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Recyclable Epoxy Resin via Simultaneous Dual Permanent/Reversible Crosslinking Based on Diels–Alder Chemistry

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Taking advantage of the reversible Diels–Alder (DA) reaction, a simple strategy to obtain recyclable epoxy resins is presented. For this purpose, blends of furan-functionalized and nonfunctionalized epoxy resin are prepared. After the addition of diamine and bismaleimide, blends are heated at 150 °C for 5 min, where the permanent amine/epoxy reaction has taken place and upon cooling to room temperature the reversible DA reaction has happened, giving rise to a dual permanent/nonpermanent network. Both reactions are confirmed by Fourier-transform infrared (FTIR) and ^{13}C-crosspolarization, magic-angle spinning (CP/MAS) nuclear magnetic resonance (NMR). Modulated differential scanning calorimetry (MDSC) shows that the epoxy/amine and bismaleimide/amine curing reaction take place, after the DA reaction, simultaneously with the retroDA reaction and before the bismaleimide homopolymerization. Therefore, under the appropriate curing conditions, the Michael's addition and the bismaleimide homopolymerization do not avoid the formation of a hybrid network, as stated in other reports. The reversibility of the DA reaction in three consecutive cycles is confirmed by DSC. Finally, the dual-cured sample is reprocessed three times without significant loss of mechanical properties.

1. Introduction

Epoxy resins are widely employed in different industrial applications, such as structural adhesives, coatings, and composites.[1] Due to their crosslinked structure, they show excellent thermal and mechanical properties.[2] However, from an environmental perspective, they present an important drawback related to their non-recyclable character.

The irreversible nature of the crosslinked network constitutes one of the main problems that not only epoxy resins but also all thermostable materials have to face in order to fulfill the requirements of the current sustainable processes.[3] Therefore, the research on different strategies to impart recyclable properties to polymeric networks is a subject of growing academic and industrial interest.

The introduction of nonpermanent crosslinking points in the network structure is the general strategy described in the literature in order to obtain a thermostable material that can be reprocessed.[4–6] Thermostable materials containing such types of linkages are known as covalent adaptable networks (CANs) and can be classified as associate (vitrimers) or dissociative. One of the most commonly used dissociative CANs involves the Diels–Alder (DA) reaction.[7–9]

Different nonpermanent crosslinking strategies have been successfully applied to epoxy-based materials. Thus, disulfide groups have been introduced into the epoxy resin to obtain reprocessable materials.[10–12] The introduction of DA adduct through the reaction between bismaleimide and furan groups has also been extensively explored.[13–15] However, according to different authors, the Michael's addition that may happen between bismaleimide and amines used as epoxy crosslinkers can limit the applicability of this strategy.[16–18] Another problem that arises when introducing DA moieties into the epoxy resin is related to the bismaleimide homopolymerization, which can take place at high temperatures, and results in a nonreversible crosslinking.[19] With the aim of avoiding these problems, several strategies have been developed. Thus, some authors have introduced the DA adduct into the epoxy resin before the crosslinking with the diamine.[16,20–22] Another strategy consists of

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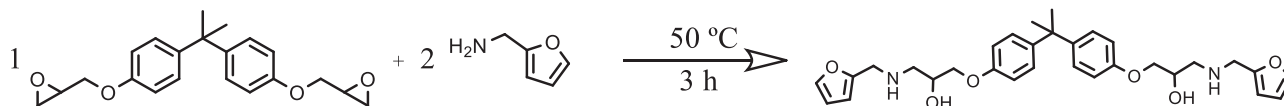
Scheme 1. Synthesis of the prepolymer.

synthesizing a diamine containing the DA adduct and using it as an epoxy resin crosslinker.[17,23,24] Finally, other authors describe the crosslinking of a furan-functionalized epoxy prepolymer with bismaleimide.[18,25–29] All these works avoid the direct contact between the bismaleimide and the amine to eliminate the possibility of the Michael's reaction. However, in recent work,[30,31] epoxy networks have been obtained by curing an epoxy resin with a conventional diamine and consecutively via DA reaction in order to get an epoxy coating with anticorrosion and self-healing properties. These studies show that the occurrence of the Michael's addition does not avoid the DA reaction and opens up the possibility of combining the DA crosslinking with conventional amine curing of epoxy resins. Nonetheless, although the self-healing properties of these systems suggest the presence of reversible linkages, there is no direct evidence of the presence of the DA adduct in the network and its reversibility in different cycles.

Taking all these considerations into account, the present work is devoted to obtain a conventional/Diels–Alder dual-cured epoxy network with reprocessing capability. For this purpose, a furan-functionalized epoxy resin was blended with a conventional epoxy resin, and the blend was simultaneously cured using diamine and bismaleimide. Therefore, a simple strategy to introduce the DA adduct into the epoxy network is described, and the curing reaction and its reversibility are studied by different techniques. The results obtained can be of great interest in order to establish the potential of the dual reversible/nonreversible curing to obtain more sustainable epoxy resins.

2. Experimental Section

2.1. Materials

Diglycidyl ether of bisphenol A (DGEBA), furfurylamine (FA), 1,1′-(methylenedi-4,1-phenylene)bismaleimide (BMI), and 4,4′-diaminodiphenylmethane (DDM) were purchased from Sigma-Aldrich. For subsequent synthesis, BMI and DDM were ground with a mortar and a pestle; meanwhile, DGEBA and FA were used directly as received.

2.2. Synthesis

2.2.1. Prepolymer Synthesis

With the aim of obtaining a polymer with the Diels–Alder adduct, the diene was first included by reacting DGEBA with FA. In order to obtain a furan-functionalized prepolymer, a large excess of FA was employed (one epoxy, two FA). **Scheme 1** shows the expected structure considering the stoichiometry employed. This reaction took place in a three-neck round bottom flask introduced in an oil bath at 50 °C and mechanically stirred (210 rpm). Once DGEBA (20 g, 58.753 mmol, 1 equivalent) was melted, FA

Table 1. Reagents used in the synthesis of different composition samples.

Polymer	Prepolymer [g (mmol)]	DGEBA [g (mmol)]	BMI [g (mmol)]	DDM [g (mmol)]
100/0	3.00 (5.611)	–	2.00 (5.581)	–
75/25	2.38 (4.452)	0.79 (2.321)	1.60 (4.465)	0.23 (1.162)
50/50	1.69 (3.161)	1.69 (4.965)	1.13 (3.153)	0.49 (2.475)
25/75	0.90 (1.683)	2.71 (7.961)	0.60 (1.674)	0.79 (3.989)
0/100	–	3.88 (11.398)	–	1.12 (5.657)

(10.4 mL, 117.685 mmol, 2 equivalents) was introduced through one of the necks. The reaction lasted 3 h.

2.2.2. Reaction of the Prepolymer via DA Chemistry

The prepolymer was reacted with BMI to produce the curing reaction via DA chemistry. In order to balance the reaction, the FA content of the prepolymer was considered. Thus, 15 g (27.981 mmol) of prepolymer and 10 g (27.981 mmol) of BMI were manually mixed at room temperature for 1 h in a mortar. A film was the prepared by hot pressing, applying 150 °C and 5 Tons for 5 min to 0.1–0.2 g of the sample. The DA adduct was formed while the film was cooled to room temperature.

2.2.3. Synthesis of Samples Using Dual Curing and Recycling

The samples were cured using a mixture of DDM and BMI. The procedure employed was similar to that described above for the DA-type reaction. The first step involved the mixing between the prepolymer and DGEBA at 60 °C for 30 min under mechanical stirring (210 rpm). The mixture was poured into a mold and cooled to room temperature. BMI and DDM were then included and mixed manually at room temperature for 1 h in a mortar and pestle. Finally, films were obtained by hot pressing, applying 150 °C and 5 Tons for 5 min to 0.1–0.2 g of the sample. During the film formation process, at 150 °C, the crosslinking reaction between the epoxy groups of the DGEBA and the amine of the DDM took place and upon cooling, the DA reaction between the prepolymer and the BMI occurred. The amounts of reagents used are shown in **Table 1**. DDM and BMI equivalents were calculated according to the epoxy and furan equivalents in the DGEBA and prepolymer, respectively. The samples were named according to the prepolymer and DGEBA content (weight percent). Thus, the polymer called 100/0 consisted of pure prepolymer and the corresponding BMI amount. It was worth mentioning that in the case of the 0/100 polymer, the synthesis was carried out by mixing DGEBA and DDM at 80 °C for 30 min, avoiding the step of the mixture with BMI at room temperature. In this process, the crosslinking did not happen, confirming literature results.[32]

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The sample was crosslinked by hot pressing about 0.1–0.2 g at 150 °C and applying 5 Tons for 5 min.

In order to recycle the samples, they were ground in a mortar and shaped by hot pressing applying 150 °C and 50 bar for 5 min.

2.3. Measurements

Proton nuclear magnetic resonance (^{1}H-NMR) spectroscopy was used to follow the reaction kinetics. When liquid samples were prepared, deuterated chloroform (CDCl$_3$) was used and spectra were obtained on a Fourier-transform Bruker 300 MHz spectrometer (Advance 300 DPX model). However, solid-state ^{13}C-NMR spectra were obtained by the crosspolarization, magic-angle spinning (CP/MAS) technique using a Bruker Advance III 400 spectrometer.

Fourier-transform infrared-attenuated total reflectance (FTIR-ATR) spectroscopy measurements were performed on a Nicolet 6700-IR (Thermo Scientific) coupled to an ATR accessory (Specac MKII Golden Gate). The spectra were the average of ten interferograms registered with a resolution of 4 cm^{-1}.

Differential scanning calorimetry (DSC) measurements were performed on a Mettler Toledo DSC3+. The sample amount used was about 3–5 mg and the scanning range was from −80 to 200 °C with a heating rate of 10 °C min^{-1} under nitrogen flow. It should be mentioned that when the reprocessing capacity was studied, only one scan was made. In the remaining cases, after the first run, the sample was cooled as quickly as possible and the second run was carried out. Modulated differential scanning calorimetry (MDSC) was used to characterize the dual curing reactions (DSC Q2000 of TA Instruments). The scanning range was from −30 to 200 °C with a heating rate of 2 °C min^{-1}, modulating ±0.80 °C every 40 s and under nitrogen flow.

Thermogravimetric analyses (TGA) were performed on the TGA Q500 V20 (TA Instrument). About 5–25 mg of the sample was introduced and heated from 30 to 800 °C, with a heating rate of 10 °C min^{-1}. A nitrogen flow rate of 90 mL min^{-1} was used.

Dynamic mechanical thermal analyses (DMTA) were performed on a Triton-2000 DA. The geometry used was the single cantilever bending, and measurements were performed from 25 to 160 °C with a heating rate of 4 °C min^{-1}. Samples of 25 mm long and 5 mm wide were used.

Matrix-assisted laser desorption-ionization/time of flight mass spectrometry (MALDI/TOF-MS) measurements were performed on a Bruker AutoFlex Speed. Samples were prepared in a matrix of 2-[(2E)-3-(4-*tert*-butylphenyl)-2-methylprop-2-enylidene]malononitrile (DCTB) and dithranol (Dith).

3. Results and Discussions

3.1. Prepolymer Synthesis

In order to follow the prepolymer synthesis reaction, samples were taken from the reactor at different reaction times and FTIR, and liquid-state ^{1}H-NMR spectra were recorded.

The FTIR-ATR spectra recorded during the reaction are shown in Figure S1 (Supporting Information). A decrease of the band attributed to the asymmetric vibration of the epoxy ring was observed at 915 cm^{-1}. However, it was overlapped with the band corresponding to the out-of-plane bending of the furan ring of furfurylamine and, therefore, the progress of the reaction could not be followed by this technique.

Figure 1a shows the ^{1}H-NMR spectra at different reaction times and Figure 1b shows the scale-expanded spectra. The assignment of the different protons of the structure is shown in Figure 1c.[33] As observed, during the reaction the signal of the epoxy ring proton 2 disappeared completely, suggesting that the reaction reached total conversion. However, the signals corresponding to "c" protons of the furfurylamine remained in the final spectrum. Accordingly, it was considered that the epoxy groups were totally opened, and the progress of the reaction was related to furfurylamine. Consequently, the areas of protons "c" and "c′" were used to calculate the reaction conversion at different reaction times (Figure 1d).

As observed, after 2 h, the reaction conversion (calculated from the signals assigned to the FA) was close to 0.75, and longer reaction time did not increase this value. Nevertheless, as explained, at high reaction times, the absence of the signal at 3.3 ppm, assigned to the epoxy ring, implied that all the epoxy rings were opened during the reaction. Conversely, NMR data showed that not all the FA reacted. This result suggests that a part of the furfurylamine did not react and remained free in the reaction media.

With the purpose of getting more accurate information about the structure of the prepolymer, a MALDI/TOF-MS measurement was performed for the final reaction product. The results are shown in **Figure 2**.

As observed, oligomers of different molecular weight were detected by this technique. The main signal at 994 umas corresponded to the oligomer containing two DGEBA and three FA units (see Figure S2 in the Supporting Information), which was larger than the expected considering the employed stoichiometry. In addition, the molecular weight difference between the consecutive oligomers was of 437 umas, which means that there were no epoxy end groups. This confirmed the NMR results. From these data, the average molecular weight was calculated,[34,35] and the results can be found in Table S1 (Supporting Information). A M_n value of 1068 g mol^{-1} was obtained, which was in accordance with the data found in the literature for the same reaction performed in toluene.[33] Therefore, as the prepolymer contained molecules with more than two furan moieties, it might be crosslinked with bismaleimide.

The prepolymer was analyzed by thermogravimetric analysis, and the results obtained can be found in Figure S3 (Supporting Information). As observed, the sample experimented a weight loss of almost 10% until 250 °C which was related to the remaining FA and the dehydrogenation as reported in literature.[36] Then, the main stage of weight loss stage started. A residue of 18% was obtained. Figure S4 (Supporting Information) shows the DSC run of the prepolymer. In the first run, the sample showed a glass transition temperature close to 0 °C and some peaks at 120 °C related to the evaporation of unreacted FA. In the second run, the T_g was slightly shifted to higher temperatures due to the removal of the FA.

Although we were conscious that the prepolymer had residual FA, we did not purify it before blending, as it could be incorporated into the network via reaction with the BMI (DA and Michael's reaction) and with epoxy moieties.
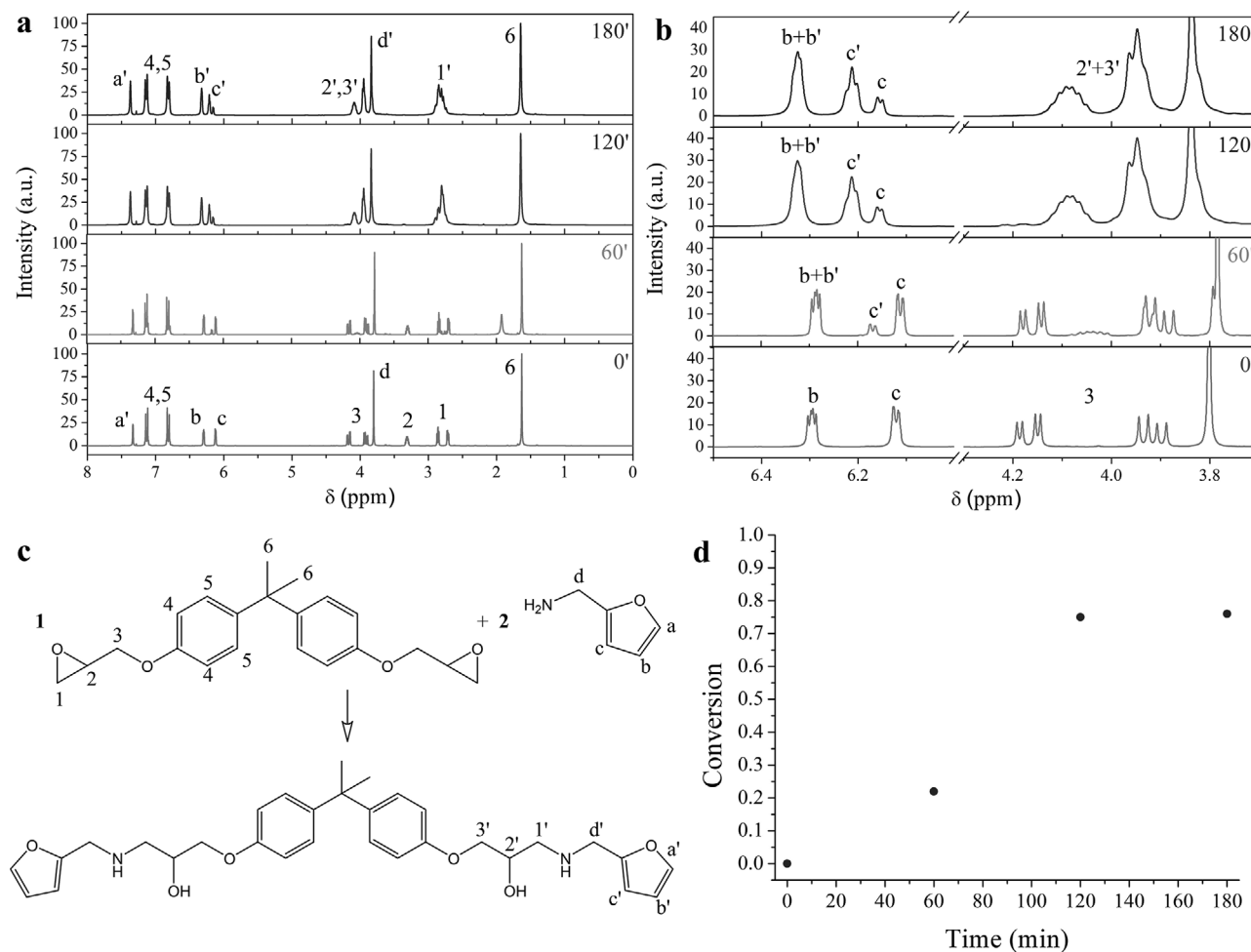
Figure 1. a) ^{1}H-NMR of the prepolymer at different reaction times, b) scale-expanded spectra, c) signal assignment to the structure, and d) reaction conversion versus time.
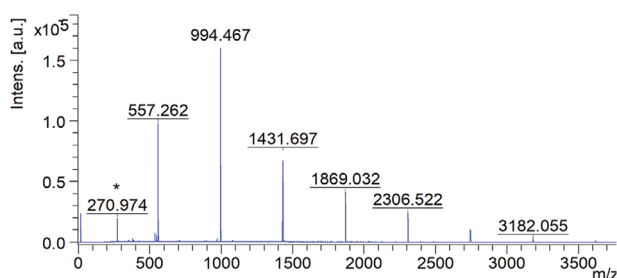

Figure 2. MALDI/TOF-MS measurement of the final prepolymer. * Signal of the matrix mixture.

3.2. Sample Crosslinked by DA Adduct

The prepolymer was mixed with BMI, and a film was obtained by hot pressing applying 150 °C and 5 Tons for 5 min. This temperature was selected considering the melting point of BMI, which is about 156—158 °C according to the supplier's data sheet. Infrared spectra were obtained before and after hot pressing, and the results are shown in **Figure 3**. Before curing, the

spectrum presented characteristic bands of the prepolymer (3500 cm^{-1}: —OH stretching; 1608, 1503, and 1418 cm^{-1}: aromatic ring stretching; 1237 and 1033 cm^{-1}: —COC symmetric and antisymmetric stretching; and 829 cm^{-1}: out-of-plane bending of the aromatic ring) and BMI (1705 cm^{-1}: carbonyl stretching; 1508 and 827 cm^{-1}: aromatic ring stretching and out-of-plane bending (both overlapped with the spectrum of the prepolymer); and 690 cm^{-1}: out-of-plane bending of the bismaleimide double bond).

However, after curing, the peak at 690 cm^{-1} was clearly reduced. This result evidenced that during the heating and cooling processes, the DA reaction between the bismaleimide and the furan occurred (**Scheme 2**). As stated in literature, 60 °C is an appropriate temperature to perform the DA reaction; however, above 110 °C the equilibrium is shifted to the retroDA reaction.[7] Consequently, it can be argued that after complete melting of BMI at 150 °C, the DA curing reaction occurred during the cooling process, which took place immediately when the sample was cooled to room temperature.

As shown in FTIR measurements, it was clear that the DA curing reaction took place in the film-making process. However, the extension of the reaction was calculated from solid-state
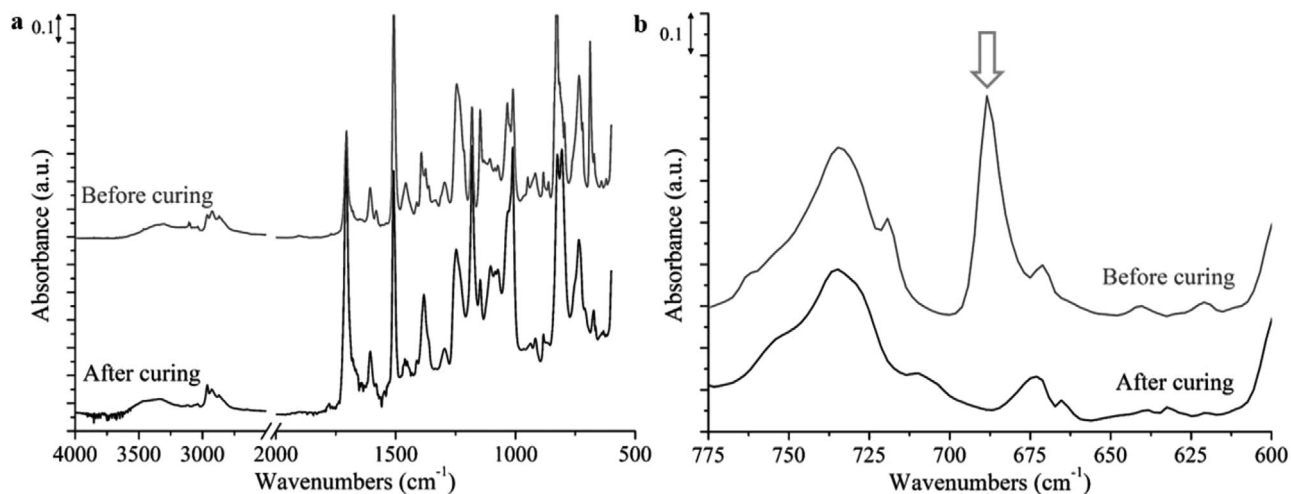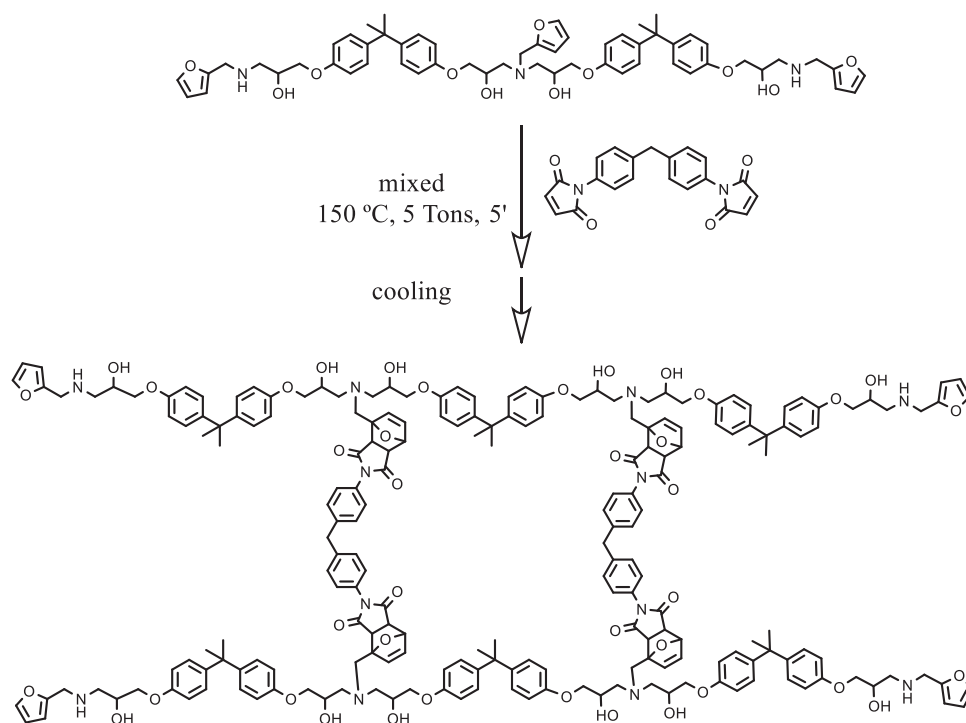
Figure 3. FTIR spectra of sample 100/0 before and after a) hot pressing and b) the scale-expanded spectra from 775 to 600 cm^{-1}.

Scheme 2. Curing of the prepolymer via DA adduct.

^{13}C-NMR. **Figure 4** shows the carbon spectrum of sample 100/0 and the corresponding nucleus signal assignment.[28,37]

The occurrence of the DA reaction was confirmed by the signals at 178, 90, and 80 ppm corresponding to carbons "a," "j," and "k" of the generated DA adduct.

The DA curing reaction was also analyzed by MDSC. By means of this technique, the total DSC curve can be split into the reversible and nonreversible parts. Thus, it is especially appropriate to study the curing processes, since the glass transition appears in the reversible part while the enthalpy associated with the curing process is recorded in the nonreversible part.[38] The MDSC run for the sample before curing is shown in **Figure 5**a. In the

reversible part, a broad glass transition between 10—50 °C could be distinguished. In the nonreversible part, two exothermic peaks were found close to 70 and 155 °C, and finally between 80 and 130 °C an endotherm was observed.

The MDSC run of the sample after curing can be found in Figure 5b. As observed in the reversible part, compared to the data obtained before curing, the onset of the glass transition was shifted to higher temperatures (Figure S5 in the Supporting Information shows an overlap of these two runs). However, in the nonreversible part, the cured sample did not show the exotherm at 70 °C (Figure S6 in the Supporting Information shows an overlap of these two runs). Accordingly, the peak at 70 °C was
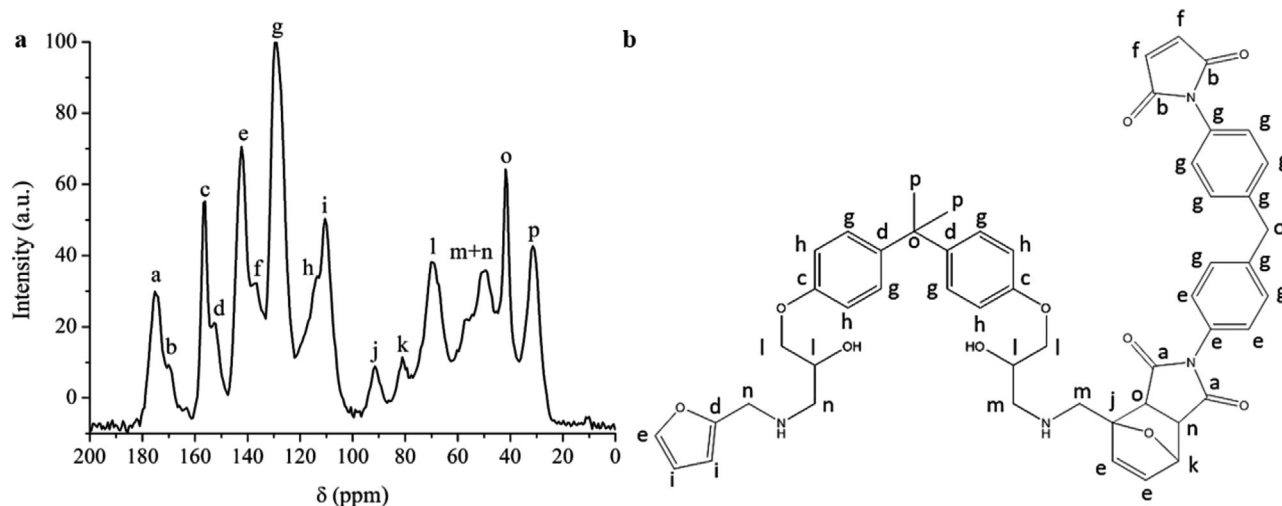
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Figure 4. Solid-state ^{13}C-NMR of sample 100/0 a) after curing and b) the peaks assignment.
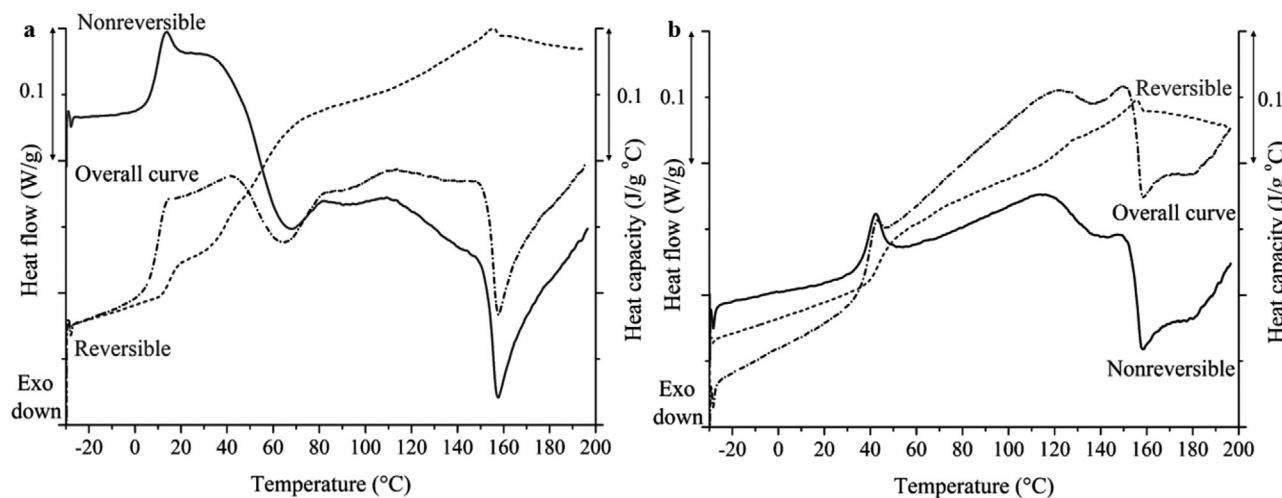

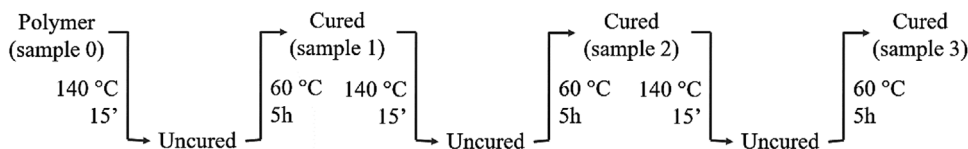**Figure 5.** MDSC of sample 100/0 a) before and b) after curing.

assigned to the occurrence of the DA reaction. This result was in accordance with the FTIR results shown in the previous section, in which it was stated that during the film-making process the DA adduct was formed. It can be highlighted that the DA reaction took place at temperature below the BMI melting (155 °C, see Figure 9b) and, consequently, the DA reaction destroyed the BMI crystals. Moreover, in the endotherm related to the retroDA reaction, two main signals could be distinguished at 80 °C corresponding to "endo" retroDA and at 110 °C referring to "exo" one as reported in literature by Canadell et al.,[13,39,40] while the last exotherm at 155 °C was assigned to the bismaleimide self-condensation.[17,18] On this basis, it is clear that at temperatures above 150 °C the sample will crosslink in a permanent way destroying the reversibility of the network and limiting the service temperature.

In order to study the reversibility of the DA reaction, different heating cycles were carried out (**Scheme 3**).[41] Therefore, the cured sample (sample 0) was placed 15 min in an oven at 140

°C in order to provoke the retroDA reaction. Subsequently, it was placed 5 h in an oven at 60 °C (sample 1). Samples 2 and 3 were obtained by repeating the same procedure twice. Conventional DSC runs were recorded for samples 0, 1, 2, and 3, and the results are shown in **Figure 6**.

As observed in **Figure 6**, all samples showed an exotherm at ≈140 °C. According to the literature, this transition was related to the retroDA reaction, which happened after the glass transition. It must be pointed out that in MDSC both transitions were registered at lower temperature. This difference was related to the higher heating rate employed in the conventional DSC run. Furthermore, in the conventional DSC run (**Figure 6**) the heat flow fell at high temperatures without showing any minimum (as attributed to the bismaleimide homopolymerization at 150 °C in MDSC). This was again due to the higher heating rate employed in conventional DSC.

The appearance of the peak assigned to the retroDA reaction in all the runs confirmed the reversibility of the DA reaction

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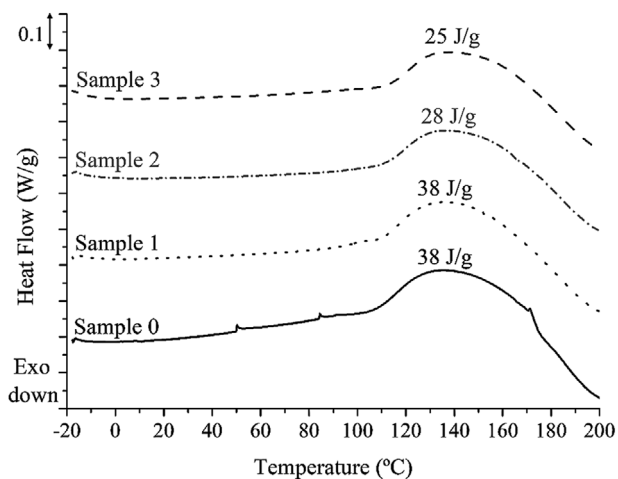**Scheme 3.** Curing treatment of the samples for DSC analysis.

Figure 6. DSC of samples after different curing cycles for polymer 100/0.

when the sample was under the thermal treatment, as shown in Scheme 3. Reversibility of the reaction in similar systems has been previously reported in the literature by rheological[18] and repetitive healing measurements.[26] However, when comparing the data between the different cycles, a reduction in the enthalpy value was detected as the sample was submitted to consecutive heating cycles. Although the absolute value of this area is probably overestimated, because of the occurrence of the BMI homopolymerization during the run, it seems that the DA–retroDA reactions lost efficiency with the cycles. Bismaleimide homopolymerization may be at the origin of this behavior. Hence, it can be supposed that when the sample was at 140 °C for 15 min, the DA adduct was broken but, in addition, part of the free bismaleimide was homopolymerized. When the temperature was lowered, the homopolymerized bismaleimide could not give rise to the DA reaction, and the stoichiometry was lost resulting in an incomplete DA reaction. In addition, according to literature,[39] the DA adduct could be aromatized at high temperatures avoiding the occurrence of the retro DA reaction. As a consequence of all these reactions, the system lost efficiency, and a reduction in the enthalpy was observed.

In order to confirm the occurrence of the maleimide homopolymerization, a small amount of BMI was placed in an oven at 150 °C for 3 h and infrared spectra were obtained (Figure S7, Supporting Information). After heating, a slight decrease of bands at 3098 and 1611 cm^{-1}, attributed to the stretching vibrations of =C—H and C=C of the bismaleimide double band, and a slight increase at 2925 cm^{-1}, attributed to the —C—H stretching, were observed. These changes evidenced the breaking of the bismaleimide double band because of its homopolymerization reaction.[42]

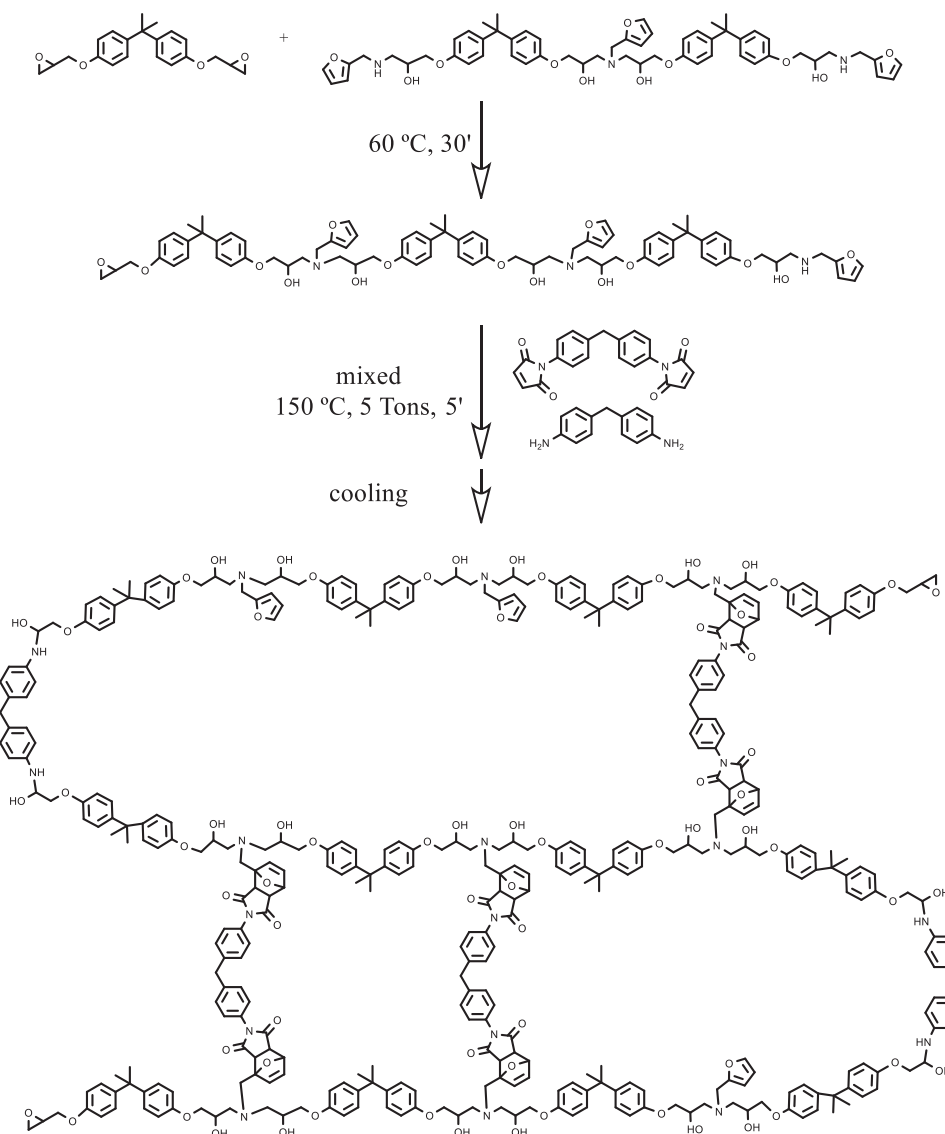## 3.3. Samples Crosslinked by DA Adduct and Conventional Curing

Different composition blends of furan-containing prepolymer and DGEBA were prepared by melting. During this process, the reaction between secondary NH of the prepolymer and DGEBA could happen. Afterward, the blends were cured using a mixture of DA curing agent (BMI), and a conventional amine (DDM). The blends were processed and cured by hot pressing applying 150 °C and 5 Tons for 5 min (**Scheme 4**).

During the cooling process, the DA reaction can occur (reversible crosslinking). However, as stated in the literature, the Michael's reaction between BMI and DDM can also open the double bond of the BMI, hindering the DA reaction.[16–18] The FTIR spectra of these materials showed a reduction of the band area at 690 cm^{-1}, which corresponds to the out-of-plane bending of the double bond of BMI (Figures S8–S11, Supporting Information). Nevertheless, the reduction of this band may be related to both, DA and Michael's addition reaction. Furthermore, the reaction between the secondary N—H of the prepolymer with the epoxy could happen (permanent crosslinking). The occurrence of all these reactions led simultaneously to a hybrid network linked by reversible (DA adduct) and nonreversible (epoxy/amine and Michael's addition) bonds.

With the aim of confirming the occurrence of Michael's reaction, a 50 wt% mixture of BMI and DDM was placed in an oven at 150 °C for 3 h. Afterward infrared spectra were recorded (Figure S12, Supporting Information). The decrease of the absorption of the bands at 1620, 3416, and 3336 cm^{-1} (related to primary amine bending and stretching vibrations) and the increase of the band of the secondary amine stretching at 3355 cm^{-1} evidenced the occurrence of the Michael's reaction.

As mentioned above, the DA reaction could be characterized by solid-state ^{13}C-NMR. **Figure 7** shows the spectra obtained after curing different composition samples. In these spectral signals assigned to the DA adduct (at 80 and 90 ppm, carbons "k" and "j") were observed, confirming the occurrence of the DA reaction.

In order to check the occurrence of Michael's addition, attention must be paid to the signal assigned to the bismaleimide carbonyl. As observed, in the 180–160 ppm region, the most unshielded signal corresponded to the DA adduct and to one of the carbonyls generated in the Michael's addition, while the most shielded signals were assigned to the unreacted bismaleimide and the other carbonyl generated in the Michael's addition. As observed, when increasing the amount of the conventional curing, the area of the most shielded signal increased. This means that, in addition to the DA reaction, the Michael's addition was taking place. This result proved that, as stated in some recent works,[30,31] the Michael's reaction does not avoid the occurrence of the DA reaction and that a dual curing can be used to crosslink the epoxy resin.

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Scheme 4. Dual curing of DGEBA and the prepolymer via maleimide and diamine.

The dual curing reaction of the samples was studied by MDSC. For this purpose, measurements were performed for the 0/100 (Figure S13, Supporting Information) and 50/50 polymers (Figure S14, Supporting Information) before curing. The reversible part of the runs of samples 0/100, 50/50, and 100/0 are shown in **Figure 8**. The sample cured with bismaleimide (100/0) showed the T_g between 10 and 75 °C in the reversible part, while the diamine-cured sample (0/100) showed the T_g between 40 and 80 °C.

The nonreversible part of the thermograms of these samples is shown in **Figure 9**a. As indicated above, sample 100/0 showed an exotherm related to the DA reaction, an endotherm related to the retroDA reaction, and finally an exotherm related to the bismaleimide homopolymerization. Sample 0/100 showed an exotherm at 110 °C related to the epoxy/amine curing reaction. No peak related to DDM melting was observed because both components were mixed at 80 °C for 30 min (Figure 9b). As expected,

this sample did not show the peak related to the bismaleimide homopolymerization. The BMI/DDM mixture presented a melting exotherm at 75 °C related to DDM and an exotherm at 130 °C related to the Michael's addition (Figure 9b). Interestingly, this exotherm was located at a higher temperature than that obtained in the epoxy/amine reaction.[17] The sample containing both curing agents showed all these transitions (the transitions related to the retroDA, the epoxy/amine curing, and bismaleimide/amine Michael's addition were overlapped). This result was especially interesting, since the epoxy/amine and bismaleimide/amine curing reactions took place, after the DA reaction, simultaneously with the retroDA reaction and before the bismaleimide homopolymerization. Thus, the possibility of side reactions, such as bismaleimide homopolymerization, was only relevant at high temperatures.

MDSC measurements were also performed for the 50/50 and 0/100 samples cured by hot pressing, and the results are shown
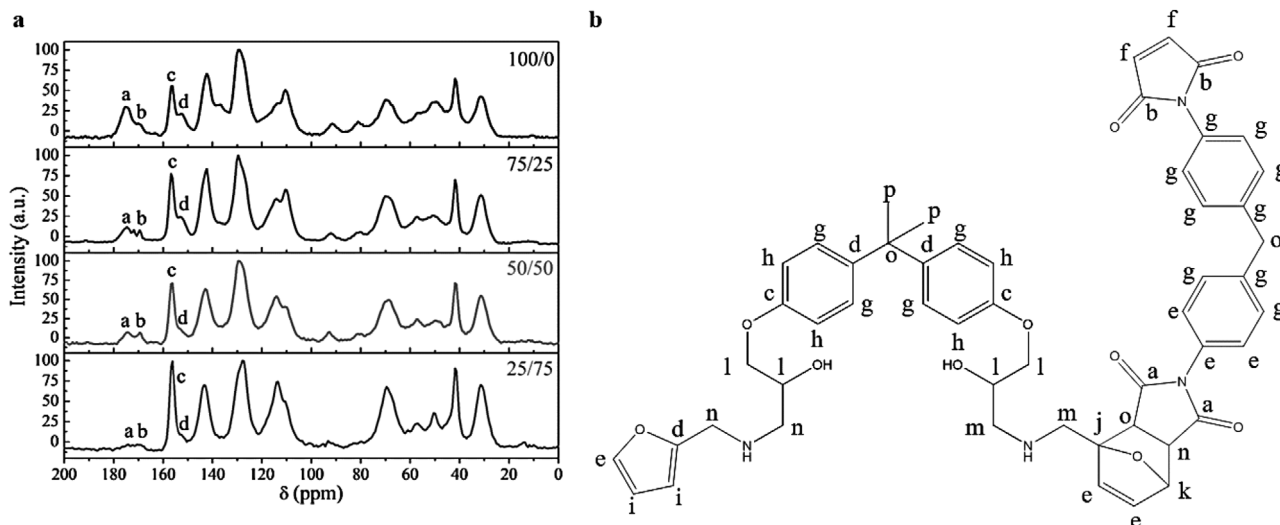
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Figure 7. Solid-state ^{13}C-NMR of different composition blends a) after curing and b) the peaks assignment.
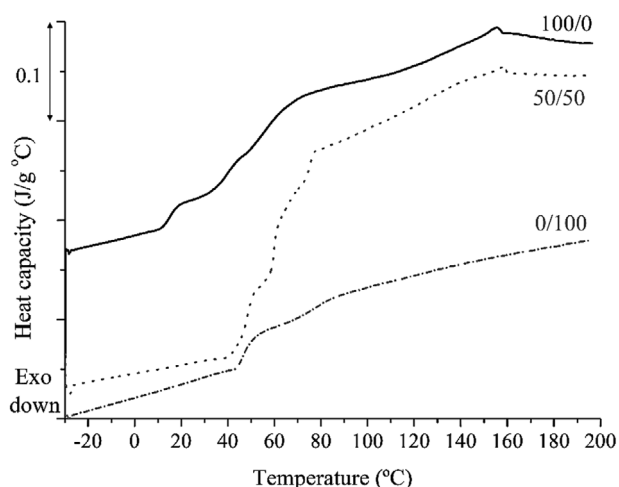

Figure 8. The reversible part MDSC of 100/0, 50/50, and 0/100 before curing.

in Figures S15 and S16 (Supporting Information). The absence of the curing exotherm in the nonreversible part of the 0/100 sample confirmed that the amine/epoxy reaction proceeded completely in the hot pressing. The behavior of sample 50/50 was more complex. **Figure 10** shows the nonreversible heat flow of this sample before and after curing.

After hot pressing, the sample showed a remaining curing endotherm, followed by the endotherm related to the retroDA reaction (which was clearly observed due to the reduction of the curing endotherm), and finally, at high temperature, the bismaleimide homopolymerization took place. In order to corroborate this, the sample was cured in the hot pressing for a longer time (15 min) and the MDSC run was performed. The results (Figure S17, Supporting Information) showed a reduction of the curing enthalpy for this sample.

Finally, to check the reversibility of the hybrid network, different heating cycles were performed with the aim of provoking the

DA and retroDA reactions (Scheme 3). DSC runs were carried out after the DA reaction (**Figure 11**).

The appearance of the peak assigned to the retroDA reaction in all the runs confirmed the reversibility of the DA reaction when the sample was under the thermal treatment as shown in Scheme 3.

3.4. Dynamic Mechanical Properties and Recycling Abilities

DMTA measurements were performed for the different samples. **Figure 12** shows the results for sample 0/100. A decrease in the storage modulus with temperature was observed and, as a consequence of the crosslinked structure, the modulus was stabilized at high temperatures.

The same measurements were made for 25/75 and 50/50 samples (available in Figures S18 and S19 in the Supporting Information). DMTA measurements of samples 100/0 and 75/25 could not be performed because the samples dripped with increasing temperature. E' values at 20 °C presented similar values, regardless of the sample composition. However, the tan δ maximum shifted toward lower temperatures as the bismaleimide concentration increased (see Table S2 in the Supporting Information).

In order to check whether the samples can be reprocessed, they were ground with a mortar and a pestle and were reshaped applying 150 °C and 50 bar for 5 min. **Figure 13** shows the images obtained during this process for sample 50/50 (the same procedure was followed for samples 100/0 and 75/25 as shown in Figure S20 in the Supporting Information). As observed, the sample could be reprocessed. However, it must be pointed out that this process was only possible with the samples containing up to 50% of DGEBA. It can be thought that during the heating in the recycling cycle, the retroDA reaction happened giving mobility to the network and allowing the reshaping of the sample. When the temperature was lowered, the DA reaction happened, and the crosslinked structure was recovered. This was not possible in the samples containing a larger amount of the diamine crosslinker because the nature of the network was more permanent.
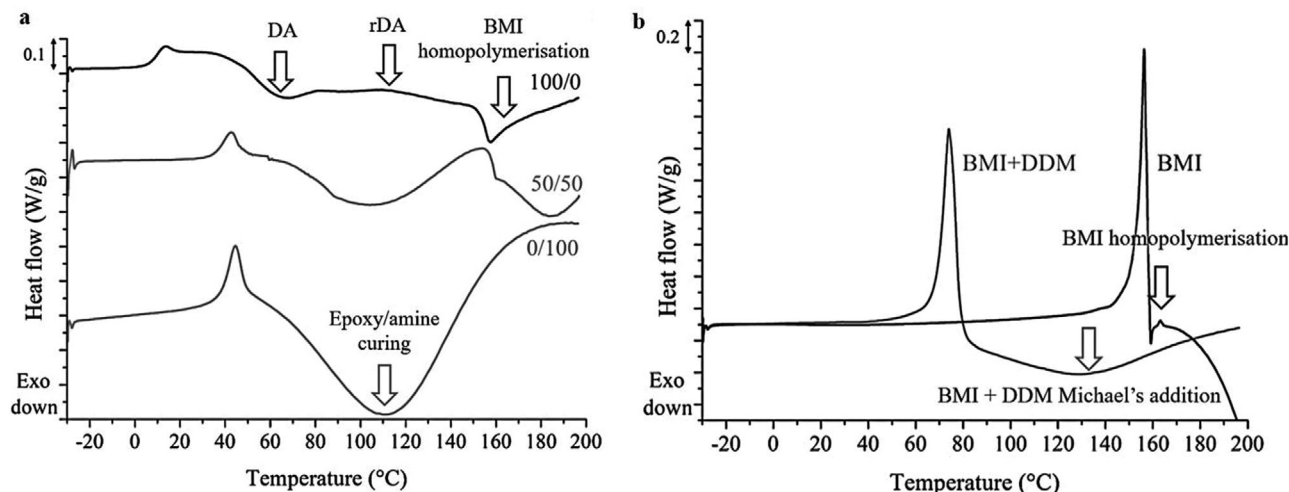
Figure 9. The nonreversible part MDSC of a) 100/0, 50/50, and 0/100 before curing. b) BMI and the 50 wt% mixture of BMI and DDM.
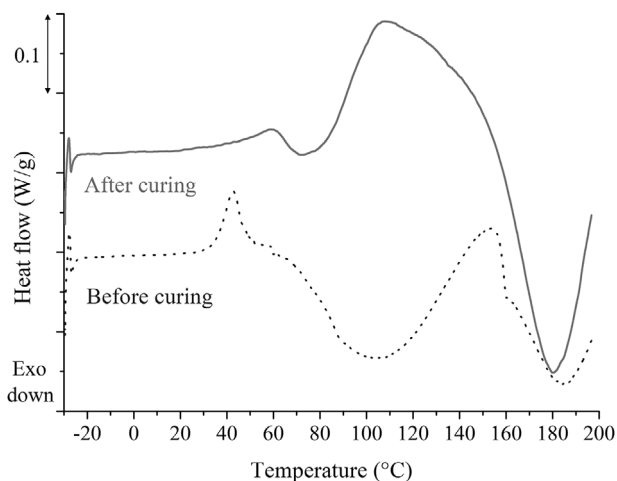

Figure 10. The nonreversible part MDSC of 50/50 before and after curing.
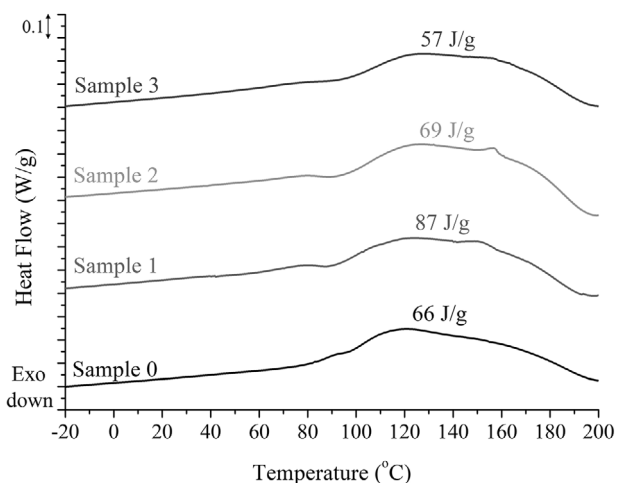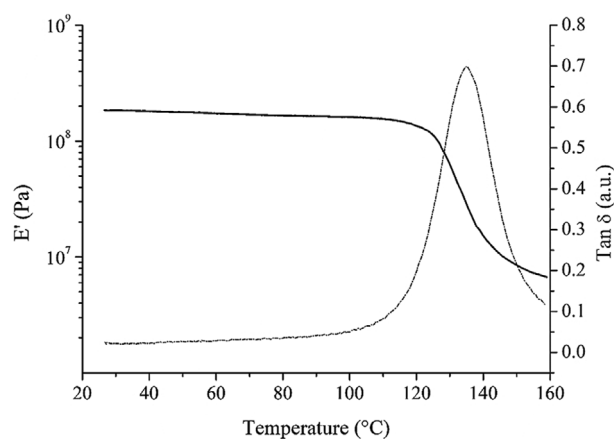

Figure 12. DMTA of 0/100 polymer.

Figure 13. a,b) Recycling of 50/50.

It was clear that sample 50/50 could be recycled. However, it was also interesting to check if the material properties were modified under this process. For this purpose, DMTA measurements of the recycled sample were performed. The results for the first recycling cycle are shown in **Figure 14**, and the results of the next two cycles are displayed in Figures S21 and 22 (Supporting Information).

As observed, the sample maintained its properties after the reprocessing process. However, the recycling process made the modulus of the sample increase. It must be considered that
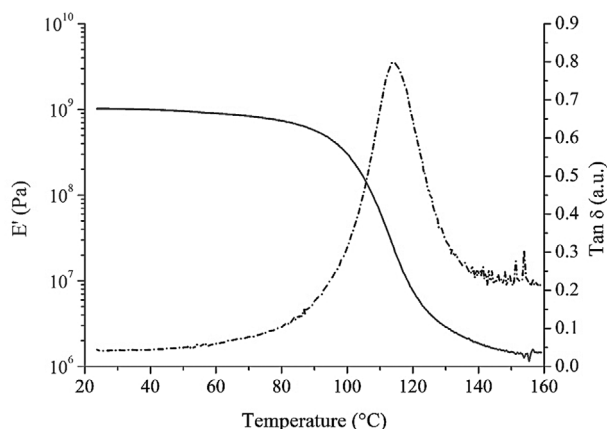

Figure 11. DSC of samples after different curing cycles for polymer 50/50.

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Figure 14. DMTA of once recycled 50/50 polymer.

the recycling of the sample was performed at 150 °C under pressure for 5 min, which was the same procedure employed to prepare the crosslinked samples. Therefore, during the recycling process, the curing degree of the epoxy could be increased and consequently a rise in the modulus took place. The increase in the curing degree after heating was confirmed by MDSC (Figure S17, Supporting Information).

4. Conclusions

In the present study, a blend of furan-functionalized and conventional epoxy was heated in the presence of a diamine and bismaleimide. Solid-state ^{13}C-NMR (CP/MAS) and MDSC experiments demonstrated that the Diels–Alder reaction could take place simultaneously with the curing of the epoxy/amine. During this dual curing process, the occurrence of the epoxy/amine, bismaleimide/amine, and furan/bismaleimide reactions gave rise to a reversible/nonreversible hybrid network. The reversible character of this network, verified by DSC measurements, allowed the samples to be recycled, which can be of great interest in order to get more sustainable epoxy resins.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Data available on request from the authors.

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