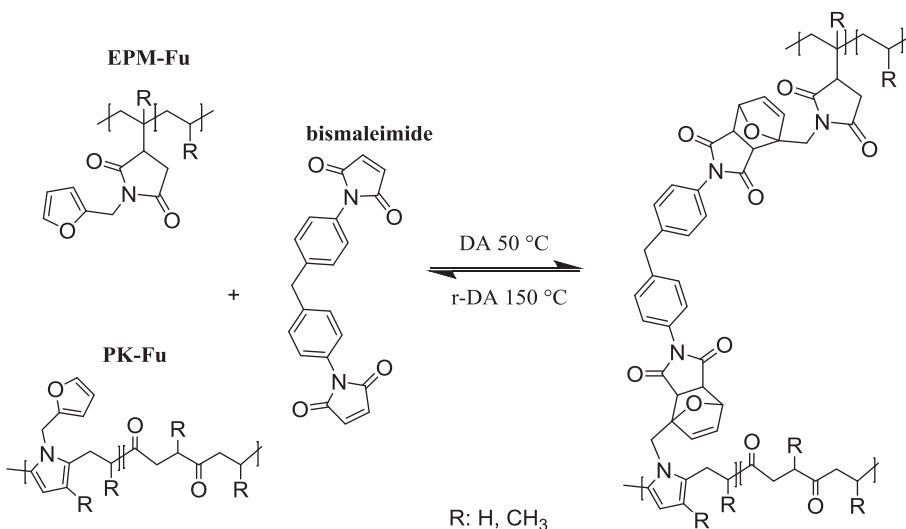
Fig. 4. Cross-linking and de-cross-linking of furan-modified polyketone PK-Fu/EPM-Fu rubber blends via Diels Alder (DA) and retro-Diels–Alder (r-DA) sequence with 1,1′-(methylenedi-4,1-phenylene)bismaleimide.
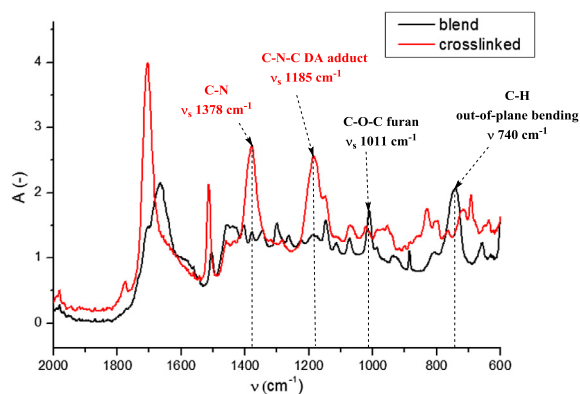
Fig. 5. FT-IR spectra of PK-Fu/EPM-Fu (80/20 wt% ratio) blend before and after cross-linking with 1,1′-(methylenedi-4,1-phenylene)bismaleimide.
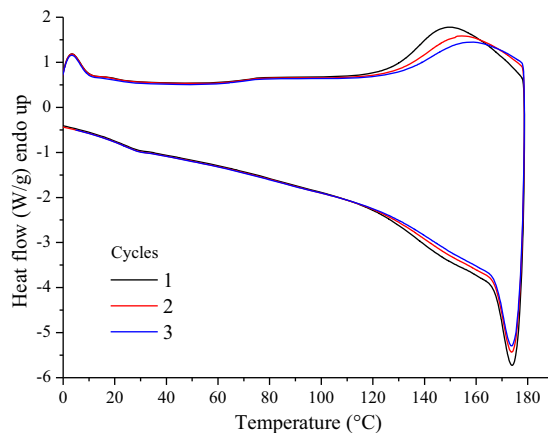

Fig. 6. DSC thermal cycles of cross-linked PK-Fu/EPM-Fu_20. Only one sample was reported for clarity.

Table 2
Calculated endothermic integral values ($Area_{rDA}$) and r-DA endothermic peak T_{rDA} in the 1st thermal cycle of PK-Fu, PK-Fu/EPM-Fu and PK-Fu/EPM-MA cross-linked with bismaleimide.

Sample	$Area_{rDA}$ (J/g)	$T_{rDA\ peak}$ (°C)
PK-Fu[a]	19.74	141.8
PK-Fu/EPM-Fu_10	17.33	149.6
PK-Fu/EPM-Fu_15	16.68	149.7
PK-Fu/EPM-Fu_20	15.38	150.4
PK-Fu/EPM-MA_20[a]	13.31	150.4

[a] Reference samples.
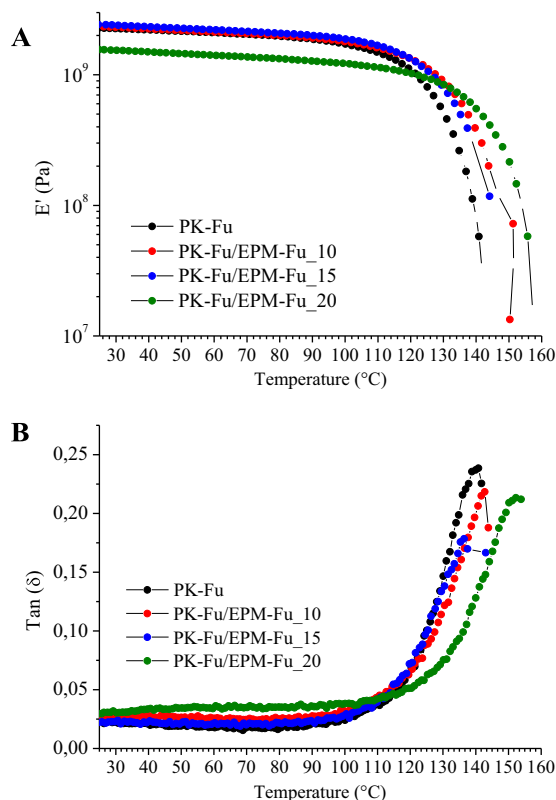
Fig. 7. Storage modulus E' (A) and damping factor $\tan\delta$ (B) in DMTA during 1st heating stage for cross-linked PK-Fu, PK-Fu/EPM-Fu_10, PK-Fu/EPM-Fu_15 and PK-Fu/EPM-Fu_20.

during the r-DA process (Table 2) decreases as the rubber content increases in the systems. This trend can be explained considering that EPM-Fu has a lower moles number of furan groups per gram than the PK-Fu, thus less amount of DA adducts are present in the blends compared to the neat cross-linked polyketone. Indeed, the lowest value in the integral was obtained from the sample PK-Fu/EPM-MA_20, which contains the maleated EPM rubber. All systems containing the rubber displayed practically the same $T_{rDA\ peak}$ and about eight degrees higher than the reference system PK-Fu. This can be possibly explained by the absorption of energy from the rubber during the process of r-DA and disentanglement [36,37].

3.5. Dynamic-mechanical Thermal Analysis

Homogeneous test-specimens for Dynamic-mechanical Thermal Analysis (DMTA) were successfully obtained from all samples, using hot compression molding. The variations in storage modulus (E') and damping factor ($\tan\delta$) as a function of the temperature and different amounts of rubber are shown in Fig. 7.

For all samples the storage modulus (E') exhibited a plateau followed by a sharp drop starting around 110 °C, implying a rubbery transition, but still cross-linked, due to a progressive softening of the entire system that probably loses some of the DA adducts during the process [8]. E' values in the plateau region were in the same order of magnitude for all the systems,
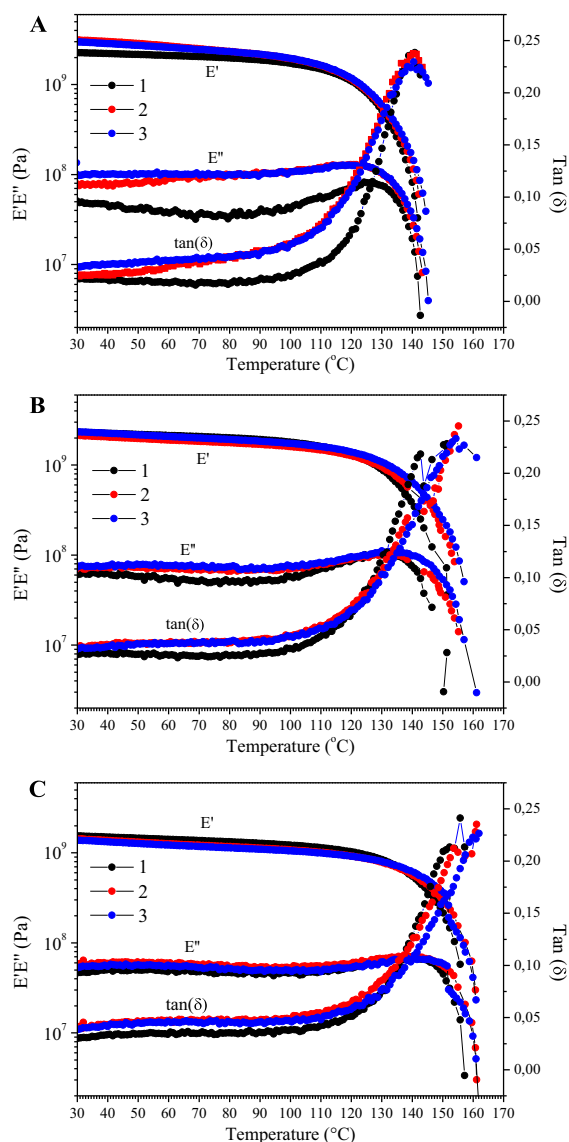
Fig. 8. Dynamic Mechanical Thermal Analysis of cross-linked samples PK-Fu (A), PK-Fu/EPMFu_10 (B) and PK-Fu/EPM-Fu_20 (C) in three consecutive cycles.

but a lower value (1.5 GPa) was observed for the sample with the highest content of rubber (PK-Fu/EPM-Fu_20), thus suggesting a less stiff material. The softening temperature, as determined from the peak of tan δ curves, was found within a narrow range (140–146 °C) for PK-Fu, PK-Fu/EPM-Fu_10, PK-Fu/EPM-Fu_15 and PK-Fu/EPM-MA_20, while significantly higher (155 °C) for PK-Fu/EPM-Fu_20.

After reaching the softening temperature, each sample was cooled down to room temperature during the first 10 min inside the DMTA chamber and tested again up to 3 heating cycles (Fig. 8).

Storage and loss moduli were quantitatively recovered in each cycle, providing further evidence of the re-workability in the systems. Notably, the softening temperature slightly shifted to higher temperatures (+5 °C) for samples containing the rubber. This shift can be attributed to a change from the kinetically *endo* to the thermodynamically more stable *exo* conformation of DA adducts after heating cycles [38].

Fig. 8 also shows that the presence of increasing amounts of rubber amplifies the system's ability to recover loss modulus between cycles. According to this, the presence of rubber increases the system's dimension stability so that modulus remains practically as the original in continuous DMTA measurements when the concentration of rubber reached 12% (PK-Fu/EPM-Fu_20). After thermo-mechanical tests, all samples were re-grinded and reshaped by compression molding for further DMTA tests, in order to further check their recyclability (figure).
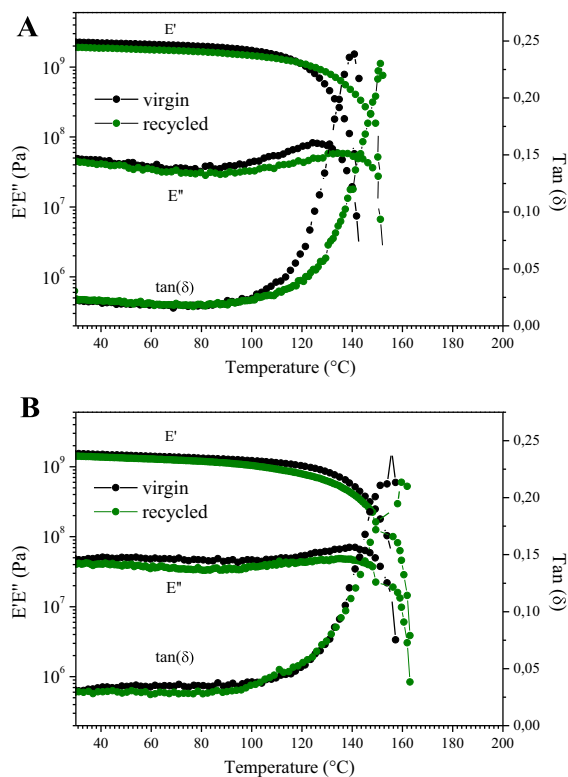
Fig. 9. DMTA of cross-linked samples PK-Fu (A) and PK-Fu/EPM-Fu_20 (B): comparison between virgin (freshly molded, in black) and recycled (grinded and remolded, in green) material. The recycled samples were reshaped at 150 °C and 40 bars for 30 min. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
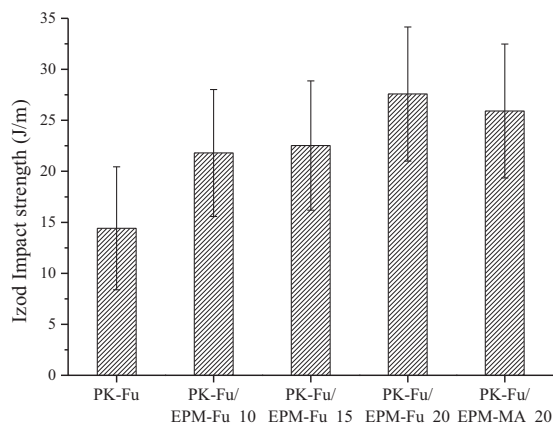
Fig. 10. Izod impact strength of all polymer samples.

It is worth noticing that both recycled samples displayed quantitative recovery of modulus and softening points. However a slightly increase in softening point was observed for the neat PK-Fu thermoset sample, possibly due to a more effective endo to exo conformation change of the DA adducts (Fig. 9). The relatively high softening point and the fully quantitative recovery of modulus and tan δ during thermo-mechanical cycles and recycling (grained samples), denotes that fully thermally reversible systems are possible to be made by the combination of furan functionalized polyketone with furan functionalized EPM rubber.
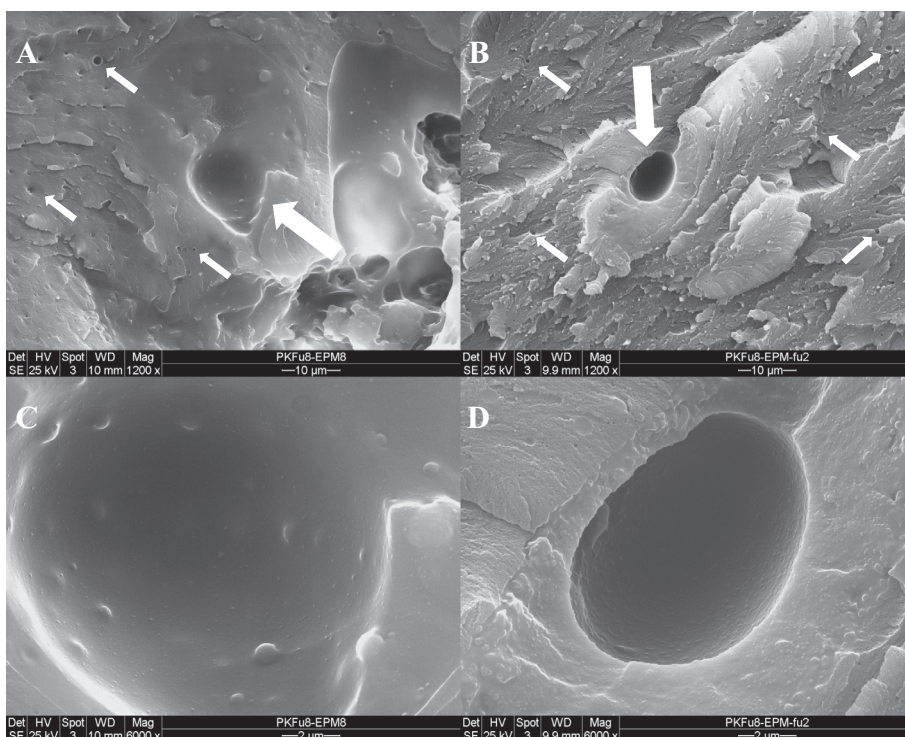
Fig. 11. SEM micrographs of freshly broken surfaces of PK-Fu/EPM-MA_20 (A and C) and PK-Fu/EPM-Fu_20 (B and D) showing cavitated particles (indicated by withe arrows) with different size and morphology.

3.6. Izod Impact strength, morphology and fractography

Izod Impact test was performed on unnotched specimens that broke completely during testing (10) (see Fig. 10).

All toughened samples display monotonous increase in the impact strength with increased rubber content, namely for the sample PK-Fu/EPM-Fu_20 (12 wt% of furan-modified rubber) a twofold increase was observed compared to the neat cross-linked polyketone. Moreover, a slightly higher value of impact strength for PK-Fu/EPM-Fu_20 compared to the reference PK-Fu/EPM-MA (12 wt% of maleated rubber) is observed. This small difference can probably indicate that both EPM rubbers provide similar toughening effect on the cross-linked polyketone. However, the DA chemical interaction between the matrix and the furan-functionalized rubber may be also taken into consideration. In order to clarify this point, a morphological study was performed by means of scanning electron microscopy SEM on fresh fractured surfaces in both toughened systems (Fig. 11). The holes observed in the micrographs are cavitated spaces of detached rubber particles after samples are broken. It is clearly noticed that EPM-MA and EPM-Fu rubber particles precipitate heterogeneously in size and morphology inside the matrix (Fig. 11A and B). The different morphologies in this case (see pictures on the left as opposed to those on the right side) stem from the differences in chemical composition. Indeed, EPM-MA rubber particles with no chemical bond with the matrix (Fig. 11A and C) leave smoother surfaces inside and around holes when removed, therefore suggesting poor compatibility between the two phases. Differently, EPM-Fu rubber particles, thus with chemical interaction between matrix and rubber particles (Fig. 11B and D), leave rough surfaces inside and around holes suggesting a well intrinsic adhesion between the phases.

Fig. 12 displays the toughening effect of EPM-MA and EPM-Fu rubber particles in the thermoset matrix after samples break. In Fig. 12B, a crack that apparently propagates from right to left (black arrow) is deflected and bridged by EPM-MA rubber particles (red[1] arrow). Moreover, some rubber particles are pulled-out or separated from the matrix as the crack propagates through the matrix. This can be explained by the weaker interaction between both phases as observed in Fig. 11C and suggested by impact test results. On the other hand, Fig. 12C and D show that crack propagation is stopped by EPM-Fu rubber particles. Deflection is also observed (black arrow, Fig. 12D) but crack separation seems to be absent. Overall, this demonstrates the effective intrinsic adhesion between the phases possibly due to the presence of DA inter-linkers between them.

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[1] For interpretation of color in Fig. 12, the reader is referred to the web version of this article.
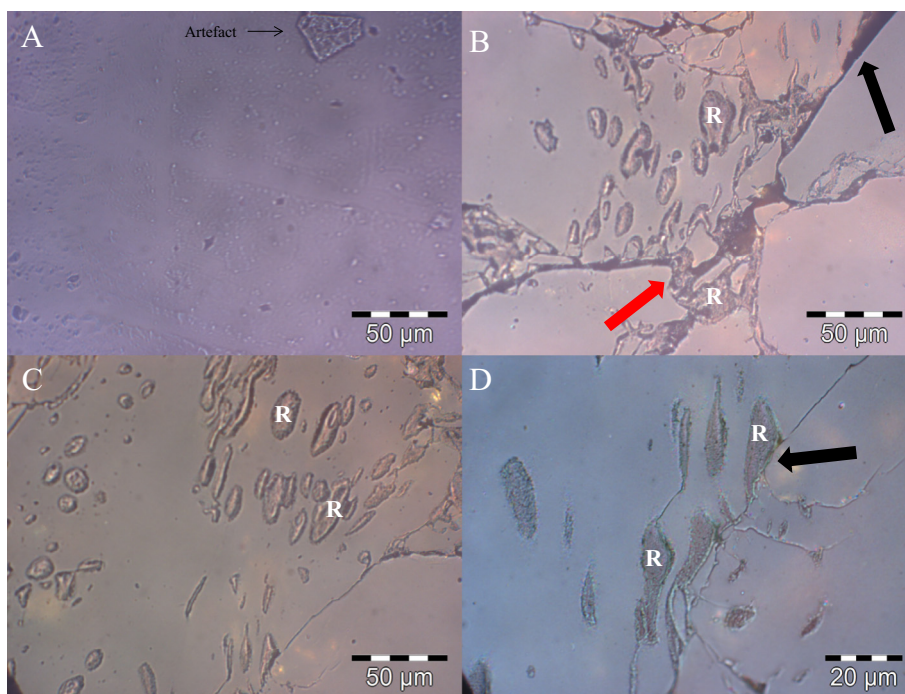
Fig. 12. Optical micrographs of PK-Fu (A) PK-Fu/EPM-MA_20 (B) and PK-Fu/EPM-Fu_20 (C and D) at different magnifications displaying the toughening effect of rubber particles. Letter R indicates rubber particles.

4. Conclusions

We have demonstrated the facile synthesis of a reversible thermoset material based on the chemical modification of aliphatic polyketones with furfurylamine by the Paal–Knorr reaction. The cross-linking and the rubber toughening with functionalized furan-EPM rubber occur via Diels–Alder chemistry. Moreover, all the processes involving polymers functionalization occur without adding any catalyst and in a conventional apparatus thus suggesting scaling up feasibility. Additionally, this approach successfully demonstrated thermo-mechanical, impact strength and recycling improvements on the neat thermoset. Indeed, the combination of DSC and DMTA experiments effectively indicates that furan functionalized polyketone in combination with furan-functionalized rubber is capable to be repeatedly cross-linked and de-cross-linked with bismaleimide by only using heat as external stimulus. Impact strength and morphological studies clearly demonstrated that the introduction of covalently bonded EPM rubber *via* Diels–Alder chemistry effectively improved the final impact strength of the toughened thermoset systems.

Acknowledgements

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