

Diels–Alder-Based Crosslinked Self-Healing Polyurethane/Urea from Polymeric Methylene Diphenyl Diisocyanate

Pengfei Du,¹ Meiyin Wu,¹ Xuanxuan Liu,¹ Zhen Zheng,¹ Xinling Wang,¹ Thomas Joncheray,² Yuefan Zhang³

¹State Key Laboratory of Metal Matrix Composites, School of Chemistry and Chemical Technology, Shanghai Jiao Tong University, Shanghai 200240, China

²Huntsman (Europe) BVBA, Everberg B-3078, Belgium

³Huntsman Chemistry R&D Center (Shanghai) Company, Limited, Shanghai 200245, China

Correspondence to: X. Wang (E-mail: xlwang@sjtu.edu.cn)

ABSTRACT: Crosslinked self-healing polyurethane/urea based on a Diels–Alder reaction (C-PMPU–DA) was synthesized from a multiple-furan monomer and a commercial bismaleimide. The multiple-furan monomer (PMPU–furan) was obtained from a functionalized prepolymer (polymeric MDI: PBA-2000 = 2:1) by furfuryl amine. The structures of both the PMPU–furan and C-PMPU–DA were characterized by attenuated total reflectance (ATR)–Fourier transform infrared (FTIR) spectroscopy, differential scanning calorimetry, thermogravimetric analysis, and ¹H-NMR. The Diels–Alder bonds enabled C-PMPU–DA thermal reversibility, which was investigated by ATR–FTIR spectroscopy, ¹H-NMR, gel–solution–gel experiments, and viscosity tests. Meanwhile, the self-healing properties of C-PMPU–DA were also investigated by the recovery of the mechanical properties. The results showed that C-PMPU–DA exhibited good thermal reversibility and self-healing properties. C-PMPU–DA exhibited thermosetting properties at room temperature, although it exhibited thermoplastic properties at higher temperatures and may find applications in self-healing materials, recyclable materials, or removable materials. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40234.

KEYWORDS: crosslinking; polyurethanes; recycling; Diels–Alder reaction

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INTRODUCTION

Polymer materials have a finite lifetime because their inherent properties degrade with continuous exposure to environmental stresses, such as chemical attack, radiation damage, mechanical abrasion, and impact and thermal decomposition alone or in combination.¹ Inspired by the self-healing phenomenon of biological organization,² the concept of self-healing polymeric materials was proposed in the 1980s to heal invisible microcracks and prolong polymeric material service life.^{3–7} Self-healing materials are able to heal and repair themselves once or multiple times, either autonomically or in response to external stimuli such as changes in pH, heat, or light.^{8,9} The thermal reversibility of the Diels–Alder (DA) reaction and the mild conditions of its retro reaction make it particularly desirable for the preparation of heat-stimuli self-healing polymeric materials. Many studies have been focused on the reaction between furan (diene) and maleimide (dienophile), presumably because of the higher reactivity of maleimide in the DA reaction.⁶ All these studies have focused on linear polymers^{10–22} and crosslinked polymers with pendant DA bonds.^{22–32} As for the later crosslinked polymer,

although it has good mechanical properties, the pendant DA bond in the polymer chain restricts their application for self-healing materials because of the relatively poor chain mobility of the starting linear polymers with pendant furan or maleimide groups.⁶

To obtain crosslinked polymers with good self-healing efficiency and mechanical properties, Wudl et al.³³ prepared a polymer network based on the DA reaction between multifunctional furan and maleimide monomers. Their study was definitely the first example of thermally mendable polymers materials. After that, many research teams have concentrated on this crosslinked thermally mendable polymer. Wudl et al.³⁴ prepared a remendable polymer network using two maleimides instead of maleimide monomers to proceed in bulk without any solvent, and the polymer exhibited good self-healing properties. Liu and Hsieh³⁵ prepared one thermosetting polymer that consisted of epoxy-based trisfurans and trismaleimides; the final polymer network exhibited good self-healing properties. Watanabe and Yoshies¹⁶ also obtained crosslinked materials with mendability via DA reaction from furfuryl telechelic polyester with trifunctional maleimide.

Gandini et al.³⁶ also prepared a multiple-furan monomer via another click reaction. A novel furan–maleimide polymer was reported by Gostsmann.³⁷ The novel polymer could switch between a rigid highly crosslinked state and a deformable fragmented state. Their polymer network has been exploited in data storage and lithographic applications. Shape-memory polymer networks were also prepared via DA reaction.^{38–41} The kinetic and thermodynamic investigation of the DA reaction between a trisfuran and a bismaleimide (BMI) was carried out via Fourier transform infrared (FTIR) spectroscopy.⁴²

The key step of preparing this type of crosslinked polymer is to form the small multifunctional monomers containing furan and maleimide separately. In this study, polymeric MDI (S5005), which has been widely used for thermosetting polyurethane, was used to prepare a multiple-furan monomer (PMPU–furan) via the reaction between isocyanate and furfuryl amine. Then a commercial BMI was added to the solution to react with PMPU–furan to form the crosslinked self-healing polyurethane/urea based on a Diels–Alder reaction (C–PMPU–DA) in a simple one-pot method. The one-pot method made it much easier to obtain C–PMPU–DA with the synthesis procedure. The DA bond enabled C–PMPU–DA to obtain a new property: thermal reversibility in which it exhibited thermosetting properties at room temperature, although it exhibited thermoplastic properties at higher temperature. The thermal reversibility provided C–PMPU–DA with the following advantages: (1) self-healing properties in response to heat stimuli, (2) a lower viscosity in solvents at higher temperatures (this makes it easier to proceed) and a higher viscosity at lower temperatures as a gel, and (3) the ability to be recycled and be good to the environment, unlike other crosslinked polyurethane. C–PMPU–DA can be potentially applied as a self-healing material or a removable material and so on.

EXPERIMENTAL

Materials

Furfuryl amine (99%) and BMI [1,1'-(methylenedi-1,4-phenylene) bismaleimide (95%)] were purchased from Aldrich and were used as received.

Polymeric MDI [S5005, a mixture of MDI, MDI dimers, MDI trimers, etc., with 2.7 NCO groups on average (99%)] was supplied by Huntsman and was used as received.

PBA-2000 (poly-1,4-butylene adipate glycol, number-average molecular weight = 2000) was supplied by Eternal Chemical and was used after 2 h of drying *in vacuo* at 90°C.

N,N-Dimethylformamide (DMF) was purchased from China National Medicines and was used after being dried with CaH₂ and purified by vacuum distillation.

Synthesis of C–PMPU–DA

Polymeric MDI [S5005, the product grade of polymeric MDI] (5.80 g, 16.0 mmol) was reacted with PBA-2000 (16.00 g, 8.0 mmol) with 22 mL of DMF as a solvent in a 100-mL, three-necked, round-bottom flask, equipped with a mechanical stirrer. The prepolymerization was carried out at 60°C under a nitrogen atmosphere. Three hours later, the flask was put in an ice–water bath to decrease the temperature. Then, furfuryl amine (2.70 g,

27.2 mmol) dissolved in 3 mL of DMF was added dropwise into the isocyanate end-capped prepolymer solution in an ice–water bath. Three hours later, the whole solution (PU–furan prepolymer) was heated to 60°C for about 30 min to make sure that all of the isocyanate was consumed by furfuryl amine. Then, BMI (5.13 g, 13.6 mmol) dissolved in 2 mL of DMF was added to the solution. Half an hour later, the whole solution was poured onto a Polytetrafluoroethylene (PTFE) plate to prevent gelling in the flask. The PTFE plate was put in a 50°C oven for about 2 days to remove the DMF solvent. Meanwhile, the crosslinking via the DA reaction proceeded during the removal of DMF. Finally, a polymer film (28.1 g) was obtained as the final product (C–PMPU–DA, yield = 94.9%).

Characterization

Attenuated Total Reflectance (ATR)–FTIR Spectroscopy. ATR–FTIR was performed on a Paragon 1000 spectrometer (PerkinElmer). ATR–FTIR spectra were recorded in the range 4000–400 cm^{−1}.

¹H-NMR. ¹H-NMR spectroscopy was performed on an Avance-400 spectrometer (Bruker, Switzerland) with hexadeuterated dimethyl sulfoxide (DMSO-*d*₆) as the solvent at 25°C.

Differential Scanning Calorimetry (DSC). DSC data was obtained from −60 to 160°C at a heating rate of 10°C/min under a nitrogen flow (TA Instruments Q2000).

Thermogravimetric Analysis (TGA). TGA of PMPU–furan and C–PMPU–DA were performed on a TGA instrument (Q5000IR, TA Instruments) at a heating rate of 20°C/min in an N₂ atmosphere from room temperature to 600°C.

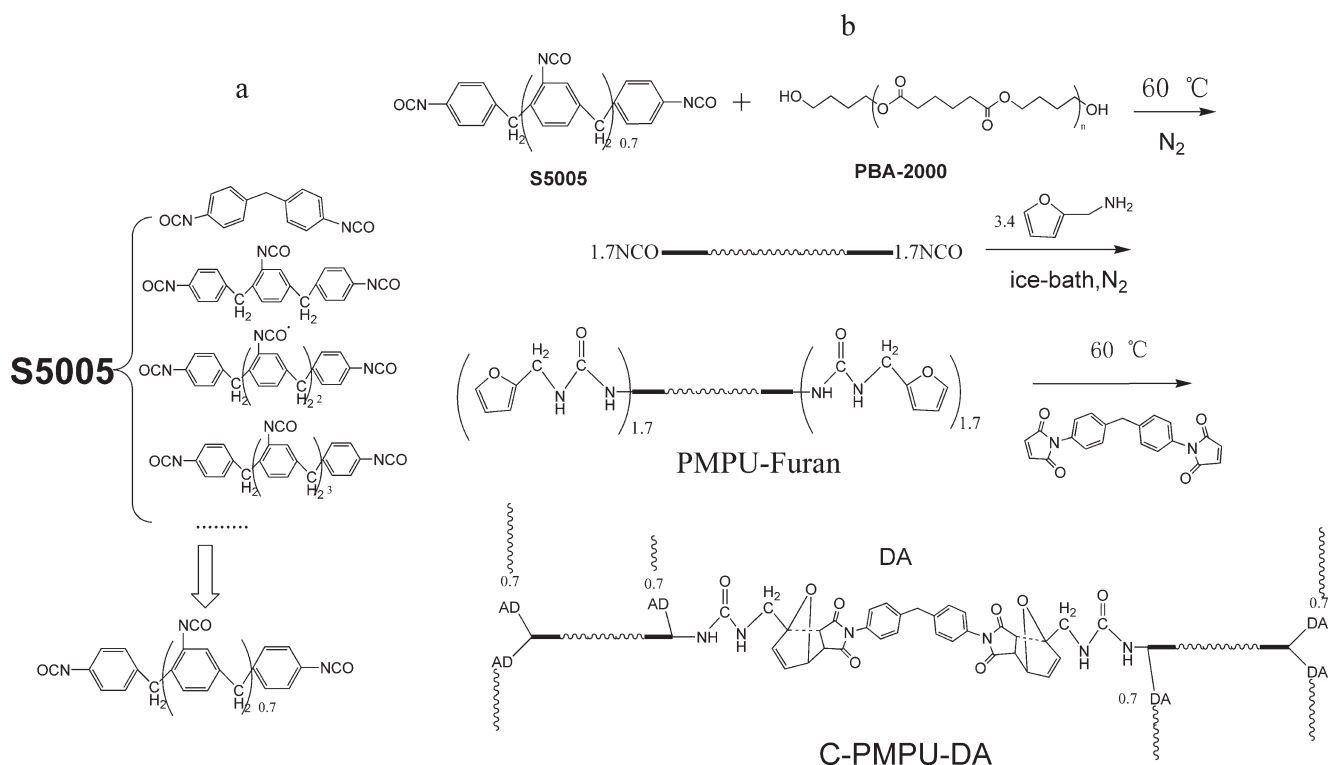
Viscosity. The viscosity was measured on a Brookfield DV-II+ Pro viscometer with an RV6 rotator. The viscosity was recorded every 10 s until the gels were obtained.

Self-Healing Properties. The tensile properties of the original and the healed samples were measured on an Instron 4465 testing machine. The elongation rate was set at 50 mm/min. The specimens were dumbbell-like with sizes of 20 × 4 × 0.4–1 mm³.

RESULTS AND DISCUSSION

C–PMPU–DA Synthesis

Polymeric MDI (S5005) was a mixture of MDI, MDI dimer, trimer, and so on (2.7 NCO on average). It was considered to have the structure shown in Scheme 1(a). S5005 reacted with PBA-2000 to form an NCO-terminated prepolymer, and this was then reacted with furfuryl amine to form the multiple-furan terminated prepolymer PMPU–furan [Scheme 1(b)]. No gels were generated in the prepolymerization because of the excess of NCO groups. Finally, the multiple-furan-terminated prepolymer was crosslinked with BMI at 60°C to form C–PMPU–DA, as shown in Scheme 1(b). Half an hour later, the whole solution was poured into a PTFE plate to prevent gelling in the flask. The polyurethane film was obtained after the removal of the DMF solvent. The whole procedure was carried out in a one-pot method; this made the synthesis procedure much easier to carry out.



Scheme 1. PMPU-furan and C-PMPU-DA synthesis.

Characterization

The structure of the PMPU-furan was first investigated via $^1\text{H-NMR}$, as shown in Figure 1. The peaks of the 8.4- and 6.5-ppm attributed to the H in urea confirmed the successful reaction between the isocyanate end-capped prepolymer and furfuryl amine. The multiple-furan monomer was obtained from the functionalized isocyanate end-capped prepolymer by furfuryl amine. The peaks at 6.2, 6.3, 7.5, and 4.2 ppm also confirmed the presence of the furan group in the intermediate

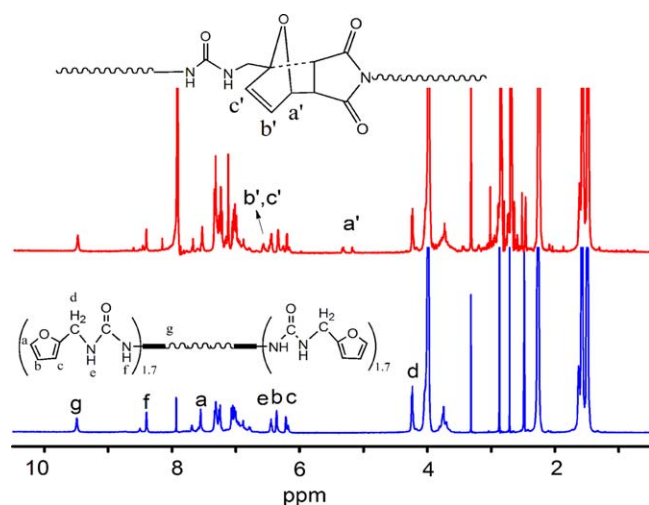


Figure 1. $^1\text{H-NMR}$ spectra of PMPU-furan and C-PMPU-DA: (A) PMPU-furan and (B) reaction solution after the addition of BMI for 0.5 h. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

PMPU-furan. The reaction of the PMPU-furan with BMI was investigated via the testing of the $^1\text{H-NMR}$ spectra of the reaction solution after 30 min at 50°C . Compared with the $^1\text{H-NMR}$ of PMPU-furan, the characteristic peaks of the DA bond appeared after 30 min at 50°C , as shown in Figure 1(a'-c'). This confirmed the successful DA reaction between PMPU-furan and BMI.

The ATR-FTIR spectra of PMPU-furan and C-PMPU-DA (Figure 2) confirmed the $^1\text{H-NMR}$ results. The absence of a peak at 2270 cm^{-1} confirmed that there were no residual isocyanate groups in PMPU-furan. Meanwhile, additional peaks at

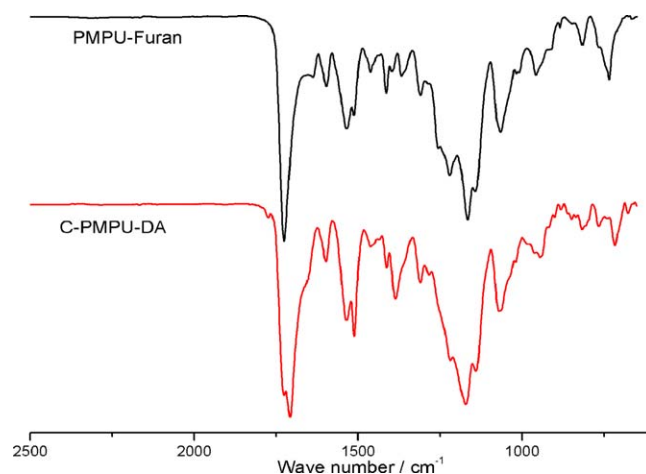


Figure 2. ATR-FTIR spectra of PMPU-furan and PMPU-DA (magnification at $2500\text{--}600\text{ cm}^{-1}$). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

1070, 720, and 810 cm^{-1} confirmed the presence of furan rings in PMPU-furan. Compared with PMPU-furan, C-PMPU-DA exhibited a shoulder peak at 1730 cm^{-1} specific to the DA adduct²⁴ and decreasing absorptions at 1070, 810, and 720 cm^{-1} , which was ascribed to the furan ring and indicated the successful crosslinking of PMPU-furan with BMI via the DA reaction.

The thermal properties of PMPU-furan and C-PMPU-DA were investigated via DSC and TGA. As shown in the DSC curves [Figure 3(a)], C-PMPU-DA exhibited a significant endothermic peak around 120°C, whereas PMPU-furan did not. The significant endothermic peaks around 120°C of C-PMPU-DA could be explained by the retro DA reaction; this confirmed the DA bonds in C-PMPU-DA. Meanwhile, PMPU-furan showed a sharp crystallization peak at 50°C, whereas C-PMPU-DA did not. This could be explained by the fact that the crosslinking via DA reaction restricted the free movement of soft-segment PBA-2000; this inhibited the formation of the crystal. All of these results confirmed the successful reaction between PMPU-furan and BMI.

From the TGA curves in Figure 3(b), C-PMPU-DA exhibited a significantly higher amount of char residue than PMPU-furan; this indicated the successful introduction of the crosslinker BMI.⁴² Meanwhile, C-PMPU-DA also showed a slow weight loss after 250°C from the weight-temperature shown in Figure 3(b); this suggested that C-PMPU-DA exhibited a higher thermal stability after crosslinking with BMI.

Thermal Reversibility of C-PMPU-DA

The thermal reversibility of C-PMPU-DA was first investigated by ¹H-NMR. Because of the crosslinking via the DA reaction, C-PMPU-DA could not be dissolved in DMSO-*d*₆. The original ¹H-NMR of C-PMPU-DA was not obtained. However, the undissolved C-PMPU-DA in DMSO-*d*₆ could be easily dissolved

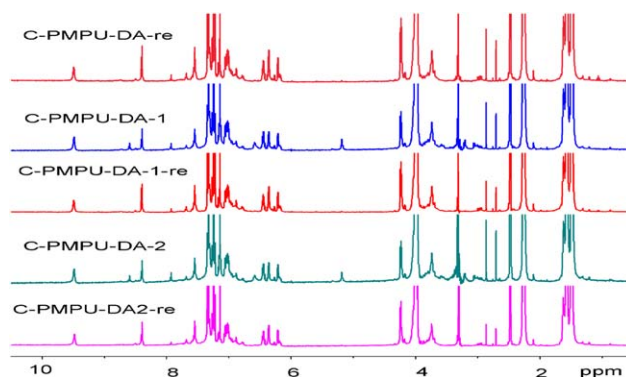


Figure 4. ¹H-NMR spectra of C-PMPU-DA during the heating and cooling procedures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

after 10 min in a 120°C oil bath because of the retro DA reaction. The retro DA reaction was confirmed by the disappearance of the four characteristic peaks at 3.1, 3.2, 5.2 and 6.6 ppm (C-PMPU-DA-re, the product of C-PMPU-DA after retro DA reaction in Figure 4). C-PMPU-DA reverted back to its starting material PMPU-furan and BMI completely after 10 min in a 120°C oil bath. After the sample was kept in 50°C oven for 2 days, the DA reaction was carried out again in an NMR tube at 50°C even at such a low concentration. This was confirmed by the reappearance of the characteristic peaks at 3.1, 3.2, 5.2 and 6.6 ppm. The retro DA reaction and DA reaction cycle could be repeated at least two times, as shown in Figure 4. The ¹H-NMR results indicated excellent thermal reversibility in C-PMPU-DA.

The thermal reversibility of C-PMPU-DA was also investigated via ATR-FTIR spectroscopy. The characteristic shoulder peak at 1730 cm^{-1} disappeared after 20 min at 120°C (C-PMPU-DA-0-re in Figure 5) because the retro DA reaction destroyed the DA bonds in C-PMPU-DA. The shoulder peak was observed again

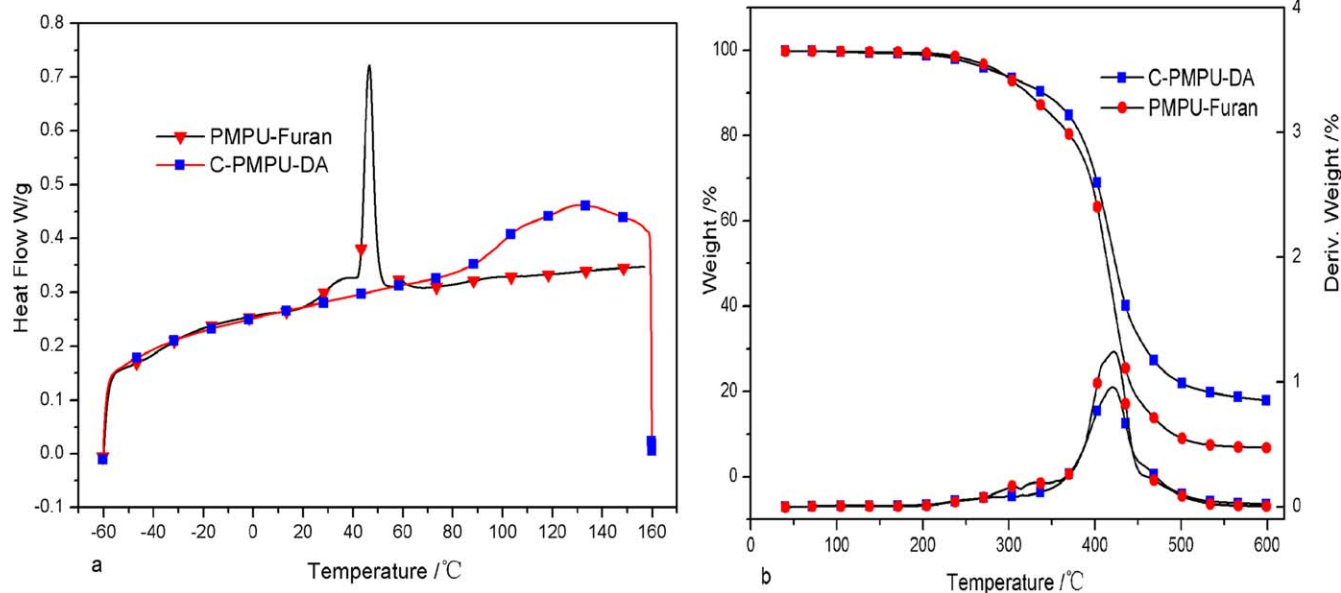


Figure 3. Thermal behavior of PMPU-furan and C-PMPU-DA as observed (a) DSC and (b) TGA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

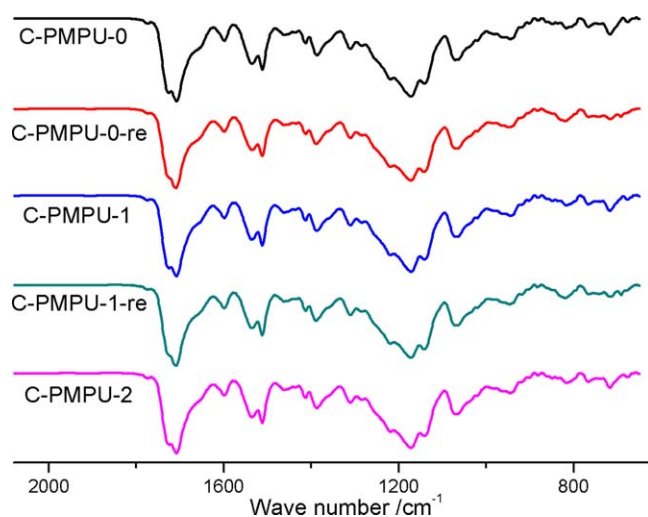


Figure 5. ATR-FTIR spectra for C-PMPU-DA during the heating and cooling procedures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

after 1 day at 50°C; this indicated the regeneration of the DA bonds. Meanwhile, the peak at 810 cm^{-1} , which was attributed to the furan ring, increased after 20 min at 120°C and decreased after 1 day at 50°C. All of this suggested that C-PMPU-DA reverted back to PMPU-furan and BMI at higher temperatures and regenerated at lower temperatures.

The thermal reversibility of C-PMPU-DA was also investigated in DMF (25 wt %). Figure 6 shows the phase changes observed versus the temperature. C-PMPU-DA was swollen after only 4 h at 50°C (picture 0 in Figure 6). Upon heating to 120°C, the swollen C-PMPU-DA was converted into a clear and low-viscosity solution (picture 1a in Figure 6) in about 15 min because of the retro DA reaction. However, the viscosity of the solution increased gradually after the solution was placed at 50°C. The fluidity of the solution was finally lost, and gels formed in about 2 h (picture 1b in Figure 6). This gel-solution-gel cycle could be repeated at least three times successfully (pictures 2a and 2b and 3a and 3b in Figure 6); this indicated good thermal reversibility in C-PMPU-DA.

Consequently, the viscosity of the C-PMPU-DA solution in DMF (25 wt %) was also recorded from low-viscosity solution to gels at 60°C on Brookfield DV-II+ Pro viscometers, as

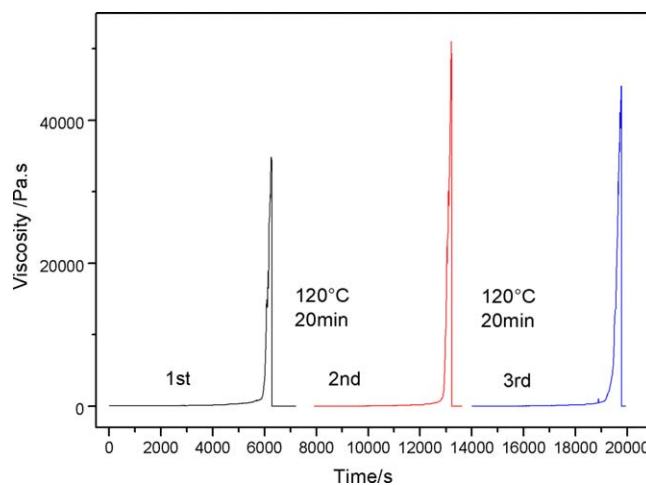


Figure 7. Viscosity changes in C-PMPU-DA during the heating and cooling procedures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

shown in Figure 7. After 20 min at 120°C and quenching to room temperature, the solution was put in a test tube at 60°C. The viscosity of the solution was very low, close to 0 Pa s; this confirmed the results of the gel-solution-gel experiment. This could be explained by the fact that C-PMPU-DA returned back to PMPU-furan and BMI after 20 min at 120°C. The low viscosity of the solution at higher temperature made it much easier to proceed. The viscosity of the solution exhibited a flat curve until it experienced a sudden significant increase at about 6000 s. The viscosity could reach about 40,000 Pa s. After that, the viscosity returned to 0 Pa s when the rotator was stopped.

The significant increase in the viscosity could be explained by the recrosslinking via the DA reaction. C-PMPU-DA was obtained again. The obtained gels returned back to low-viscosity solutions for the second time at 120°C in about 20 min, and the low-viscosity solution exhibited a flat curve of viscosity and a sudden significant increase in the test tube at 60°C, as shown in Figure 7, and this phenomenon (gel-low-viscosity solution-gel) was repeated at least three times.

All of the previous results confirmed the good thermal reversibility of C-PMPU-DA and highlighted the fact that C-PMPU-DA could potentially be used as self-healing, removable, or recyclable materials.

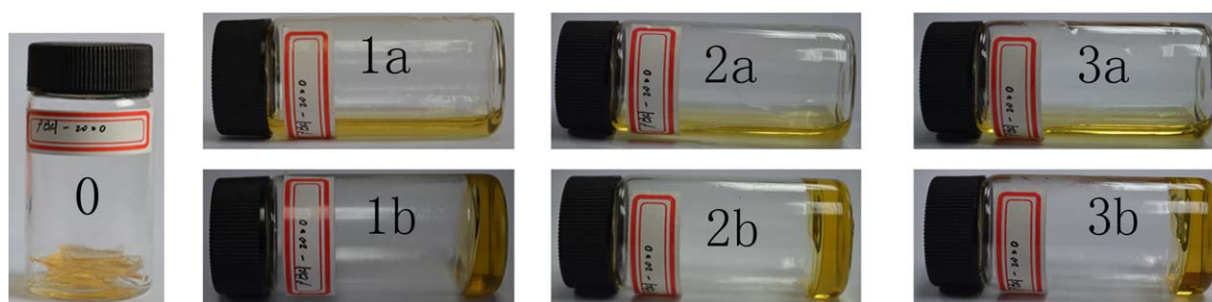


Figure 6. (0) C-PMPU-DA at 50°C for 2 h, (1a,2a,3a) soluble solution after 10 min at 120°C (cycles 1, 2, and 3, respectively), and (1b,2b,3b) gel formation after 2 h at 50°C (cycles 1, 2, and 3, respectively). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

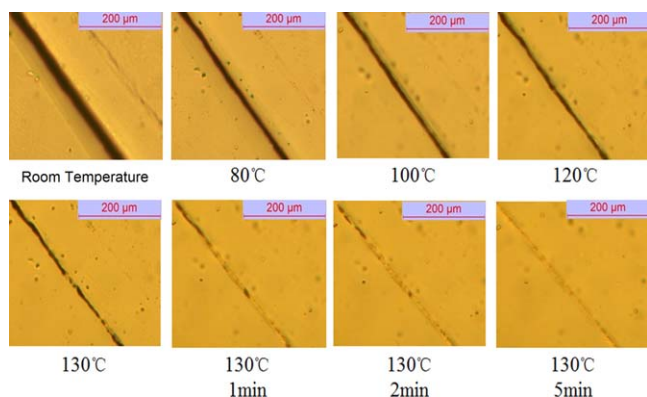


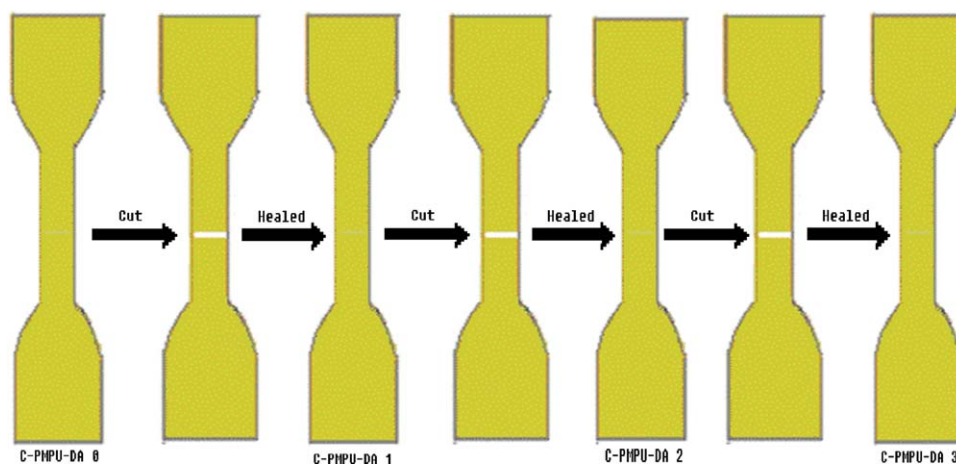
Figure 8. Polarizing optical microscopy photographs of a crack in C-PMPU-DA during the healing process. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Self-Healing Properties

The self-healing properties behavior of C-PMPU-DA under thermal treatment was first investigated by observation of the evolution of a crack under polarizing optical microscopy equipped with a heating stage. The C-PMPU-DA film was cut through with a surgical blade and put on a heating stage under an N_2 flow. The temperature was increased at a rate of $10^\circ C/min$ and held at $130^\circ C$ until the crack disappeared. Photographs were taken at different time intervals during the healing process, as shown in Figure 8.

The crack did not change much below $120^\circ C$ but only when the temperature got close to $130^\circ C$. When the sample was kept at $130^\circ C$, the crack disappeared gradually in about 5 min; this indicated that C-PMPU-DA exhibited excellent self-healing properties.

As for self-healing materials, healing efficiency is a good measure for evaluating the healing process. In this article, the self-healing efficiency of C-PMPU-DA was obtained by the measurement of the breaking (tensile) strength before damage and after healing, as our previous works.^{43,44} A series of treatments were performed on C-PMPU-DA to evaluate the healing efficiency, as shown in Scheme 2.



Scheme 2. Thermal healing procedure for testing the self-healing efficiency of C-PMPU-DA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

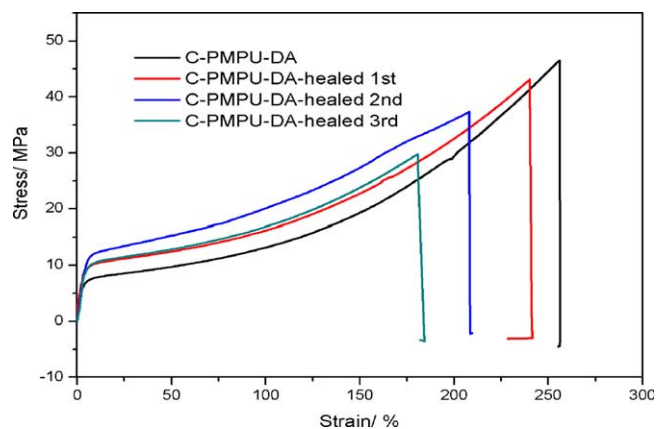


Figure 9. Mechanical properties of the C-PMPU-DA and healed samples. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The original sample was cut through in its center with a surgical blade, and it was healed at $130^\circ C$ for about 5 min followed by 1 day at $55^\circ C$. The healed samples were named C-PMPU-DA-1, C-PMPU-DA-2, and C-PMPU-DA-3. The breaking (tensile) strength of C-PMPU-DA (as shown in Figure 9) reached 46.5 MPa; this was much higher than our previous linear polyurethane with DA bonds.^{44,45} This could be explained by the crosslinking with BMI. According to the breaking (tensile) strength of the damaged and healed samples, the healing efficiency [breaking (tensile) strength] of the first healed sample reached about 92.4%, whereas the third healed sample also exhibited a significant healing efficiency of about 64.5%. All of these results indicated that C-PU-DA exhibited good mechanical properties and self-healing properties.

CONCLUSIONS

Crosslinked polyurethane containing DA bonds (C-PMPU-DA) was synthesized from a multiple-furan monomer (PMPU-furan) and BMI. PMPU-furan was prepared from a functionalizing prepolymer (S5005-PBA-2000) with furfuryl amine. The structures of both PMPU-furan and C-PMPU-DA were

confirmed by ATR–FTIR spectroscopy, DSC, TGA, and ¹H-NMR. According to the results of the ATR–FTIR spectroscopy, ¹H-NMR, gel–solution–gel experiments, and viscosity tests, C-PMPU–DA exhibited good thermal reversibility. C-PMPU–DA reverted back to PMPU–furan and BMI at 120°C and recrosslinked at 50°C to form C-PMPU–DA again. The breaking (tensile) strength of the original and the healed samples revealed excellent mechanical properties, with a breaking (tensile) strength of about 46.5 MPa for the original C-PMPU–DA, and significant recovery after healing (92.4% after damage and healing for the first time and 64.5% for the third time).

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