

Polyether-maleimide-based crosslinked self-healing polyurethane with Diels-Alder bonds

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ABSTRACT: The Diels-Alder (DA) reaction is particularly desirable for the preparation of heat-stimuli self-healing polymeric materials because of its thermal reversibility, high yield, and minimal side reactions. Some attempts were conducted to synthesize polyether-maleimide-based crosslinked self-healing polyurethane with DA bonds (C-PEMIPU-DA) through the reactions of the prepolymer (polymeric MDI/PBA-1000) functionalized by furfuryl amine and polyether-maleimide without benzene in this study. The structures of intermediates and C-PEMIPU-DA were first confirmed by $^1\text{H-NMR}$, Fourier transform infrared spectroscopy, and differential scanning calorimetry. Next, the thermal reversibility and the self-healing performance of C-PEMIPU-DA were studied by $^1\text{H-NMR}$, polarizing optical microscopy, tensile testing, and a sol-gel process. The results show that C-PEMIPU-DA exhibited interesting properties of thermal reversibility and self-healing. The polymers could be applied to self-healing materials or recyclable materials in the fields of the repair of composite structures and aging parts because of their thermosetting properties at room temperature and thermoplasticity at higher temperatures. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41944.

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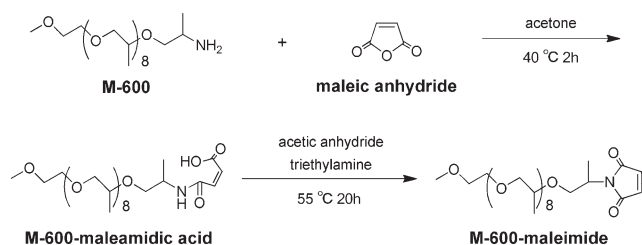
INTRODUCTION

Polymeric materials are applied in multiple aspects of everyday life, including food processing, electronics, automotive industry, coating, medical supplies, and sports equipment. However, during processing, transportation, and storage and usage processes, the combined effects of internal and external factors often lead to microscopic or macroscopic damage of materials, and this ultimately damages the mechanical properties.^{1,2} Cracks in polymeric materials are often deep inside and difficult to detect.³ Therefore, many studies have focused on self-healing polymeric materials, which can heal themselves after microcracks appear, either automatically or under external stimuli, such as changes in the temperature, light, pH, and ionic strength.^{4–24}

The Diels-Alder (DA) reaction is particularly desirable for the preparation of heat-stimuli self-healing polymeric materials because of its thermal reversibility, high yield, minimal side reactions, and mild reaction condition.^{17–27} Crosslinked polymeric materials are desirable because of their excellent mechanical properties, thermal stability, and insolubility in solvents. However, crosslinked polymeric materials cannot be reprocessed or repaired after fracture.¹⁷ To overcome this problem, some studies have been done to create self-healing crosslinked polymeric materials based on DA chemistry.^{18–24} The resulting

crosslinked polymers behave like thermosets at ambient conditions and thermoplastics at increased temperature. Most studies have focused on the DA reaction between furan (diene) and maleimide (dienophile) because the maleimide group shows a relatively high reactivity in DA reactions.¹⁷ There are two main methods for synthesizing self-healing crosslinked polymers based on DA chemistry. One is to form a linear polymer chain with pendant functional groups (diene and dienophile) first, and then, the linear polymer chain is crosslinked via a reaction with difunctional molecules (dienophile or diene). The other method relies on the reaction of multifunctional monomers containing furan groups and maleimide to form DA-based crosslinked polymers via step-growth polymerization.

Our previous studies have shown that DA bonds can be introduced into polyurethane with furfuryl amine (FA) and bismaleimide.^{25–27} In one study, crosslinked self-healing polyurethane was synthesized from polymeric MDI (S5005), PBA-1000 [poly(1,4-butylene adipate glycol), number-average molecular weight = 1000 g/mol], and bismaleimide. However, because of the high content of hard segments (benzene) and high crosslinking density, the product was hard and brittle, and its mechanical properties and self-healing performance were not so good. In our previous study,²⁷ we substituted PBA-1000 with



Scheme 1. Synthesis of M-600-maleimide.

PBA-2000 to increase the soft-segment content, obtaining a softer product with better mechanical properties and self-healing performance. In this study, we developed another method to increase soft-segment content by substituting bismaleimide with polyether-maleimide (PEMI) without benzene.

The polyether backbone of Jeffamine polyetheramine contains both ethylene oxide and propylene oxide or only propylene oxide. There are primary amino groups at the end of a polyether backbone of Jeffamine polyetheramine. Jeffamine polyetheramine can be easily converted into PEMI through typical amine reactions.

In this study, a multiple-furan prepolymer (PMPU-furan) was synthesized similarly as in our previous work.²⁷ Jeffamine polyetheramine was converted to PEMI by amidation and dehydration reactions. Finally, PEMI was reacted with PMPU-furan to form a polyether-maleimide-based crosslinked self-healing polyurethane with DA bonds (C-PEMIPU-DA) in a simple one-pot method. The newly synthesized C-PEMIPU-DA exhibited good thermal stability, mechanical properties, and self-healing properties. All of these properties will extend the application area and prolong the lifetime of C-PEMIPU-DA, which has broad prospects for development.

EXPERIMENTAL

Materials

Jeffamine polyetheramines [M-600 (monoamine, weight-average molecular weight = 600 g/mol), D-400 (diamine, weight-average molecular weight = 430 g/mol), and T-403 (triamine, weight-average molecular weight = 440 g/mol)] were supplied by Huntsman and were used as received.

Maleic anhydride was purchased from Sigma-Aldrich and was used as received.

Triethylamine, acetic anhydride, trichloromethane, anhydrous ether, and acetone were purchased from China National Medicines and were used as received.

Poly(1,4-butylene adipate glycol) (PBA-1000, number-average molecular weight = 1000 g/mol) was supplied by Eternal Chemical and was used after the removal of water.

Polymeric MDI (99%, S5005, a mixture of MDI, MDI dimers, MDI trimers, etc., with 2.7 NCO groups on average; weight-average molecular weight = 362.3 g/mol.) was provided by Huntsman and was used as received.

FA (99%) was purchased from Aldrich and was used as received.

N,N-Dimethylformamide (DMF) was purchased from China National Medicines and was used after the removal of water.

Synthesis of PEMI

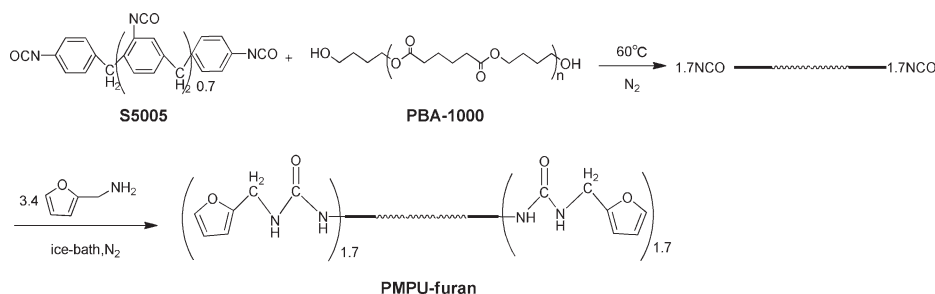
Maleic anhydride (1.05 g, 10.5 mmol) was dissolved in 3 mL of acetone in an ice-water bath. Then, M-600 (6.00 g, 10 mmol) diluted with 6 mL of acetone was added dropwise to the maleic anhydride solution. The temperature of the reaction system was maintained below 35 °C during the addition. The ice-water bath was removed after 0.5 h, and the solution was heated to 40 °C in an oil bath and kept at that temperature for about 2 h. Here, the intermediate M-600-maleic acid (6.30 g) was obtained (yield = 90.3%). After the solution was cooled to room temperature (RT), triethylamine (1.00 g, 10 mmol) as the catalyst was added. Then, the solution was heated to 55 °C, and acetic anhydride (5.00 g, 50 mmol) as the dehydrating agent was added dropwise to the solution. The whole solution was maintained at 55 °C for 20 h to ensure completion of the dehydration reaction (as shown in Scheme 1).

After the reaction finished, impurities were removed by repeated water and alkali washing, water was removed with anhydrous sodium sulfate, and the solvent was removed by rotary evaporation under reduced pressure. Finally, M-600-maleimide (3.86 g) was obtained (yield = 56.8%).

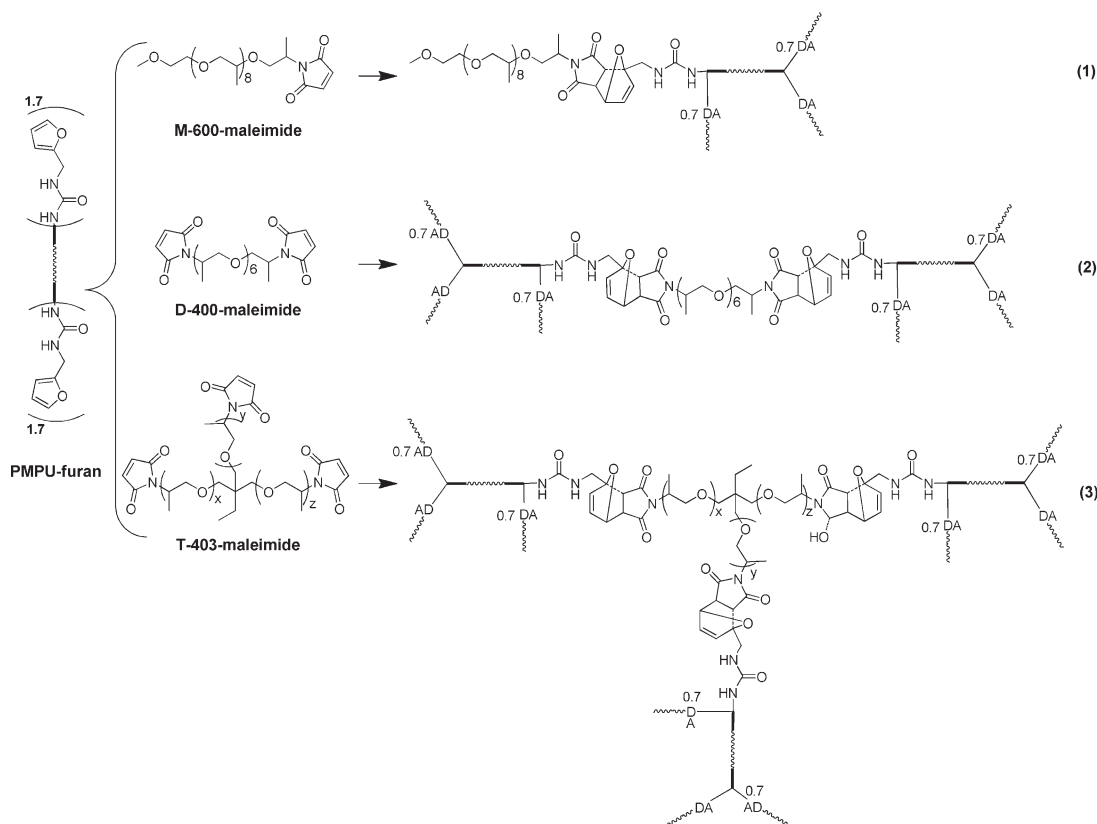
D-400-maleimide (yield = 57.5%) and T-403-maleimide (yield = 58.1%) were obtained in the same way as done previously based on D-400 and T-403.

Synthesis of C-PEMIPU-DA

Polymeric MDI (S5005, 3.60 g, 10 mmol), PBA-1000 (5.00 g, 5 mmol), and FA (1.70 g, 17 mmol) were used to prepare a multiple-furan prepolymer (PMPU-furan) via the reaction between isocyanate and FA as in our previous studies [Scheme 2].²⁷ Then, M-600-maleimide (10.90 g, 17 mmol) dissolved in 11 mL of DMF was added to the solution, and the whole solution was heated to 60 °C. Three hours later, the whole solution was poured onto a polytetrafluoroethylene plate to prevent gelling in the flask. The polytetrafluoroethylene plate was



Scheme 2. Synthesis process of PMPU-furan.



Scheme 3. DA reaction between PMPU-furan and PEMI: (1) M-600-PEMIPU-DA, (2) D-400-PEMIPU-DA, and (3) T-403-PEMIPU-DA.

kept at 60°C for about 2 days to remove the DMF solvent. Meanwhile, crosslinking via the DA reaction proceeded during the removal of DMF. Finally, the polymer film (20.13 g) was obtained as the final product (C-PEMIPU-DA, yield = 95.0%) [Scheme 3]. The whole synthesis was carried out by a one-pot reaction, and this made the synthesis procedure much easier.

M-600-maleimide with only one maleimide group reacted with PMPU-furan without accompanying crosslinking; this was convenient for studying the DA reaction between PMPU-furan and PEMI. However, the mechanical properties of M-600-PEMIPU-DA were limited. When M-600-maleimide was proportionally replaced by D-400-maleimide or T-403-maleimide, D-400-maleimide and T-403-maleimide were crosslinked with PMPU-furan through DA reaction, so it was necessary to shorten the reaction time to 2 h to prevent gelling in the flask.

Characterization

Fourier Transform Infrared (FTIR) Spectroscopy. FTIR was performed on a Paragon 1000 spectrometer (PerkinElmer). FTIR spectra were recorded from 4000 to 400 cm^{-1} . PMPU-furan and final PU product were tested via FTIR to confirm the DA reaction between PMPU-furan and PEMI.

$^1\text{H-NMR}$. $^1\text{H-NMR}$ spectroscopy was performed on an Avance-400 spectrometer (Bruker, Switzerland) with hexadeuterated dimethyl sulfoxide ($\text{DMSO-}d_6$) or deuterated chloroform (CDCl_3) as the solvent. All intermediates and final PU product were tested via $^1\text{H-NMR}$ to confirm their structures. And the thermal reversibility of PEMIPU was investigated via $^1\text{H-NMR}$.

Differential Scanning Calorimetry (DSC). DSC was performed on a TA Instruments Q2000 from -60 to 160°C at a heating rate of $10^\circ\text{C}/\text{min}$ under a nitrogen atmosphere. The thermal properties of PMPU-furan and final PU product were investigated via DSC.

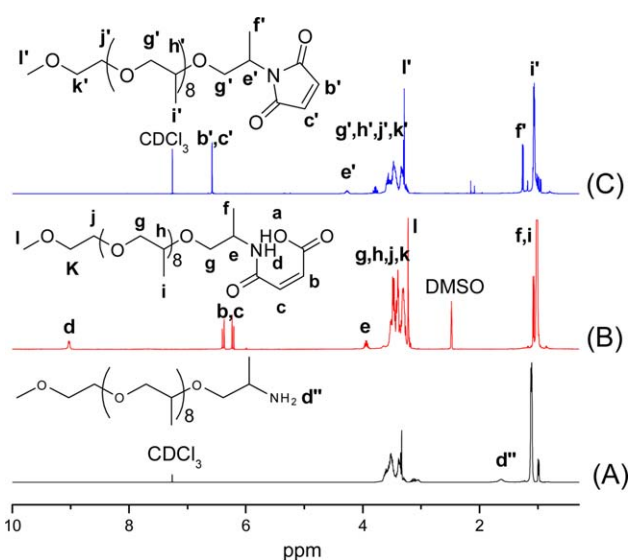


Figure 1. $^1\text{H-NMR}$ spectra of (A) M-600, (B) M-600-maleamic acid, and (C) M-600-maleimide (DMSO = dimethyl sulfoxide). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

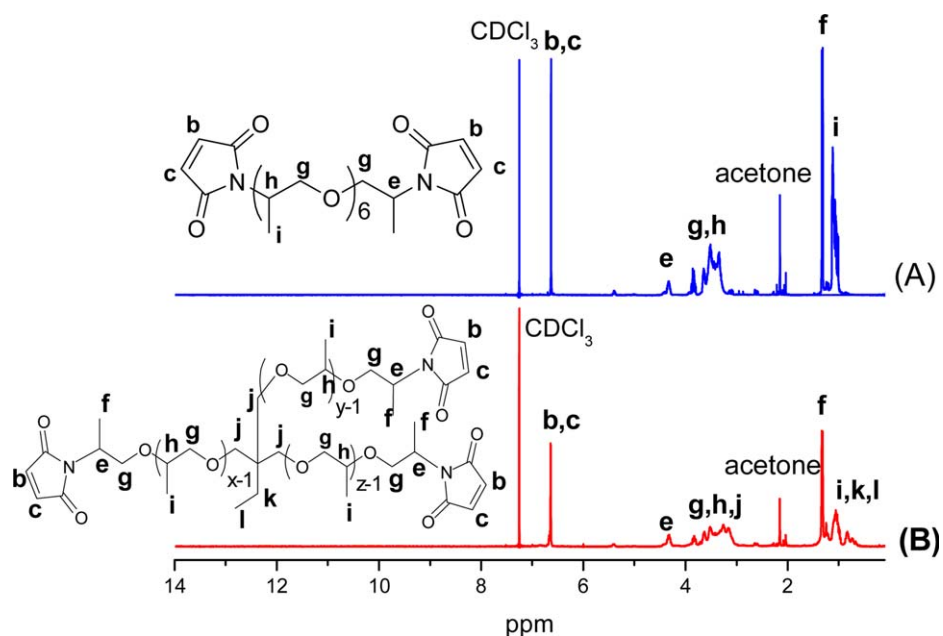


Figure 2. $^1\text{H-NMR}$ spectra of D-400-maleimide and T-403-maleimide. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Self-Healing Properties. (1) The tensile properties of the original and healed samples were measured on an Instron 4465 testing machine with an elongation rate of 50 mm/min at 25°C and 55% relative humidity. The sizes of the dumbbell-like specimens were 20 mm \times 4 mm \times 0.5–1 mm (thickness). Five specimens were tested from each sample. (2) The polarizing optical microscopy (POM) photographs of a crack in C-PEMIPU-DA during the healing process were obtained from RT (25°C) to 130°C at a heating rate of 10°C/min and maintained at 130°C for 5 min (Leica DM LP, Leica Instruments).

RESULTS AND DISCUSSION

PEMI Synthesis

The structure of M-600, M-600-maleamic acid, and M-600-maleimide were investigated via $^1\text{H-NMR}$, as shown in Figure 1.

The peaks at 6.37 and 6.24 ppm [b and c in Figure 1(B)] confirmed the C=C bond in M-600-maleamic acid. Meanwhile, the peak at 1.60 ppm [d' in Figure 1(A)] disappeared, and the peak at 9.02 ppm [d in Figure 1(B)] appeared. This confirmed the successful amidation reaction between M-600 and maleic anhydride.

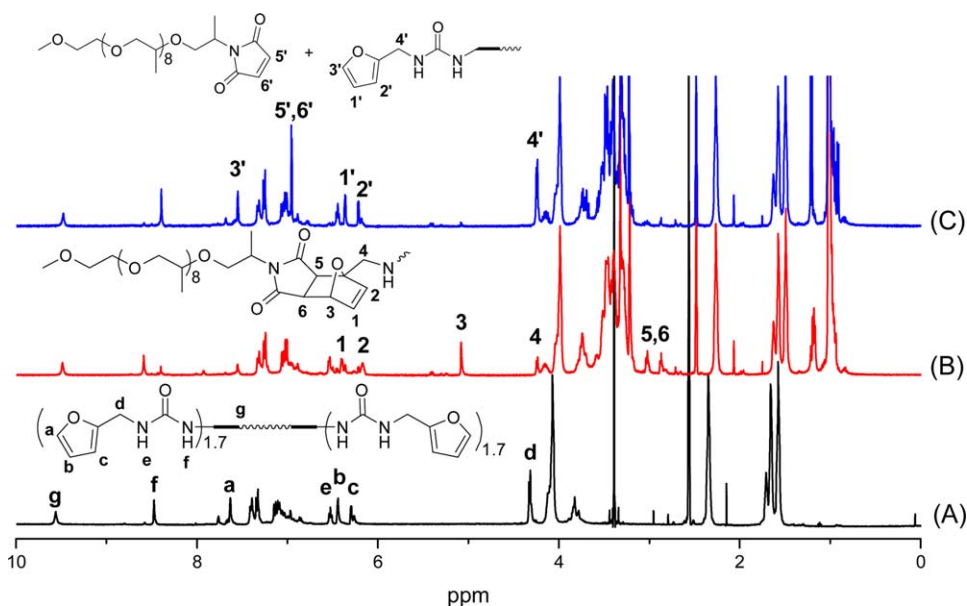


Figure 3. $^1\text{H-NMR}$ spectra of the (A) PMPU-furan, (B) M-600-PEMIPU-DA, and (C) M-600-PEMIPU-DA reaction solution after 10 min at 120°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

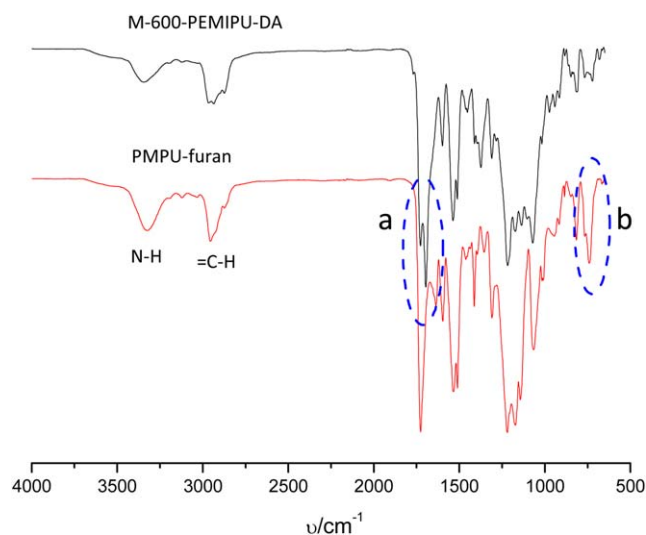


Figure 4. FTIR spectra of the PMPU-furan and M-600-PEMIPU-DA: (a) carbonyl absorption band and (b) furan absorption band. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Comparing the spectrum of M-600-maleimide to that of M-600-maleamic acid, we found that the peak at 9.02 ppm [d in Figure 1(B)] disappeared in the spectrum of M-600-maleimide [Figure 1(C)]. In addition, the peaks at 6.37 and 6.24 ppm [b and c in Figure 1(B)] merged into a peak at 6.55 ppm [b' and c' in Figure 1(C)]. All these confirmed the successful dehydration cyclization reaction of the intermediate M-600-maleamic acid.

The synthesis and characterization of D-400-maleimide and T-403-maleimide were similar to those of M-600-maleimide. Their structures were investigated via $^1\text{H-NMR}$ spectroscopy, as shown in Figure 2.

The $^1\text{H-NMR}$ results show that PEMI with different functional groups (M-600-maleimide, D-400-maleimide, and T-403-maleimide) were successfully synthesized.

C-PEMIPU-DA Synthesis

The structure of PMPU-furan was first investigated via $^1\text{H-NMR}$, as shown in Figure 3(A). The peaks at 8.50 and 6.53 ppm (peaks e and f, respectively), due to the protons of urea, confirmed the successful reaction between the isocyanate and amino group. The peaks at 6.28, 6.45, 7.63, and 4.16 ppm (peaks a, b, c, and d, respectively) confirmed the presence of the furan group in PMPU-furan. Take M-600-PEMIPU-DA, for example; the structure of C-PEMIPU-DA was also investigated via $^1\text{H-NMR}$, as shown in Figure 3(B). Compared with

Table I. Polyurethane Samples Obtained from PEMI

Sample	—OH/—NCO (molar ratio)	Chain extender
PMPU-furan	1/2.7	—
D-400-PEMIPU-DA	1/2.7	D-400-maleimide
T-403-PEMIPU-DA	1/2.5	T-403-maleimide

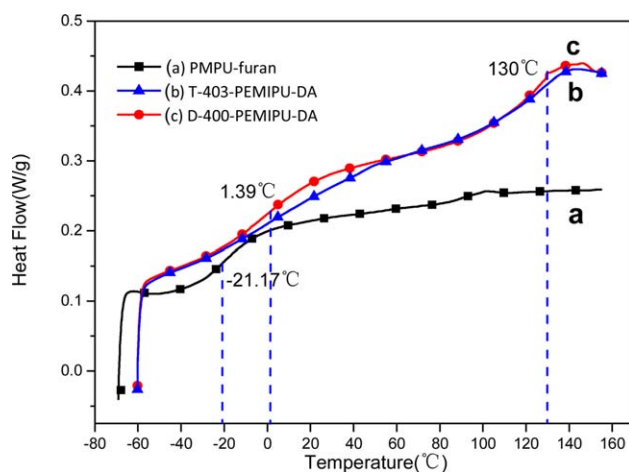


Figure 5. DSC curves of the (a) PMPU-furan and (b,c) C-PEMIPU-DA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the $^1\text{H-NMR}$ spectrum of PMPU-furan, C-PEMIPU-DA exhibited the characteristic peaks of the DA bonds at 2.87, 3.02, and 5.08 ppm (peaks 3, 5, and 6, respectively); this confirmed the successful DA reaction between PMPU-furan and PEMI. The retro DA reaction of C-PEMIPU-DA was investigated via testing of the $^1\text{H-NMR}$ spectrum of the C-PEMIPU-DA reaction solution after 10 min at 120°C, as shown in Figure 3(C). The characteristic peaks of DA bonds (2.87, 3.02, and 5.08 ppm) nearly disappeared. The characteristic peaks of the initial raw materials PMPU-furan and PEMI appeared, as shown in Figure 3(C) (peaks 3', 5', and 6'). These indicated that C-PEMIPU-DA had a great thermal reversibility.

The FTIR spectra of the PMPU-furan and M-600-PEMIPU-DA (Figure 4) confirmed the $^1\text{H-NMR}$ results. The FTIR spectrum of PMPU-furan confirmed that there were no residual isocyanate groups in PMPU-furan by the absence of a peak at 2270 cm^{-1} . Meanwhile, additional peaks at 3428, 1725, and 1534 cm^{-1} specific to the allophanate groups confirmed the successful reaction between the isocyanate and amino group. Compared with PMPU-furan, M-600-PEMIPU-DA exhibited

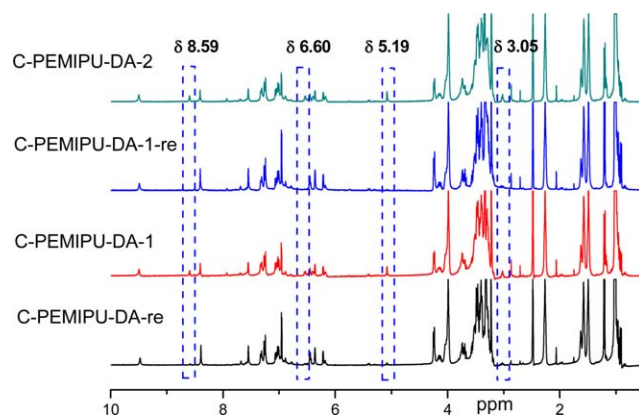


Figure 6. $^1\text{H-NMR}$ spectra of D-400-PEMIPU-DA and D-400-PEMIPU-DA-re during the heating and cooling procedures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

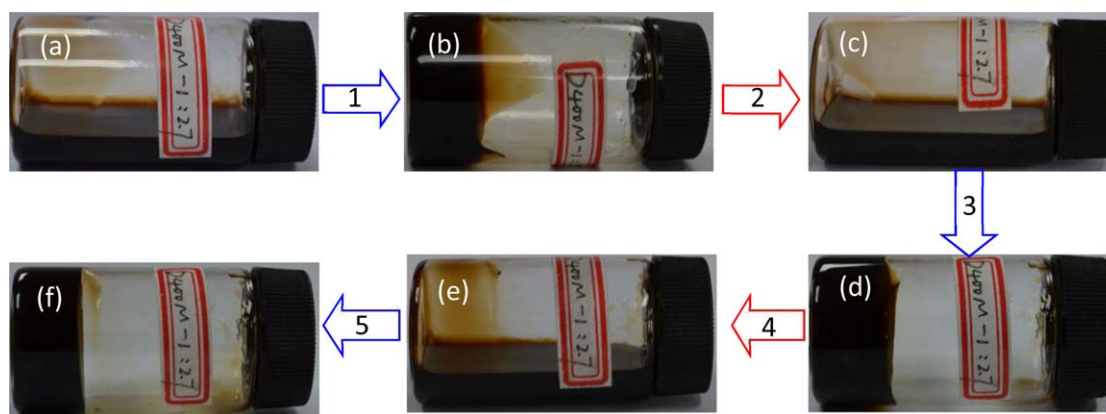


Figure 7. Photographs of D-400-PEMIPU-DA during the sol-gel process: (a) C-PEMIPU-DA-re, (b) C-PEMIPU-DA-1, (c) C-PEMIPU-DA-1-re, (d) C-PEMIPU-DA-2, (e) C-PEMIPU-DA-2-re, and (f) C-PEMIPU-DA-3. Arrows 1, 3, and 5 represent 180 min at 60°C, and arrows 2 and 4 represent 20 min at 120°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

two major differences. First, a shoulder peak specific to the DA adduct appeared at 1730 cm^{-1} [Figure 4(a)]. Second, the absorption at 740 cm^{-1} decreased; this was ascribed to the decrease of furan rings [Figure 4(b)]. These indicated the successful crosslinking of PMPU-furan with PEMI via the DA reaction.

With the samples shown in Table I as examples, the thermal properties of PMPU-furan and C-PEMIPU-DA were investigated via DSC. As shown in the DSC curves (Figure 5), C-PEMIPU-DA exhibited a significant endothermic peak around 130°C, whereas PMPU-furan did not. The significant endothermic peaks around 130°C of C-PEMIPU-DA could be explained by the retro DA reaction; this confirmed the DA bonds in C-PEMIPU-DA. D-400-PEMIPU-DA had a glass-transition temperature of 1.39°C, which was much higher than that of

PMPU-furan (-21.17°C). This could be explained by the fact that the crosslinking via DA reaction restricted the movement of soft-segment PBA-1000. The glass-transition temperature of T-403-PEMIPU-DA was not obvious as the segmental motion was mostly restricted because of the high crosslinking density.

Thermal Reversibility of C-PEMIPU-DA

The thermal reversibility of C-PEMIPU-DA was first characterized by $^1\text{H-NMR}$ (Figure 6). Take D-400-PEMIPU-DA as an example; because of the crosslinking via DA reaction, C-PEMIPU-DA could not be dissolved in $\text{DMSO-}d_6$. Thus, the original $^1\text{H-NMR}$ spectrum of C-PEMIPU-DA was not obtained. However, C-PEMIPU-DA could be easily dissolved in $\text{DMSO-}d_6$ after 10 min at 120°C because of the retro DA reaction. C-PEMIPU-DA-re (the product of C-PEMIPU-DA after

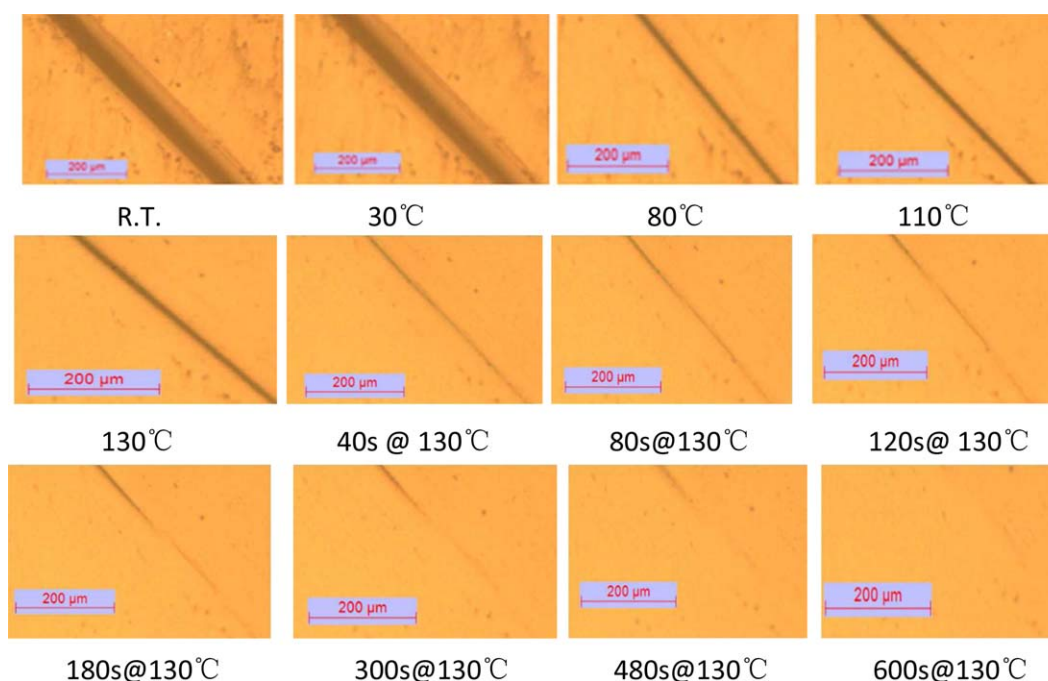


Figure 8. Self-healing study of D-400-PEMIPU-DA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

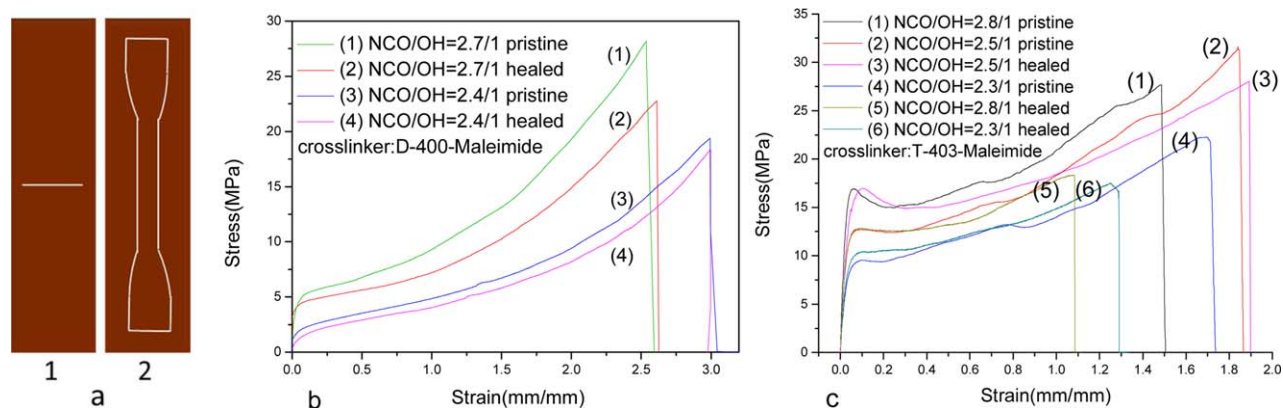


Figure 9. (a) Testing method for healing efficiency, (b) stress–strain curves of the D-400–PEMIPU–DA and healed samples, and (c) stress–strain curves of the T-403–PEMIPU–DA and healed samples. NCO/OH indicates the molar ratio of isocyanate groups to hydroxyl. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the retro DA reaction) did not exhibit the characteristic peaks of DA adducts at 3.05, 5.19, 6.60, and 8.59 ppm; this confirmed the retro DA reaction of C-PEMIPU–DA. C-PEMIPU–DA reverts to C-PEMIPU–DA through the DA reaction after 7 days at 60°C. This was confirmed by the reappearance of the characteristic peaks at 3.05, 5.19, 6.60, and 8.59 ppm (C-PEMIPU–DA-1 in Figure 6). The cycles of DA and the retro DA reaction could be repeated at least two times, as shown in Figure 6; this indicated the excellent thermal reversibility of C-PEMIPU–DA.

With D-400–PEMIPU–DA as an example, the thermal reversibility of C-PEMIPU–DA was also investigated by a sol–gel process. Figure 7 shows the phase changes that came with the DA and retro DA reactions. C-PEMIPU–DA was swollen in DMF after 4 h at 60°C (33 wt %). Upon heating to 120°C, the swollen C-PEMIPU–DA was completely converted into a dark solution in about 20 min because of the retro DA reaction [Figure 7(a)]. The solution was gradually converted into a gel in about 3 h at 60°C because of the DA reaction [Figure 7(b)]. Upon heating, the gel was converted back to a dark solution again [Figure 7(c)]. This gel solution–gel cycle could be repeated at least three times successfully [Figure 7(a–f)]; this indicated that C-PEMIPU–DA was fully thermally reversible. At the same concentration, T-403–PEMIPU–DA formed gels in about 2 h because of the higher crosslinking density.

These results confirmed that C-PEMIPU–DA exhibited excellent thermal reversibility and highlighted the potential applications of C-PEMIPU–DA in self-healing and recyclable materials.

Self-Healing Properties of C-PEMIPU–DA

With D-400–PEMIPU–DA as an example, the self-healing behavior of C-PEMIPU–DA under thermal treatment was first characterized by the POM study (Figure 8). A deliberate scratch 5 mm in length was made on the C-PEMIPU–DA film by a surgical blade. The scratched film was placed on a heating stage under an N₂ flow and heated to 130°C with a constant heating rate of 10°C/min and kept at 130°C until the crack disappeared. The sample was characterized by POM analysis at different time intervals during the healing process, as shown in Figure 8. The

sample softened gradually, and the crack narrowed slightly when the sample was heated up to 80°C. When the sample was kept at 130°C, the crack disappeared gradually in about 10 min. This could be explained by the retro DA reaction of C-PEMIPU–DA at 130°C. When the sample was kept at 130°C, the DA bonds were broken, and the crosslinked C-PEMIPU–DA gradually transformed into PMPU–furan and PEMI. Because of the small molecular weight and nonrigid structure of D-400–maleimide, it was easy for the molecular chain to move; this was favorable for crack repair. This indicated the excellent self-healing properties of C-PEMIPU–DA.

The self-healing behavior of C-PEMIPU–DA was also characterized by the measurement of the healing efficiency obtained through the measurement of the tensile strength of the original and healed samples, as shown by our previous studies.^{25–27} The original sample was cut through its center with a surgical blade [Figure 9(a-1)]. Afterward, it was healed at 130°C until the crack disappeared, and then, it was placed at 60°C for 3 days. Then, the healed sample was cut into a dumbbell-shaped sample, as shown in Figure 9(a-2). The stress–strain curves of the pristine and healed D-400–PEMIPU–DA samples are shown in Figure 9(b). The stress–strain curves of the pristine and healed T-403–PEMIPU–DA samples are shown in Figure 9(c).

The data of the mechanical properties were obtained from Figure 9, as shown in Tables II and III. A comparison of the

Table II. Mechanical Properties of the D-400–PEMIPU–DA

Property	–NCO/–OH (molar ratio)			
	2.4:1		2.7:1	
	Pristine	Healed	Pristine	Healed
Yield strength (MPa)	2.3	1.7	5.3	4.5
Tensile strength (MPa)	19.4	18.3	28.2	22.8
Elongation at break (%)	299	299	254	261
Healing efficiency	94.3%		80.8%	

The chain extender was D-400–maleimide.

Table III. Mechanical Properties of the T-403-PEMIPU-DA

Property	-NCO/-OH (molar ratio)					
	2.3/1		2.5/1		2.8/1	
	Pristine	Healed	Pristine	Healed	Pristine	Healed
Yield strength (MPa)	9.6	10.4	12.7	17.0	16.9	12.9
Tensile strength (MPa)	22.3	17.4	31.7	28.0	27.9	18.3
Elongation at break (%)	171	129	186	189	150	109
Healing efficiency (%)	78.0		88.3		65.6	

The chain extender was T-403-maleimide.

yield strength of the pristine T-403-PEMIPU-DA samples indicated that the yield strength increased with increasing -NCO/-OH ratio. This was because the hard-segment content increased with increasing -NCO/-OH ratio; this was favorable for raising the strength and hardness. However, a comparison of the tensile strengths indicated that the T-403-PEMIPU-DA sample with a -NCO/-OH ratio of 2.5:1 had the highest tensile strength. This was because the polyurethane with an -NCO/-OH ratio of 2.8:1 contained too many hard segments, which hardened the polyurethane and reduced the sample's tensile strength and elongation at break. Compared to the T-403-PEMIPU-DA samples, the D-400-PEMIPU-DA samples had a lower tensile strength and higher elongation at break, especially compared to that with a lower -NCO/-OH ratio. This could be explained by the high crosslinking density of T-403-PEMIPU-DA, which improved the tensile strength and reduced the flexibility and ductility of the sample. The previous results show that for the PEMI-based polyurethanes, the crosslinking density was not the higher the better.

A comparison of the healing efficiencies of the D-400-PEMIPU-DA samples showed that the sample with an -NCO/-OH ratio of 2.4/1 exhibited a healing efficiency of 94.3%, and the sample with an -NCO/-OH ratio of 2.7/1 exhibited a healing efficiency of 80.8%. This was because the polyurethane with a higher -NCO/-OH ratio needed more calories to break the covalent bonds during the self-healing process; this could give rise to unfavorable side reactions and could, thus, reduce the healing efficiency. Also, a higher -NCO/-OH ratio indicated more rigid groups; this restricted the movement of segments at the healing temperature and thus reduced the healing efficiency.

CONCLUSIONS

Jeffamine polyetheramine with amino ends were converted to PEMI by amidation and dehydration reactions. PMPU-furan was prepared from a functionalized prepolymer and FA. Finally, crosslinked polyurethane containing DA bonds (C-PEMIPU-DA) was synthesized from PMPU-furan and PEMI. The structures of PEMI, PMPU-furan, and C-PEMIPU-DA were confirmed by ¹H-NMR, FTIR spectroscopy, and DSC. The thermal reversibility and self-healing performances of C-PEMIPU-DA

were studied by ¹H-NMR, a sol-gel process, POM, and tensile testing. The obtained results indicate that the C-PEMIPU-DAs had excellent mechanical properties (with a tensile strength of up to 19–32 MPa), great thermal reversibility (the gel solution-gel cycle could be repeated at least three times successfully), and self-healing capability (the healing efficiency was up to 80–95%). Because the retro-DA reaction temperature was around 130°C, C-PEMIPU-DA could maintain its mechanical properties under 130°C. All of these properties extended the application area and prolonged the lifetime of C-PEMIPU-DA; this has broad prospects for development.

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