

Slightly crosslinked polyurethane with Diels–Alder adducts from trimethylolpropane

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ABSTRACT: Diels–Alder (DA) reactions between furan and maleimide have been widely applied in thermally remendable polymeric materials. Crosslinked polyurethane with DA adducts exhibited much better mechanical properties than linear polyurethane with DA adducts. However, the highly crosslinked polyurethane needs a higher temperature and a longer healing time. This will increase the possibility of side reactions proceeding during the healing procedure. In this paper, slightly crosslinked polyurethane with DA adducts was synthesized by incorporating trimethylolpropane into linear polyurethane with DA adducts. The structure of the intermediate and final products was characterized by Fourier transform infrared spectroscopy, ¹H-NMR, and differential scanning calorimetry, confirming that the synthesizing process proceeded successfully. The images from the polarizing optical microscope demonstrated that the final product with slight crosslinking needed less time and a lower healing temperature to complete the healing procedure. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43971.

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INTRODUCTION

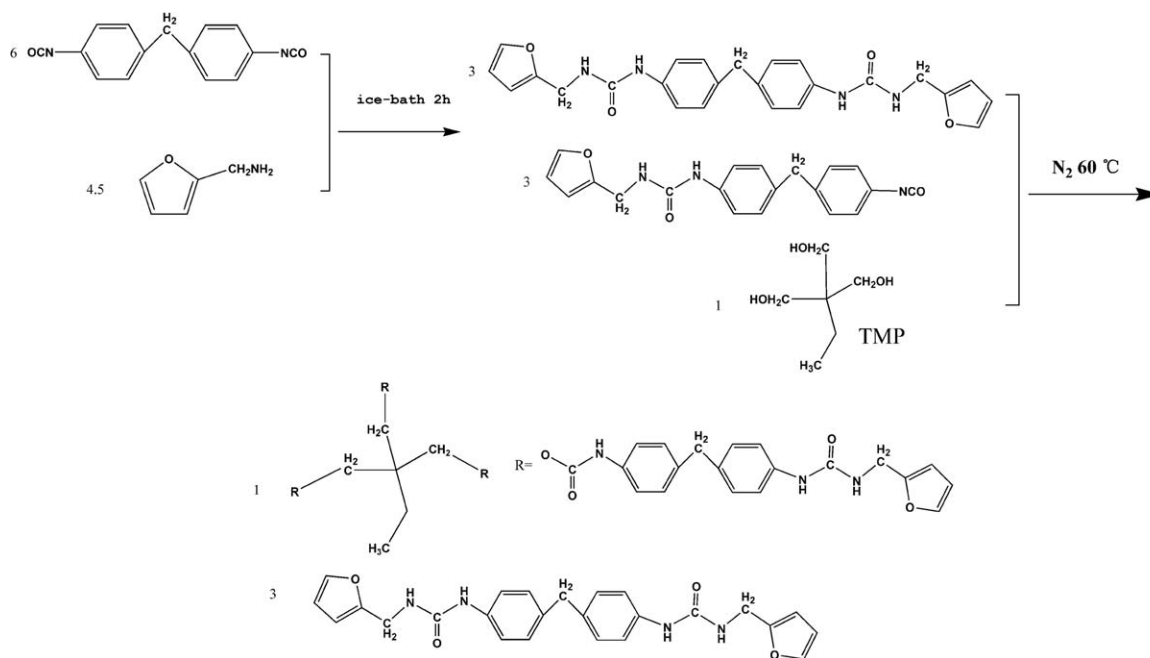
Diels–Alder (DA) reactions between furan and maleimide have been widely applied in thermally remendable polymeric materials^{1–21} because of their excellent thermal reversibility and the mild reaction conditions under which the retro-DA reaction occurs. Because of the good mechanical properties and the flexible formula of the polyurethane, many researchers^{22–30} have concentrated on polyurethane with DA adducts, including linear^{24–26,29} and crosslinked^{22,23,25,28,30,31} polyurethane.

Previous research⁴ demonstrated that crosslinked polyurethane with DA adducts exhibited much better mechanical properties than linear polyurethane with DA adducts. However, the highly crosslinked polyurethane with DA adducts needed a higher healing temperature and a longer healing time than the linear polyurethane with DA adducts because of its higher content of hard segments (benzene) and higher degree of crosslinking. This will increase the possibility of side reactions proceeding during the healing process. Two methods have been used to decrease the crosslinking density of the polyurethane with DA adducts. One was to increase the molecular weight of the polyester polyol³⁰; the other was to synthesize bismaleimide without benzene to decrease the rigidity of the crosslinked polyurethane.³¹ However, the healing temperature was still higher than for the linear

polyurethane (130 to 120 °C). The healing still needed 5 to 10 min to complete the healing process, while the linear polyurethane needed about 5 min.

In this paper, slightly crosslinked polyurethane with DA adducts was synthesized via incorporating trimethylolpropane (TMP) into the linear polyurethane with DA adducts. TMP, a traditional polyurethane curing agent, can incorporate crosslinking into polyurethane feasibly. However, when we tried to incorporate crosslinking into the linear polyurethane with terminal NCO groups by adding TMP into the polyurethane prepolymer solution directly, gels were generated during the synthesizing procedure of polyurethane prepolymer. This can be explained by the higher percentage of the MDI or polyurethane prepolymer with two isocyanates.

To reduce the possibility of generating gels during the synthesis procedure of the polyurethane prepolymer with terminal furan groups, our key ideas were as follows. (1) First, 75% isocyanate in polyurethane prepolymer was consumed by furfuryl amine to reduce the percentage of the MDI or polyurethane prepolymer with two isocyanates. (2) The remaining 25% isocyanate was consumed by TMP, generating polyurethane prepolymer (MDI-PBA-FA-TMP) with two or three furan-terminated groups. (3) MDI-PBA-FA-TMP was crosslinked with bismaleimide (BMI) to



Scheme 1. Synthesis of model compound MDI-FA-TMP.

form slightly crosslinked polyurethane with DA adducts (MDI-PBA-TMP-DA).

The incorporation of the slight crosslinking via TMP will improve the mechanical properties of the polyurethane on one hand and decrease the healing temperature and healing time on the other hand. All of these improvements will reduce the possibility of side reactions proceeding during the healing process.

EXPERIMENTAL

Materials

Furfurylamine (99%, AR) and BMI [1,1-(methylene-1,4-phenylene)bismaleimide, 95%, AR] were purchased from Aldrich, Shanghai, China and used as received. MDI [4,4'-diphenylmethane diisocyanate, 99%, CP] was supplied by Huntsman, Shanghai, China and used as received. Polybutyleneglycol adipate (PBA; $M_n = 1000$, CP) was supplied by Eternal Chemical, Shanghai, China and used after 2 h drying under vacuum at 90 °C. Trimethylolpropane (99%, AR) was purchased from Aladdin, Shanghai, China and used as received. *N,N*-Dimethylformamide (DMF) (99%, AR) was purchased from China National Medicines, Shanghai, China and was used after drying with CaH_2 and purification by vacuum distillation.

Characterization

Fourier transform infrared spectroscopy (FTIR) and ATR-FTIR were performed on a Paragon 1000 spectrometer (Perkin-Elmer, Waltham, Massachusetts USA). The FTIR spectra were recorded in the range 4000 to 400 cm^{-1} .

$^1\text{H-NMR}$ spectroscopy was performed on an Avance-400 spectrometer (Bruker, Switzerland, Zürich) with hexadeuterated dimethyl sulfoxide ($\text{DMSO-}d_6$) as solvent at 25 °C.

The thermal behavior of MDI-PBA-TMP-DA was studied by differential scanning calorimetry (DSC). The DSC data were

obtained from -60 to 160 °C at a heating rate of 10 °C min^{-1} under nitrogen flow (TA Instruments Q2000, New Castle city, Delaware, USA).

To evaluate the self-healing property of MDI-PBA-TMP-DA, a crack in the polyurethane film was observed under a polarizing optical microscope (Leica Camera AG, Wetzlar, Germany) equipped with a temperature-programmed heating stage (TMS 94). The mechanical properties of the original and the healed samples were measured on an Instron 4465 testing machine (INSTRON CORPORATION, Canton, Massachusetts, USA). The elongation rate was set to 50 mm/min. The specimens were dumbbell-like (20 mm \times 4 mm \times 0.4–1 mm). The healing efficiency was calculated by the recovery of the breaking (tensile) strength.

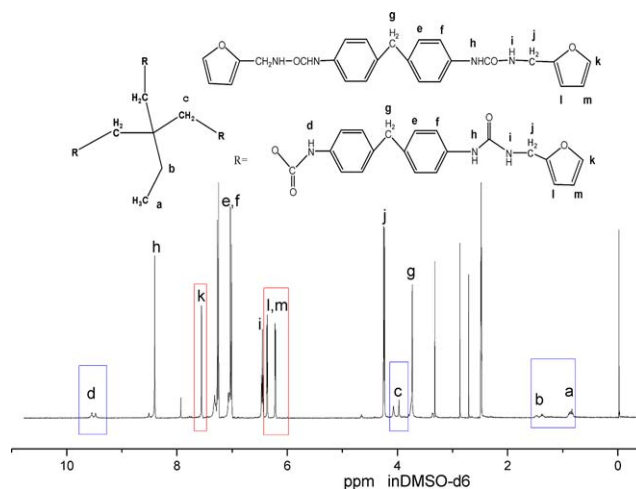
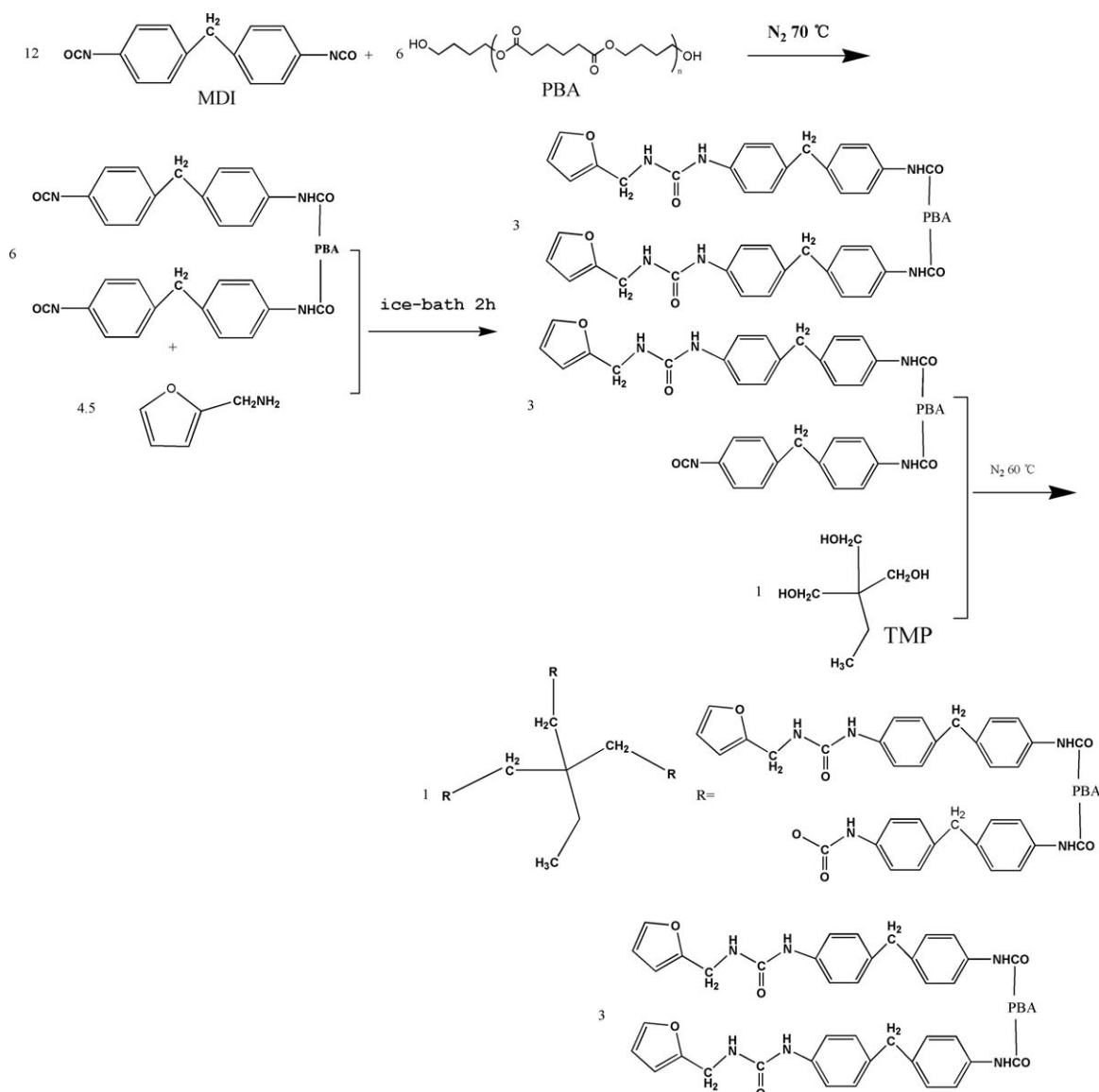


Figure 1. $^1\text{H-NMR}$ spectra of MDI-FA-TMP. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



Scheme 2. Synthesis of furan-terminated prepolymer MDI-PBA-FA-TMP.

Synthesis of Model Compound: Furan-Terminated MDI Containing TMP (MDI-FA-TMP)

MDI-FA-TMP was synthesized through the following procedures: (1) MDI (4 g, 16 mmol) was dissolved in 10 mL DMF in a 100 mL three-necked round-bottom flask equipped with a mechanical stirrer and dropping funnel. (2) Furfurylamine (2.4 g, 24 mmol) dissolved in 3 mL DMF was added dropwise into the solution in an ice-water bath for 0.5 h, followed by 1 h at 60 °C. (3) TMP (0.37 g, 2.7 mmol) was then added to the flask and kept at 60 °C for 3 h. (4) After cooling down to room temperature, the solution was poured into excess diethyl ether and was filtered and dried under vacuum at room temperature, and a white solid polymer (MDI-FA-TMP) was obtained.

Synthesis of Furan-Terminated Polyurethane Prepolymer Containing TMP (MDI-PBA-FA-TMP)

MDI-PBA-FA-TMP was synthesized through the following procedures: (1) MDI (4 g, 16 mmol) reacted with PBA-1000 (8 g, 8

mmol) in 10 mL DMF as solvent in a 100 mL three-necked round-bottom flask, equipped with a mechanical stirrer and dropping funnel. The reaction was carried out at 60 °C under nitrogen atmosphere for 3 h and then cooled in an ice-water bath. NCO-terminated polyurethane prepolymer (MDI-PBA-MDI) was obtained. (2) Furfurylamine (1.2 g, 12 mmol) dissolved in 2 mL DMF was added dropwise into the solution in an ice-water bath for 0.5 h, followed by 1 h at 60 °C, generating furan-terminated polyurethane prepolymer (MDI-PBA-FA). (3) TMP (0.18 g, 1.3 mmol) was added to the flask and kept at 60 °C for 3 h. (4) After cooling down to room temperature, the solution was poured into excess diethyl ether and was filtered and dried under vacuum at room temperature, and a white solid polymer (MDI-PBA-FA-TMP) was obtained.

Crosslinking of MDI-PBA-FA-TMP with BMI

BMI (2.1 g, 6 mmol) dissolved in 2 mL DMF was added to the solution of MDI-PBA-FA-TMP at 60 °C. After 5 h, the whole solution was poured into a polytetrafluoroethylene plate and

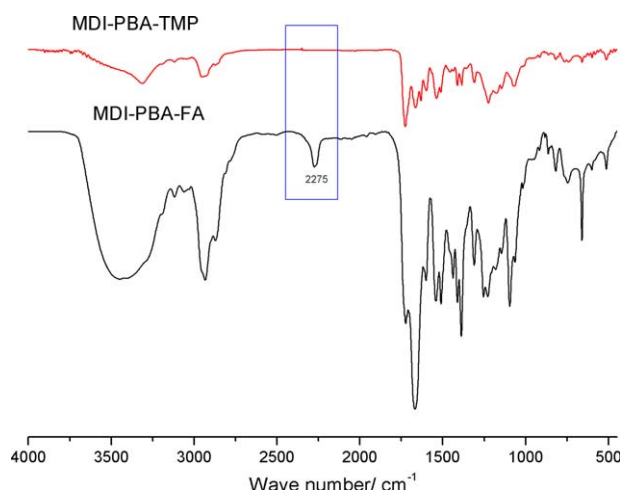


Figure 2. Monitoring the reaction process via FTIR. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

was put in an oven at 50 °C for about 2 days to evaporate the DMF. A polyurethane film was obtained as the final product (MDI-PBA-TMP-DA).

RESULTS AND DISCUSSION

Synthesis and Characterization of Model Compound

MDI-FA-TMP

First, 75% of the isocyanate in MDI was consumed by furfuryl amine, generating MDI terminated with furan groups and isocyanate groups. The residue 25% isocyanate was consumed by TMP, resulting in MDI-FA-TMP with two and three furan terminal groups, as shown in Scheme 1.

As furfuryl amine is a monoprimary compound, the side reaction between the generated urea and the residue isocyanate can

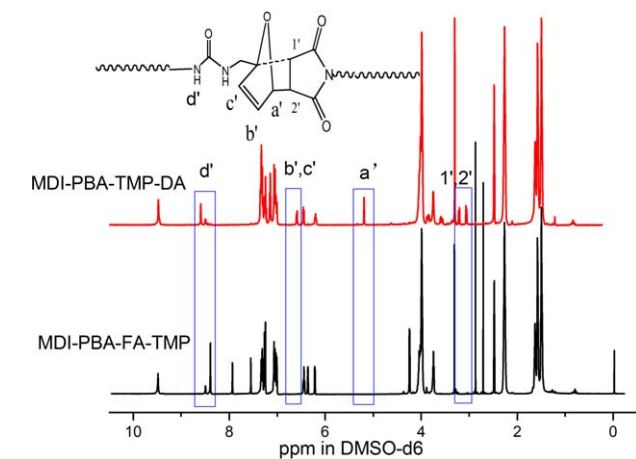


Figure 4. $^1\text{H-NMR}$ spectra of MDI-PBA-FA-TMP and MDI-PBA-TMP-DA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

be avoided conveniently via the same method as was described in our previous work.²⁹ After 2 h in an ice bath, the solution was kept at room temperature for about 1 h to make sure the furfuryl amine reacted with the isocyanate completely. Only the MDI with one isocyanate group can react with TMP, generating MDI-FA-TMP, as shown in Scheme 1.

The structure of MDI-FA-TMP was characterized by $^1\text{H-NMR}$, as shown in Figure 1. MDI-FA-TMP exhibited chemical shifts at $\delta = 7.55$ ppm [$-\text{O}-\text{CH}=\text{CH}$ in the furan ring; hydrogen (k) in figure], 6.37 ppm [$-\text{O}-\text{CH}=\text{CH}$ in the furan ring; hydrogens at (l) and (m)], as well as at $\delta = 4.25$ ppm [furan- CH_2 ; (j)], indicating the presence of the furan ring. MDI-FA-TMP also exhibited chemical shifts at $\delta = 8.40$ ppm and 6.45 ppm, which were assigned to the hydrogens in the urea

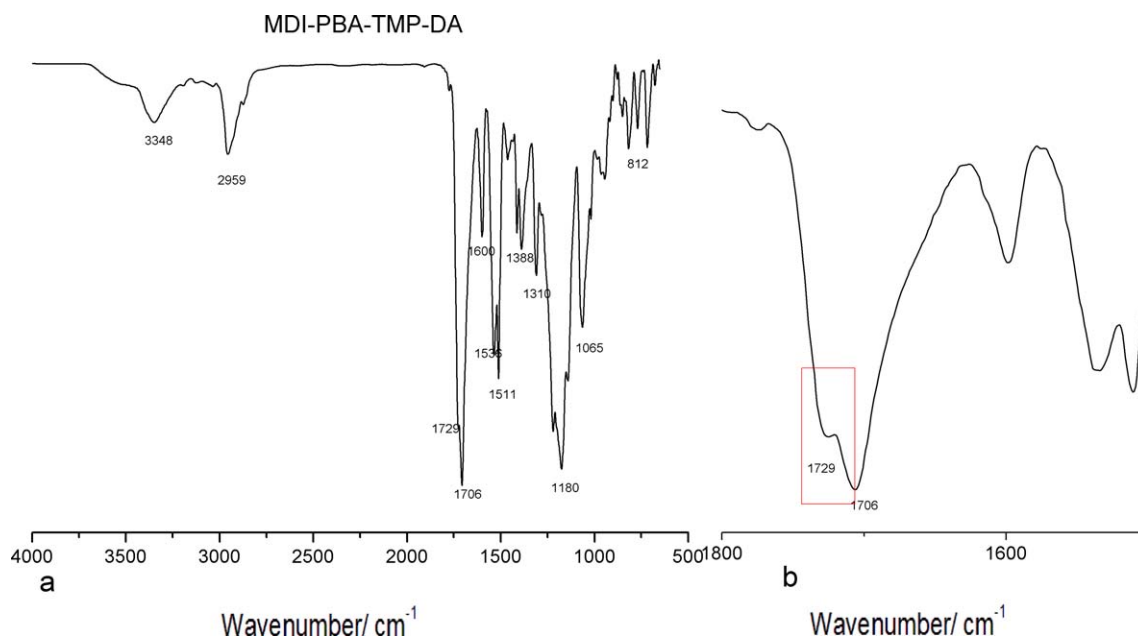


Figure 3. (a) ATI-FTIR spectra of MDI-PBA-TMP-DA; (b) magnification of 1800–1500 cm^{-1} . [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

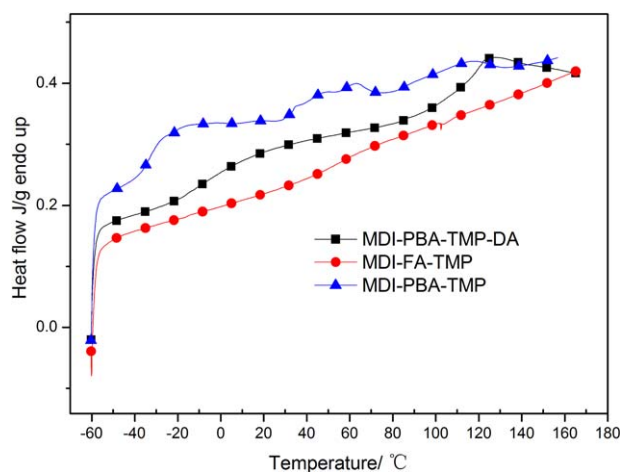


Figure 5. DSC curves of MDI-PBA-TMP-DA and MDI-PBA-TMP-DA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

group [(h) and (i)]. These peaks confirmed that the reaction between MDI and furfuryl amine had occurred completely without side reactions. The peaks at $\delta = 9.50$ ppm were attributed to the hydrogen in the urethane group [hydrogen at (d)]. The peaks at $\delta = 4.00$ ppm, 1.40 ppm, and 0.85 ppm were attributed to TMP [hydrogens at (a–c)]. These peaks confirmed the reaction between the hydroxyl groups in TMP and the remaining 25% isocyanate in MDI. All of these results confirmed that MDI-FA-TMP was a mixture of polyurethane prepolymer with two and three terminal furan groups.

The results of the $^1\text{H-NMR}$ demonstrated that MDI-FA-TMP can be feasibly synthesized as shown in Scheme 1 and provided a theoretical basis for analyzing the $^1\text{H-NMR}$ spectra of the subsequent polyurethane prepolymer mixture with two and three terminal furan groups (MDI-PBA-FA-TMP) and its subsequent DA adduct (MDI-PBA-TMP-DA).

Synthesis and Characterization of MDI-PBA-FA-TMP and MDI-PBA-TMP-DA

In this section, MDI-PBA-FA-TMP was synthesized via the same method as MDI-FA-TMP in the previous section, using MDI-PBA-MDI as the starting material (as shown in Scheme 2). The incorporation of PBA will increase the proportion of the soft segments in polyurethane and improve the elasticity and toughness of the polyurethane.

First, the process of synthesizing MDI-PBA-FA-TMP was monitored via FTIR, as shown in Figure 2. The intensity of the peaks at 2275 cm^{-1} attributed to the NCO groups in the polyurethane prepolymer decreased significantly after reaction with furfuryl amine, indicating most of the isocyanate in MDI-PBA-MDI prepolymer was consumed by the furfuryl amine. There was still residue isocyanate in the MDI-PBA-FA prepolymer solution, confirmed by the fact that the characteristic peaks did not disappear completely in Figure 2. However, the characteristic peaks of the isocyanate group at 2275 cm^{-1} disappeared completely after reaction with TMP, indicating the residue isocyanate in the MDI-PBA-FA prepolymer solution was consumed by TMP. The FTIR results demonstrated that TMP was incorporated into the polyurethane prepolymer successfully, generating MDI-PBA-FA-TMP, as shown in Scheme 2.

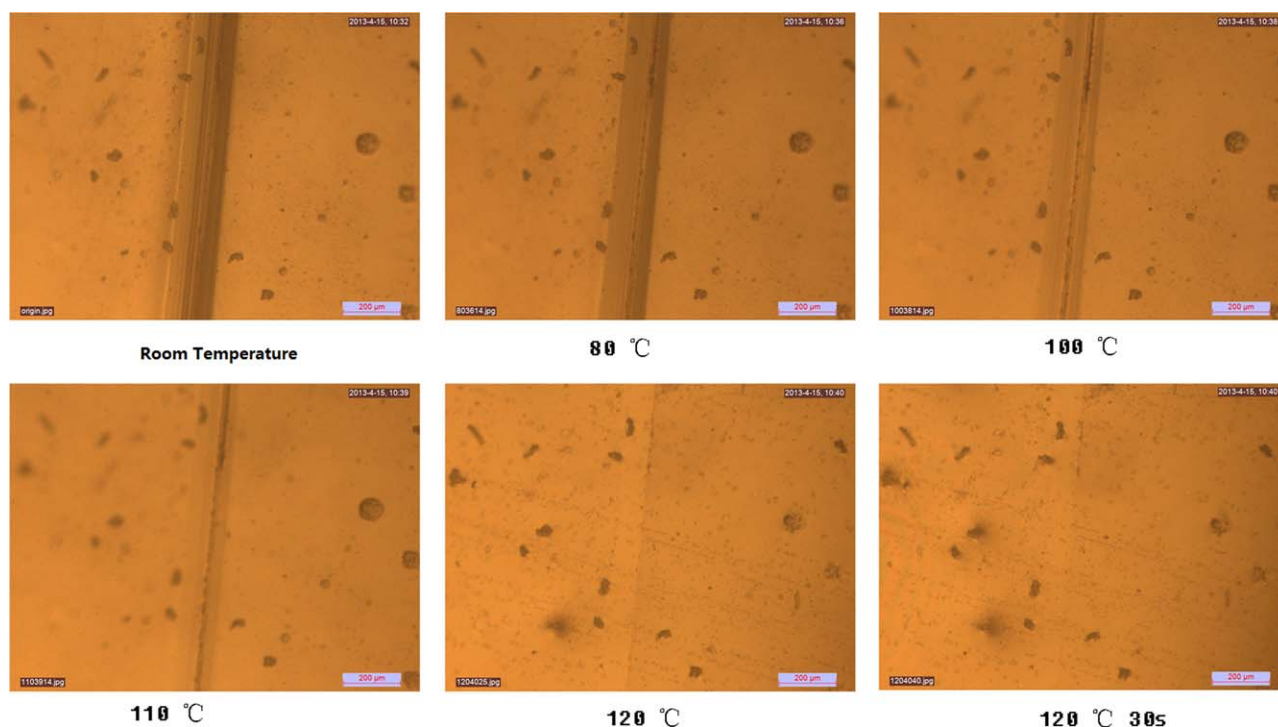


Figure 6. Polarizing optical microscope photographs of a crack in MDI-PBA-TMP-DA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

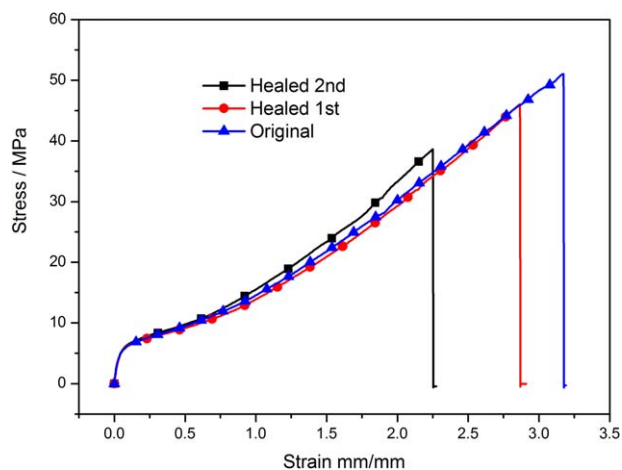


Figure 7. Stress–strain curves of MDI-PBA-TMP-DA and its healed samples. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

After purification in excess ether, MDI-PBA-TMP-DA was characterized by ATR-FTIR, as shown in Figure 3. The peaks at 3348 cm^{-1} (N–H) confirmed the generation of the urethane groups from MDI and PBA. The peaks at 3529 cm^{-1} (N–H) confirmed the generation of urea groups from NCO groups and furfuryl amine. The peaks at 1600 cm^{-1} demonstrated the presence of the phenyl ring attributed to the MDI. Meanwhile, the peaks at 1706 cm^{-1} , 2959 cm^{-1} , and 1065 cm^{-1} indicated the presence of the soft polyester segment PBA. More importantly, the presence of the characteristic shoulder peak at 1729 cm^{-1} attributed to the DA adducts demonstrated that the DA reaction occurred successfully. The ATR-FTIR results qualitatively confirmed the introduction of the DA adducts into the polyurethane.

Second, the structure of MDI-PBA-FA-TMP was characterized via $^1\text{H-NMR}$, as shown in Figure 4. MDI-PBA-FA-TMP exhibited the characteristic peaks of TMP at $\delta = 3.88\text{ ppm}$, 1.26 ppm , and 0.79 ppm , confirming that TMP was incorporated into the polyurethane prepolymer. MDI-PBA-FA-TMP also exhibited the characteristic peaks of the furan ring at $\delta = 7.55\text{ ppm}$ [–O–CH=CH in furan ring; hydrogen at (a)], 6.39 ppm [–O–CH=CH in furan ring; hydrogen at (b)] and 6.25 ppm [–O–CH=CH in furan ring; hydrogen at (c)], as well as at $\delta = 4.28\text{ ppm}$ [furan–CH₂; (e)], demonstrating the incorporation of the furan ring into MDI-PBA-FA-TMP. The

incorporation of the furan ring can also be demonstrated by the presence of peaks at $\delta = 8.43$ and 6.47 ppm [(d), (f)], attributed to the urea groups from the reaction between isocyanate in the polyurethane prepolymer and furfuryl amine. Meanwhile, the characteristic peaks at $\delta = 4.00\text{ ppm}$ (–COOCH₂; hydrogens at (k), (o)), 2.30 ppm [–CH₂–COO–; (g), (j)], and 1.55 ppm (–CH₂; (h), (i), (m), (n)) confirmed the presence of the soft segment PBA. The peaks at $\delta = 9.50\text{ ppm}$ were attributed to the urethane generated from the reaction between PBA and MDI. All of these peaks demonstrated the presence of TMP and the furan ring in the polyurethane prepolymer MDI-PBA-FA-TMP.

After crosslinking with BMI, the final product MDI-PBA-FA-TMP exhibited the characteristic peaks at $\delta = 5.19\text{ ppm}$ [hydrogen at (a')], 6.60 ppm [(b'), (c')], 3.05 ppm (1'), and 3.22 ppm (2'), as shown in Figure 4. The presence of these characteristic peaks of DA adducts^{28,29} confirmed the generation of the DA adducts in the final product. Meanwhile, the decrease of the intensity of the peaks at $\delta = 7.55\text{ ppm}$ [–O–CH=CH in furan ring; hydrogen at (a)], 6.39 ppm [–CH=CH in furan ring; (b)], 6.25 ppm [–O–CH=CH in furan ring; (c)], and 4.28 ppm [furan–CH₂; (e)] also confirmed the consumption of the furan ring in MDI-PBA-FA-TMP. All of these results demonstrated that the DA reaction had occurred successfully and the polyurethane with DA adducts had formed successfully.

Furthermore, the thermal properties of MDI-PBA-FA-TMP and MDI-PBA-TMP-DA were investigated via DSC, as shown in Figure 5. The final product MDI-PBA-TMP-DA exhibited a significant endothermic peak at 120°C , while the two intermediates MDI-PBA-FA-TMP and MDI-FA-TMP did not exhibit any endothermic peak. The endothermic peak at 120°C can be explained by the retro-DA reaction during the heating process, demonstrating the presence of the DA adducts in MDI-PBA-TMP-DA. Meanwhile, the intermediate MDI-PBA-FA-TMP exhibited a significant endothermic peak at -30°C . This can be explained by the glass transition of the soft segment PBA, confirmed by the fact that MDI-FA-TMP did not exhibit any endothermic peak during the whole heating process. However, the final product exhibited a more flat glass transition at 0°C , which can be explained by the fact that the slight crosslinking via the DA reaction restricted the free movement and decreased the chain segment activity of the soft segment in polyurethane. The results of the DSC demonstrated that the DA reaction between MDI-PBA-FA-TMP and BMI occurred successfully.

Table I. Mechanical Properties of MDI-PBA-TMP-DA and Its Healed Samples

	Yield strength (MPa)	Breaking (tensile) strength (MPa)	Elongation at break (%)	Healing efficiency (%)
C-PU-DA ²⁸	6.8	40.3	239	—
C-PMPU-DA ³⁰	7.8	46.5	255	—
PU-DA ²⁹	8.0	25.6	440	—
MDI-PBA-TMP-DA	6.5	51.0	320	—
Healed 1st	6.5	46.1	288	90.4
Healed 2nd	6.5	38.6	225	75.7

The self-healing property of MDI-PBA-TMP-DA was first investigated by observing the evolution of a crack under a polarizing optical microscope equipped with a heating stage via the same method as was described in our previous work.^{28,29} Photographs were taken at different time intervals during the healing process (as shown in Figure 6).

The crack did not change much below 80 °C and began to disappear at 100 °C, 20 or 30 °C lower than the linear polyurethane²⁹ and the crosslinked polyurethane²⁸ in our previous research. When the temperature reached 120 °C, the crack disappeared completely in 30 s. The healing of the polyurethane film was attributed to the debonding of the DA adducts in MDI-PBA-TMP-DA after the temperature reached 80 °C, and the debonding of DA adducts was accelerated with the increase of the temperature. The generated MDI-PBA-FA-TMP and BMI exhibited good chain segment activity under the healing temperature. This is why MDI-PBA-TMP-DA needed much less time than the polyurethanes in our previous research^{28,29} to complete the healing procedure. All of these results indicated that MDI-PBA-TMP-DA exhibited excellent self-healing properties.

The mechanical properties and the healing properties of MDI-PBA-TMP-DA were also investigated. The stress–strain curves of the original sample as well as the healed samples are shown in Figure 7. The healing efficiency was calculated by the recovery of the breaking (tensile) strength after healing.

According to the mechanical properties of the four polyurethanes with DA adducts listed in Table I, the breaking (tensile) strength of MDI-PBA-TMP-DA reached up to 51.0 MPa, which was much higher than our previous linear polyurethane with DA adducts (about two times). Even comparing with the two crosslinked polyurethanes with DA adducts, MDI-PBA-TMP-DA also exhibited higher breaking (tensile) strength. Meanwhile, the elongation at break was also higher than the two crosslinked polyurethanes, indicating good elasticity and toughness of the slightly crosslinked polyurethane MDI-PBA-TMP-DA. According to the breaking (tensile) strength of the damaged and healed samples, the healing efficiency [breaking (tensile) strength] of “Healed 1st” reached 90.2%, while “Healed 2nd” also exhibited a significant healing efficiency of 75.6%. All of these results indicated that MDI-PBA-TMP-DA exhibited good mechanical and self-healing properties.

CONCLUSIONS

Slightly crosslinked polyurethane with DA adducts was synthesized via incorporating trimethylolpropane into linear polyurethane with DA adducts. The synthesizing method was first investigated using pure MDI as a model compound and was confirmed by the results of ¹H-NMR. Finally, MDI-PBA-FA-TMP and MDI-PBA-TMP-DA were prepared with the same method and were characterized by FTIR, ¹H-NMR, and DSC. The results from FTIR, ¹H-NMR, and DSC demonstrated that the furan groups and DA adducts were incorporated into the intermediate and the final product, respectively. The results from polarizing optical microscopy demonstrated that MDI-PBA-TMP-DA with

slight crosslinking needed a lower healing temperature and much less time than the crosslinked polyurethane with DA adducts to complete the healing process.

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