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Thermally Self-Healing Polymeric Materials: The Next Step to Recycling Thermoset Polymers?

Youchun Zhang, Antonius A. Broekhuis,* and Francesco Picchioni

Department of Chemical Engineering/Product Technology, University of Groningen, Nijenborgh 4, 9747 AG, Groningen, The Netherlands

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ABSTRACT: We developed thermally self-healing polymeric materials on the basis of furan-functionalized, alternating thermosetting polyketones (PK-furan) and bis-maleimide by using the Diels–Alder (DA) and Retro-Diels–Alder (RDA) reaction sequence. PK-furan can be easily obtained under mild conditions by the Paal–Knorr reaction of the polyketones with furfurylamine. The highly cross-linked polymers can be thermally remended to complete recovery in fracture loading, whereas the remending process can be repeated multiple times without any loss in mechanical properties. It is found that the achieved self-healing ability of this easily accessible system provides full recyclability and reworkability, which often is perceived to be difficult or impossible for thermosetting polymers. The simplicity of the synthesis, the broad range of available polyketone precursors, and the striking healing ability (kinetics and efficiency of mechanical properties recovery) of this system could expand the scientific understanding of self-healing materials and introduce the cradle-to-cradle concept for thermoset-based plastics and composites.

Introduction

Inspired by the phenomenon of self-healing in biological systems, the synthesis of man-made self-healing polymeric materials has become a newly emerging paradigm and a fascinating area of research.^{1–3} Self-healing materials have the capability of repairing or recovering themselves when suffering mechanically or thermally induced damage, which can occur autonomously^{4,5} or be activated by external stimuli^{6–8} (e.g., heat) once or multiple times. This valuable characteristic could extend the lifetime use of various polymeric products. However, costly and complex synthetic pathways and the loss of mechanical properties^{1–8} after self-healing or remending has limited their further development so far. The Diels–Alder (DA) reaction and its Retro-Diels–Alder (RDA) analogue represent a highly promising route to introducing self-healing properties to polymeric systems.^{1–3} The earliest work dealing with a thermally reversible polymeric network that contains DA functionalities was reported by Craven et al. in 1969.⁹ During the last few decades, two different strategic applications of this reaction sequence have been studied: (i) the polymerization of multifunctional monomers,^{6,7,10–15} for example, a di- or trifunctional furan derivative and a bis-maleimide; (ii) the formation of cross-linked polymer networks^{16–25} from linear thermoplastics bearing pendant furan or maleimide groups. However, limited thermal reversibility and costly synthesis pathways in both of the strategic approaches prohibit their practical applications as self-healing materials.^{6,7,10–25} In contrast, we report a simple polymer system that could resolve these problems. The starting materials for this system consist of alternating polyketones (1,4 arrangement of carbonyl groups), a new class of thermosetting polymers, obtained by alternating co- or terpolymerization of carbon monoxide, ethylene, and propylene using homogeneous palladium-based catalysis.^{26–28} These polyketones can be easily converted to furan derivatives (PK-furan) via the Paal–Knorr reaction with furfurylamine. The PK-furan is successively converted by the DA reaction with the indicated bis-maleimide, resulting in a highly cross-linked polymeric network. Subsequently, the dissociation of the network can be accomplished at elevated temperature by the RDA reaction. Therefore, the sequence of cross-linking (DA), de-cross-linking (RDA), and

re-cross-linking (DA) processes makes this thermosetting polymer system not only remendable but also reworkable.

Nowadays, thermosetting resins are used in a wide range of applications including adhesives, coatings, polymer composites, electrical insulation, printed circuit boards, etc. However, the recycling at the end of their life cycle is a very difficult challenge because of the cross-linked nature.^{29–33} The cross-linked thermosetting resins cannot be remelted or reshaped like thermoplastics because the heating leads to decomposition and degradation of the materials. Furthermore, thermoset-based products, in particular, thermoset composites, are usually formulated with various additives such as fillers (e.g., mineral powders, fire retardants) and fibrous reinforcement (e.g., glass or carbon fiber), which results in complex mixtures that are difficult or impossible to separate. Therefore, most of the thermoset-based products end up in landfills or are incinerated after their functional use. Owing to the serious concern regarding the environment and the finite natural resources, new recycling technologies for thermosetting resins are urgently needed. In the present work, the before-mentioned thermally self-healing concept could address these issues well.

Here we first investigated the chemical reactivity of the polyketones with furfurylamine under different reaction conditions. A model component reaction was used for this study to facilitate the structure characterization for the prepared polymeric material. We thoroughly studied the DA and RDA reactions between PK-furan and bis-maleimide by measuring gelation time and gel content and by performing NMR and FTIR spectroscopy. We also performed thermal analysis of the cross-linked PK-furan by using differential scanning calorimetry (DSC), whereas we evaluated the self-healing efficiency by dynamic mechanical analysis (DMA) and three-point bending tests. To the best of our knowledge, the use of polyketone precursors for the Diels–Alder reactions, the ultrafast kinetics of such reactions for the polymeric system, and the outstanding efficiency in the mechanical properties recovery (no changes are observed up to seven thermal cycles) constitute clear novelties of the present work.

Experimental Section

Materials. The alternating polyketones, co- and terpolymers of carbon monoxide, ethylene, and propylene, with 0% ethylene (PK0,

* Corresponding author. E-mail: A.A.Broekhuis@rug.nl.

MW 1680), 30% ethylene (PK30, MW 3970), and 50% ethylene (PK50, MW 5350) on the basis of the total olefin content were synthesized according to a reported procedure.^{27,28} Furfurylamine (Aldrich, $\geq 99\%$), 2,5-hexanedione (Aldrich, $\geq 99\%$), bis-maleimide (1,1'-(methylenedi-1,4-phenylene)bismaleimide-95%, *N,N'*-(1,3-phenylene)bismaleimide-97%, Aldrich), chloroform (Laboratory-Scan, 99.5%), dichloromethane (Laboratory-Scan, 99.8%), and dimethyl sulfoxide (DMSO, Acros, 99.7%) were purchased and used as received.

Furan Functionalization of Alternating Polyketones. The reaction between polyketones (80 mg) and furfurylamine (in equimolar ratio between the 1,4-dicarbonyl groups of the polyketones and the amino groups) was first carried out in CDCl_3 at 50 °C for 12 h in an NMR tube. The progress of the reaction was monitored with ^1H NMR spectroscopy, and the spectra were recorded at regular time intervals of 30 min. The chemical modifications of the polyketones with furfurylamine were also carried out in bulk in a sealed 250 mL round-bottomed glass reactor with a reflux condenser, a U-type anchor impeller, and an oil bath for heating. After the polyketones (40 g) were preheated to the liquid state at the employed reaction temperature (100 °C), furfurylamine was added dropwise to the reactor in the first 10 min. The stirring speed was set at a constant value of 500 rpm, and the employed reaction time was 4 h. After reaction, the color of the reaction mixtures changed from colorless to brown because of the presence of pyrrole unit in the polymer backbone. The conversion of furfurylamine was determined by ^1H NMR and reported as the average of four different values (different spectra). The resulting experimental error (standard deviation) on the average value was $<1\%$. Moreover, the conversion was found to be in full agreement with the results determined by potentiometric titration.³⁴ The resulting polymers (after modifications) were washed several times with deionized Milli-Q water to remove unreacted furfurylamine. After filtering and freeze drying, light-brown polymers were obtained as the final products (PK-furan). Elemental analysis for PK-furan (PK50 at the amine/diketone ratio of 0.8): Calcd: C, 75.18; H, 7.10; N, 6.31; Found: C, 75.08; H, 7.14; N, 6.37.

Synthesis of Model Compound. Pyrrolic furan was first obtained by the reaction of 2,5-hexanedione (5 g, 44 mmol) and furfurylamine (4.26 g, 44 mmol) without using any solvent in a 50 mL round-bottomed flask equipped with a magnetic stirrer. The reaction mixture was heated to 70 °C for 20 h with vigorous stirring. After the reaction, the mixture was diluted with dichloromethane (150 mL) and dried over sodium sulfate. The solvent was removed under vacuum to yield pyrrolic furan (7.06 g, 94% yield). ^1H NMR (400 MHz, CDCl_3 , δ): 7.33 (dd, 1H, $J = 1.8$ Hz, $J = 1.1$ Hz), 6.29 (dd, 1H, $J = 3.2$ Hz, $J = 1.8$ Hz), 6.03 (m, 1H), 5.81(s, 2H), 4.91 (d, 2H, $J = 0.7$ Hz), 2.27 (s, 6H). ^{13}C NMR (100.6 Hz, CDCl_3 , δ): 151.3, 142.1, 127.8, 110.2, 106.9, 105.3, 40.4, 12.3. Elemental analysis for $\text{C}_{11}\text{H}_{13}\text{NO}$: Calcd: C, 75.40; H, 7.48; N, 7.99; Found: C, 75.12; H, 7.38; N, 7.89.

Model Diels–Alder and Retro-Diels–Alder Reaction. The Diels–Alder (DA) reaction of pyrrolic furan (0.5 g, 2.85 mmol) and bis-maleimide (0.54 g, 1.43 mmol) was carried out in chloroform (5 mL) in a 50 mL round-bottomed flask equipped with a magnetic stirrer. The reaction mixture was heated to 50 °C for 24 h with vigorous stirring. After the reaction, the solvent was removed under vacuum to afford the model adduct as a yellowish solid. The Retro-Diels–Alder (RDA) reaction of the model adduct was performed in an NMR tube. The model adduct (50 mg) was dissolved in $\text{DMSO}-d_6$ (0.6 mL) in a 4 mL glass vial. After transferring the solution in the NMR tube, the latter was immersed in a 150 °C oil bath for 5 min, followed by quenching in an ice-water bath. After that, ^1H NMR spectra were immediately recorded.

Polymer Diels–Alder and Retro-Diels–Alder Reaction. The DA reaction of PK-furan (15 g) and bis-maleimide using chloroform (150 g) as solvent (10 wt % polymer based on solvent) was carried out in a 250 mL round-bottomed flask equipped with a magnetic stirrer. In this article, 1,1'-(methylene-di-1,4-phenylene)bis-maleimide was used in all of the experiments unless otherwise stated. The gelation time was determined to be the point at which the

magnetic stirrer stopped rotating. We obtained the cross-linked polymers by drying the polymer gel to a constant weight at 50 °C under vacuum. The gel content was determined by Soxhlet extraction with boiling dichloromethane for 20 h. The DA and RDA reactions of the polymers were also performed in an NMR tube. PK-furan (25 mg) and bis-maleimide (21.5 mg) in equimolar ratio (between furan and maleimide groups) were dissolved in $\text{DMSO}-d_6$ (0.7 mL) and then transferred to an NMR tube. The reaction mixture was heated to 50 °C for 24 h to form the polymer adduct. After the reaction, the NMR tube was immersed in a 150 °C oil bath for 5 min, followed by quenching in an ice–water bath. ^1H NMR spectra were instantly recorded after quenching. For the cross-linked PK-furan after Soxhlet extraction and the removal of the solvent, the sample (50 mg) was added to $\text{DMSO}-d_6$ (0.7 mL) in a small glass vial and then heated to 150 °C in an oil bath for 5 min. After quenching in an ice–water bath, the completely dissolved polymer solution was transferred to an NMR tube, and ^1H NMR spectra were then instantly recorded.

Characterization. ^1H NMR spectra were recorded on a Varian Mercury Plus 400 MHz apparatus using CDCl_3 or $\text{DMSO}-d_6$ as a solvent. FTIR spectra were recorded using a Perkin-Elmer Spectrum 2000 equipped with a heating stage and temperature controller. Element analysis was performed with an Euro EA elemental analyzer. DSC was performed on a Perkin-Elmer differential scanning calorimeter Pyris 1 under a N_2 atmosphere. The sample for DSC was weighed (ca. 8 mg) in an aluminum pan, which was then sealed. The sample was first heated from 25 to 180 °C and then kept at 180 °C for 1 min, followed by cooling to 25 °C. Four cycles were performed, and the heating and cooling rates were set to 10 °C/min throughout the DSC measurements.

Quantifying Healing Efficiency. Dynamic mechanical analyses were conducted on a rheometrics scientific solid analyzer (RSA II) under an air environment using the dual cantilever mode at an oscillation frequency of 1 Hz at a heating rate of 5 °C/min with the specimen size of 6 mm in width, 1.4 mm in thickness, and 54 mm in length. The three-point bending test was performed on a 4301 Instron machine using a 1 kN power sensor at a crossing head speed of 1 mm/min with the specimen size of 12.7 mm in width, 4 mm in thickness, and 64 mm in length. At least eight specimens of every formulation for three-point bending were tested with the standard deviation of fracture load less than 0.02 kN. The fracture surface of the samples after three-point bending was examined by scanning electron microscopy (SEM) (JSM-6320 instrument). The samples were sputtered with Pt/Pd prior to SEM observation. The specimens for three-point bending were prepared by compression molding of the cross-linked PK-furan into rectangular bars at 120 °C for 20 min under a pressure of about 4 MPa, followed by the thermal treatment at 50 °C for 24 h in an oven.

Results and Discussion

Synthesis of Furan-Functionalized Polyketones. The classic Paal–Knorr reaction, in which the 1,4-dicarbonyl moiety of the polyketones reacts with a primary amine function yielding a pyrrole unit, is one of the dominating reaction routes for the functionalization of alternating polyketones.³⁴ In the present work, a class of low-molecular-weight polyketones (MW 1500–5500), alternating co- and terpolymers of carbon monoxide, ethylene, and propylene were used as starting materials for chemical modifications. We synthesized the furan-functionalized polyketones (PK-furan), which have *N*-substituted 2,5-pyrrolediyl groups incorporated into the backbone with a furan group pendant from the main chain, by reacting the polyketones with furfurylamine (Figure 1). The mechanism of the Paal–Knorr reaction between a 1,4-dicarbonyl compound and a primary amine involves three steps: addition to the first carbonyl, addition/elimination and rearrangement steps, and stable product formation.³⁵ In contrast with various polymerization techniques,²⁵ chemical modifications of polyketones provide a feasible, simple, and highly efficient route for preparing furan-functionalized polymers.

Figure 1. Scheme of the Paal–Knorr reaction between polyketones and furfurylamine.

Figure 2. NMR tube reactions between polyketones (PK0, PK30, and PK50) and furfurylamine at 50 °C: (a) ¹H NMR spectra (PK50 and furfurylamine) before reaction (I) and after 12 h (II); (b) furfurylamine conversion, determined by ¹H NMR.

The Paal–Knorr reaction between polyketones (PK0, PK30, and PK50) and furfurylamine was first investigated at equimolar ratio between furfurylamine and the 1,4-dicarbonyl groups of the polyketones in the NMR tubes. NMR spectra of the starting reaction mixture (PK50 and furfurylamine) (I) and that after 12 h reaction time at 50 °C (II) are shown in Figure 2a. The broad absorbance peaks at 5.8 and 4.9 ppm are assigned to the pyrrole ring in the backbone and the $-\text{CH}_2-$ group attached to the pyrrole ring, respectively. The broad absorbance peaks at 7.3, 6.2, and 5.9 ppm can be ascribed to the hydrogens on the furan ring attached to the polymer backbone. By using the intensity ratio of the $-\text{CH}_2-$ peak of furfurylamine before and after reaction, the reaction conversion of furfurylamine can be

Figure 3. FTIR spectra of polyketones (PK50) (I) and furan-functionalized PK50 (II).

Table 1. Conversion Data of Furfurylamine (X_{NH_2}) and Carbonyl Groups of Polyketones (X_{CO}) at the Effect of Different $I_{\text{NH}_2/\text{CO}}$ and Different Types of Polyketones^a

PK-furan	polyketones	$I_{\text{NH}_2/\text{CO}}$	X_{NH_2} (%)	X_{CO} (%)
PK50f-1	PK50	0.8	98	78
PK50f-2	PK50	0.6	100	60
PK50f-3	PK50	0.4	100	40
PK50f-4	PK50	0.2	100	20
PK30f	PK30	0.8	75	60
PK0f	PK0	0.8	62	50

^a Reaction temperature: 100 °C; reaction time: 4 h.

calculated as a function of reaction time (Figure 2b). It is interesting to observe that the Paal–Knorr reaction for the polyketones with furfurylamine can easily take place, even under mild conditions (50 °C). The reaction conversions of the polymers after 12 h of reaction time reach 17.5% (PK0), 35% (PK30), and 68% (PK50), respectively. The reaction rates and conversion values were found to increase with the ethylene content of the polyketones, which is due to lower steric hindrance of the carbonyl groups and a reduced C–C rotation barrier for the polymers with higher ethylene content.³⁴ Furthermore, FTIR spectra of polyketones (PK50) before and after chemical modifications (Figure 3) also demonstrated the presence of pyrrole rings (3112 and 1596 cm^{-1}) in the backbone and the bearing of furan rings (734 cm^{-1}) at the side chain for the furan-functionalized polyketones.

The bulk reactions between polyketones and furfurylamine (without the use of any catalysts or additives) were studied at 100 °C using a reaction time of 4 h while varying the amine/diketone ratio ($I_{\text{NH}_2/\text{CO}}$) and the ethylene content of the polyketones. The conversion data for furfurylamine (X_{NH_2}) and carbonyl groups (X_{CO}) are shown in Table 1. All reactions with PK50 proceeded exceedingly well with conversion values up to 98% for $I_{\text{NH}_2/\text{CO}} = 0.8$ and 100% for $I_{\text{NH}_2/\text{CO}}$ of 0.6, 0.4, and 0.2, respectively. The degree of furan functionality can be tuned simply by varying the $I_{\text{NH}_2/\text{CO}}$. With respect to the effect of ethylene content of the polyketones, amine conversions of 75 and 62% for PK30 and PK0 were obtained under the applied reaction conditions, respectively, which also indicates that a higher ethylene content resulted in higher conversion values. This is in line with the results obtained for the reactions carried out in the NMR tubes.

Diels–Alder and Retro-Diels–Alder Reaction of PK-furan. The cross-linking of PK-furan with bis-maleimide via the DA reaction (Figure 4) was studied as a function of the initial molar ratio between maleimide and furan groups ($I_{\text{ma/fur}}$)

Figure 4. Scheme of the Diels–Alder (DA) and Retro-Diels–Alder (RDA) reactions between PK-furan and bis-maleimide.

Table 2. Cross-Linking of PK-furan with Bis-Maleimide via the DA Reaction at the Effect of Maleimide/Furan Ratio ($I_{ma/fur}$) and the Degree of Furan Functionality^a

PK-furan	$I_{ma/fur}$	gelation time (h)	gel content (%)
PK50f-1	0.25	9	59
PK50f-1	0.5	3	92
PK50f-1	0.75	2.5	95
PK50f-1	1	2.2	93
PK50f-2	1	2.5	95
PK50f-3	1	3	87
PK50f-4	1	8.5	68

^a Reaction temperature: 50 °C; reaction time: 24 h; polymer coding as in Table 1.

Figure 5. (a) Gelation and its reversal for PK50f-1 with bis-maleimide at $I_{ma/fur} = 1$ in DMSO solvent: (1) initial reaction mixture, (2) gel formation at 50 °C after 2 h, (3) back to soluble solution in 5 min at 150 °C; (b) insoluble cross-linked PK50f-1 at $I_{ma/fur} = 1$ in DMSO (upper) at 50 °C and fully soluble solution (bottom) in 5 min at 150 °C.

and the degree of furan functionality on the polymer backbone (Table 2). The PK-furan derived from PK50 can be easily cross-linked with bis-maleimide to form a gel, irrespective of $I_{ma/fur}$ and the amount of furan functionalities along the polymer backbone. The fastest gelation time was about 2 h for PK50f-1 at $I_{ma/fur}=1$. It is worth noticing that the gelation time increases with decreasing the $I_{ma/fur}$ and the degree of furan functionality. This is related to the fact that the reaction kinetics at a fixed weight content of the polymers strongly depend on the initial concentration of furan and maleimide groups. With respect to gel content (corresponding to the number of cross-linking points) for all of the studied samples, it is found that high gel contents (in the range of 92–95%) were obtained at high maleimide/furan ratios and a high degree of furan functionality, clearly indicating the high conversion level for the DA reaction.

The cycles of the DA and RDA reaction of PK-furan with bis-maleimide were first investigated in solvent. Figure 5a shows the photographs of the DA and RDA reactions in DMSO (10 wt % of PK-furan based on solvent) for PK50f-1 at $I_{ma/fur} = 1$. The forward reaction occurred at low temperature and led to gel formation (2 of Figure 5a). Upon heating, the resulting polymer gels were completely reversed to clear and fluid solutions (3 of

Figure 6. (a) NMR spectra of model adduct (I) and reversal of model adduct (II); (b) NMR spectra of initial reaction mixture of PK50f-1 with bis-maleimide at $I_{ma/fur} = 1$ (I), polymer adduct after 24 h at 50 °C (II), and reversal of polymer adduct after 5 min at 150 °C (III).

Figure 5a), which show the same appearance as the starting mixture (1 of Figure 5a). Contrary to the results^{16–25} described in the literature for thermoplastic polymers bearing pendant furan or maleimide groups, the DA and RDA reactions here are characterized by ultrafast kinetics (gel formation in 2 h at 50 °C and its reversal in 5 min at 150 °C or in 10 min at 120 °C), which in turn can also be tuned by adjusting the maleimide to furan molar ratio. We repeated the cycle of gelation and its reversal four times without noticing any relevant changes in appearance, thus giving a clear preliminary indication that the PK-furan/bis-maleimide system is fully thermally reversible. Moreover, the fast kinetics of the RDA reaction were further confirmed (Figure 5b) by the initial insolubility of the highly cross-linked polymers (PK50f-1 at $I_{ma/fur} = 1$) after Soxhlet extraction and the removal of the solvent in DMSO (upper part in Figure 5b). Upon heating, in less than 5 min, the precipitated polymer was converted back to a clear solution (bottom part in Figure 5b).

¹H NMR spectroscopy was used to study the forward and reverse DA reaction of PK-furan with bis-maleimide. To facilitate structure identification, the model DA adduct of pyrrolic furan with bis-maleimide was first used to study the thermal behavior. It is observed that the reaction product after DA reaction (I of Figure 6a) contains the endo and exo forms of the DA adduct and some of the unreacted starting materials. According to the relative intensity ratio of the reacted and unreacted pyrrolic furan, the yield of the DA (including exo and endo forms) adduct was found to be 96% with an exo/endo ratio of around 70/30. Upon heating at 150 °C for 5 min, the RDA reaction on the model compound proceeded almost completely, as demonstrated by the corresponding NMR

Figure 7. FTIR spectra of the cross-linked PK-furan (PK50f-1 at $I_{\text{ma/fur}} = 1$) before heat treatment at room temperature (I), upon heating to 150 °C for 5 min (II), and after cooling to room temperature in 20 min (III).

spectrum (II of Figure 6a), where only peaks from the pyrrolic furan and the bis-maleimide could be identified. For the polymeric systems, the features of the DA adduct that are in line with the model study, namely, H1 and H2 at 3.2 ppm, H3 at 5.1 ppm, and H4 and H5 at 6.5 ppm, appeared after the reaction (II of Figure 6b). The RDA reaction of the polymer adduct was performed using the same conditions as those for the model adduct. No features of the DA adduct could be detected after RDA reaction (III of Figure 6b). Another NMR study for the RDA reaction was carried out for the cross-linked PK50f-1 at $I_{\text{ma/fur}} = 1$ after Soxhlet extraction and removal of the solvent. Upon heating, in less than 5 min at 150 °C or 10 min at 120 °C, a clear polymer solution in DMSO- d_6 was obtained. The NMR spectrum of this polymer solution was found to be practically the same as I of Figure 6b, which only consists of absorptions assigned to PK50f-1 and bis-maleimide. All of these results provide strong evidence of 100% or full thermal reversibility of the cross-linked polymer systems.

In addition, FTIR spectroscopy was used to study the cycle of the DA and RDA reactions of PK-furan with bis-maleimide in the solid state. The following steps were used: DA-RDA-DA (Figure 7). The striking phenomenon during the heating and cooling cycles is the up and down switch of the intensity of the absorption peak at 1182 cm^{-1} . The spectrum of the cross-linked PK-furan (PK50f-1 at $I_{\text{ma/fur}} = 1$) after solvent extraction and removal of the solvent is shown in I of Figure 7. Upon heating to 150 °C for 5 min, a significant intensity decrease in the absorption peak at 1182 cm^{-1} (II of Figure 7) was observed, which could be ascribed to the debonding of the DA adduct (C–O–C) via the retroreaction. No change of the spectra could be detected after a further increase in heating time to 20 min at 150 °C, indicating the complete debonding of the DA adduct in the short time frame of 5 min, which is in line with our study in the liquid state. After slow cooling from 150 °C to room temperature in 20 min, III in Figure 7 shows the recovery of intensity at 1182 cm^{-1} with the same characteristics as those given in I of Figure 7. This can be explained by the regeneration of the DA adduct (C–O–C) during the cooling step. Four cycles of RDA and DA reactions were performed, and similar results (i.e., up and down switch of intensity at 1182 cm^{-1}) were obtained. Therefore, it can be concluded that the PK-furan can be repeatedly de-cross-linked and re-cross-linked with bis-maleimide in the solid state by simple heating and cooling cycles.

The high efficiency of the DA and RDA process is further confirmed by the thermal behavior of the cross-linked PK-furan (Figure 8), as measured by the repeated DSC cycles. DSC thermograms display an overlapping of the endothermic (as-

Figure 8. Thermal behavior of the cross-linked PK-furan (PK50f-1 at $I_{\text{ma/fur}} = 1$).

cribed to the RDA reaction) and exothermic transitions (ascribed to the DA reaction) during the successive thermal cycles. The slight deviations of the absorption profile, especially in the heating cycles, can be attributed to the relatively short time scale of the DSC experiment, which does not allow a full reconstitution of the DA network. With respect to thermal behavior of previously reported DA polymer products,^{10,13–15,17} none of them was able to show any endothermic transition at a second heating cycle, which suggests limited reversibility or very slow kinetics of the DA adduct formation during the first cooling scan. This highlights the capability of the current system as a self-healing material.

Thermally Self-Healing. The fact that cross-linked PK-furan is thermally remendable is further demonstrated by compression molding of small granules of the cross-linked PK-furan into uniform bars at elevated temperature (typically 110–150 °C, 10–30 min processing time). When exposed to heat, the polymers display the relevant properties of linear thermoplastics, such as remeltability, reprocessability, and recyclability because of the opening of the DA adduct. After slowly cooling to room temperature (30–40 min), a rigid structural polymer network can be achieved because of the regeneration of the DA adduct. In this process, polymer chains are able to reorganize and therefore reconstruct or remodel themselves into any desired physical shape. Besides the remendability, a breakthrough has been made here in terms of full recyclability and reworkability of this system. Nowadays, recycling of thermosetting materials at the end of the life cycle is often considered to be difficult and remains an unresolved issue.^{29–33} The recycling techniques in current polymer recycling industries mainly involve mechanical (the use of grinding techniques to comminute thermoset recyclates as reinforcing fillers in new composites) and thermal processing steps (the use of heat to break the scarp composites down to recover the energy and feedstock), but they do not represent convenient choices from the economic and environmental point of view.^{29–33} In contrast, our system can provide a feasible way to resolve the recycling issues of thermosetting polymers.

The thermal self-healing ability of the cross-linked PK-furan was further studied by using DMA. Dynamic mechanical properties of the cross-linked PK-furan (storage modulus G' , loss modulus G'' , $\tan \delta$ versus temperature) are shown in Figure 9. We observed that dynamic mechanical properties can be easily modulated by adjusting $I_{\text{ma/fur}}$. It can be seen in Figure 9a that there is a gradual increase in G' and a decrease in G'' with the increase in $I_{\text{ma/fur}}$ from 0.5 to 1 at the glassy state, indicating that the stiffness of the polymers increases with $I_{\text{ma/fur}}$. The shift of $\tan \delta$ to a higher level with $I_{\text{ma/fur}}$ also gave an indication of fewer damping characteristics or less flexibility at higher $I_{\text{ma/fur}}$ values. The observed dynamic mechanical

Figure 9. Dynamic mechanical properties of the cross-linked PK-furan (PK50f-1): (a) at different maleimide to furan molar ratio, (b) in response to continuous heating cycle scanning at $I_{\text{ma/fur}} = 1$, and (c) upon heat treatment at 50 °C for 24 h (for the sample after the six-cycle study).

properties can be ascribed to the fact that the change in $I_{\text{ma/fur}}$ leads to the difference in cross-linking density and therefore the number of formed DA adducts. The glass-transition (T_g) or softening temperature, as determined from the inflection point of the G' curves for the cross-linked PK50f-1 at $I_{\text{ma/fur}}$ of 1, 0.75, and 0.5, are around 100, 96, and 87 °C, respectively, thus indirectly confirming the change in cross-linking density. The obtained T_g is found to be comparable to or even higher than other DA-related polymer systems reported in the literature.^{7,12} Nevertheless, the relatively low T_g in comparison with some commercial thermosetting resins (e.g., epoxy) may limit the use of the proposed materials for applications that require softening points of >100 °C. DMA was also performed in a cyclic manner to check reworkability of the DA and RDA sequence on the sample PK50f-1 at $I_{\text{ma/fur}} = 1$ (Figure 9b). When reaching its glass-transition temperature, the sample starts to become soft because of the occurrence of the RDA reaction but can still retain its original shape. Upon cooling in 10 min, the G' and G'' of the samples recover because of the reformation of the DA adduct. The cycle was repeated sequentially six times. Even

Figure 10. Representative "load to displacement" behavior of the original and healed samples (PK50f-1): (a) at different maleimide to furan molar ratio, (b) upon multiple healing cycles at $I_{\text{ma/fur}} = 0.75$, and (c) using different intermaleimide structures (1,1'-(methylenedi-1,4-phenylene)bismaleimide)-structure A and N,N' -(1,3-phenylene)bismaleimide-structure B) at $I_{\text{ma/fur}} = 0.75$.

without using antioxidants in the formulation, it is shown that the dynamic mechanical properties of the tested sample (Figure 9b) remain almost unchanged after the repeated six cycles, although a small drop in the T_g value of 3 to 4 °C is observed after the first cycle. This effect could be attributed to the discrepancy in the time scale between the measurement time of the DMA and the kinetics of the DA adduct formation, in analogy to the results found in the DSC study. The confirmation for this hypothesis was obtained by thermal treatment of the same six-cycle sample at 50 °C for 24 h to fully recover the DA adduct qualities. When testing again, the behavior of cycle seven (Figure 9c) almost matches that of cycle one in terms of the G' , G'' , and $\tan \delta$, which proves that this polymer system is 100% self-repairable under heat treatment.

Self-healing efficiency⁴ (e.g., remended to original value of fracture load) of the repaired polymers was further studied using a three-point bending test at room temperature (23 °C). Representative "load to displacement" curves show typical

Figure 11. SEM images of fracture surface of the polymers after three-point bending test: (a) original fracture surface and (b) healed fracture surface.

thermosetting mechanical behavior (linear load to displacement relationship) of the samples prepared according to different maleimide-to-furan molar ratios (Figure 10). Mechanical strength (40–100 MPa) and modulus (~ 4 GPa) can be derived from the “load-to-displacement” curves and are found in the range of typical engineering thermosetting resins.³⁶ It can be seen in Figure 10a that a lower amount of bis-maleimide can lead to a higher fracture load, which could be due to a more efficient formation of the cross-linked network and higher toughness at relatively low cross-linking densities. After the bending test, the fractured samples were shredded into small granulates using a table-top hammer mill and then remended into rectangular bars by using compression molding at 120 °C for 20 min. When testing the remended samples once again, a full recovery of the fracture load with a healing efficiency of approximately 100% was achieved (Figure 10a). The healing performance was also evaluated for multiple cycles, indicating that the polymers, after three cycles, do display full recovery to the original fracture load (Figure 10b). We further studied the self-healing ability of this system by varying the chemical structure of bis-maleimide (Figure 10c), indicating not only the 100% self-healing efficiency but also that fracture load values can be tailored by molecular design. For other self-healing systems reported in the literature,^{1–3} in contrast with the present one, the recovery efficiency could not reach a full completion and a relevant deterioration of the mechanical behavior was found. SEM examination of the fracture surface of the original and healed samples after three-point bending test indicates that the polymers have the ability to recover to the original microstructure (Figure 11). Both fracture surfaces gave similar appearances, that is, sharp, clear, and ligament shapes, which are characteristics of a brittle or thermosetting material.^{37–39}

Conclusions

We have developed a thermally self-healing polymeric material using a simple and efficient processing method. To the best of our knowledge, this system introduces a new and practically applicable concept to recycle thermosetting polymers through a Diels–Alder and Retro-Diels–Alder reaction sequence. The polyketones can easily be converted to furan derivatives in bulk without the need for a catalyst or a solvent just by using mild conditions, whereas the degree of furan functionality can be tuned well by changing the initial reaction conditions. The NMR and FTIR spectroscopy as well as thermal analysis indicated that the furan-functionalized polyketones could be repeatedly cross-linked and de-cross-linked with bis-maleimide by using only one external stimulus (heat). DMA analysis and three-point bending tests demonstrated that this polymeric system can repeatedly heal or repair itself to the extent of 100% multiple times. We hope that our polymer system will move the research on self-healing materials to a new stage, for example, the recycling of thermoset-based plastics and composites.

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