Effect of Diisocyanate on Pyridine Containing Shape Memory Polyurethanes Based on N,N-Bis(2-hydroxylethyl)isonicotinamide

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ABSTRACT: This article demonstrates a comparative investigation about the effect of diisocyanate on pyridine containing shape memory polyurethanes (Py-SMPUs), which are synthesized with N,N-bis(2-hydroxylethyl)isonicotinamide (BINA) and four different diisocyanates: 1,6-hexanediisocyante (HDI), isophorone diisocyanate (IPDI), methylene diphenyl diisocyanate (MDI), and tolylene diisocyanate (TDI). Results show that all BINA–SMPU systems have amorphous reversible phase. Comparatively, the MDI–BINA and TDI–BINA systems show higher T_g, and the HDI–BINA and IPDI–BINA systems show better thermal stability. In addition, the HDI–BINA and the IPDI–BINA systems exhibit good thermal-induced shape memory effect and good moisture-sensitive shape memory effect due to their better moisture absorption properties. Particularly, the HDI–BINA system has better response speed and better shape recovery. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40721.

INTRODUCTION

Shape memory polymer is one kind of attractive smart materials that can "remember" their origin shapes.[1,2] Particularly, shape memory polyurethane (SMPU) draws much attention of researchers due to its excellent biocompatibility and great potential biomedical applications.[1,3] The reported SMPUs are generally segmented block copolymers, comprising of soft- and hard-segment blocks. The soft segment is composed of long-chain, mainly polyester or polyether diols, whereas the hard segment is generally formed in a polyaddition reaction of diisocyanate with short-chain alcohols or amines that act as chain extender or crosslinker.[4] As an important composition of hard segment, diisocyanate influences greatly the structure and properties of polyurethane. The effect of diisocyanate has been widely studied in past decades.[5,6] For example, Gradinaru et al.[7] had studied the effect of isocyanate on physical properties of thermal reversible poly(isopropyl lactate diol)-based polyurethane hydrogels. Peruzzo et al.[8] studied the influence of diisocyanate structure on the morphology and properties of waterborne polyurethane-acrylates. Angeles Corcuera et al.[9] studied the effect of diisocyanate structure on thermal properties and microstructure of polyurethane based on polyols derived from renewable resources. Recently, Ahmad et al. had studied systematically the effects of

diisocyanate concentration on material properties of SMPUs, such as crystallinity, transition temperature, shape memory effect, and tensile strength. They found that a high methylene diphenyl diisocyanate (MDI) content results in better shape-memory effect, whereas increasing isophorone diisocyanate (IPDI) content leads to a weaker shape-memory effect.[10] These studies suggest that the diisocyanates play a very important role on the structure and properties of SMPUs.

In addition, it is reported that pyridine-containing polyurethanes synthesized from N,N-bis(2-hydroxylethyl)isonicotinamide (BINA) and 1,6-hexanediisocyantes (HDI) are widely used to build supramolecular liquid crystalline polyurethane complex.[11,12] BINA is a very useful chain extender for preparing functional polyurethanes like antibacterial polyurethanes.[13] Pyridine-containing polyurethane shows great promise applications in many fields, and it provides a new strategy to synthesize smart polymers or other functional polymers. Most recently, we had reported one kind of novel supramolecular SMPUs containing pyridine moieties derived from the BINA.[14] Being different from the common segmented SMPUs, the main composition BINA is a monomer containing hydroxyl groups and the resulted BINA-based SMPUs (BINA–SMPUs) are synthesized directly from the BINA and diisocyanates. Thus, the

Table I. Composition, Molecular Weight, Thermal Properties, and Thermal Stability of BINA–SMPUs with Various Diisocyanates

Samples code	Components		Molecular weight		Glass transition		Thermal stability	
	BINA (g)	Diisocyanates (g)	M_n (×10,000)	PDI	T_g (°C)	ΔC_p (J/g°C)	T_i (°C)	T_e (°C)
HDI-BINA	5.0	4.20	9.52	1.75	56.50	0.35	218	385
IPDI-BINA	5.0	5.54	7.65	1.73	73.49	0.29	202	422
TDI-BINA	5.0	4.35	5.80	1.77	74.59	0.26	180	438
MDI-BINA	5.0	6.24	5.56	1.78	74.53	0.50	133	478

M_n is the number-average molecular weight; PDI = M_w/M_n; T_g is glass transition temperature; ΔC_p is step change of specific heat; T_i is the onset decomposition temperature; T_e is the end decomposition temperature.

BINA–SMPUs are nonsegmented copolymers having no soft block. However, the hydrogen bonding formed between pyridine ring with NH of urethane groups greatly influences the glass transition and shape recovery process, serving as supramolecular molecular switch, whereas the hydrogen bondings between C=O and NH of urethane groups serve as physical netpoints.[15] Thus, the BINA–SMPUs exhibit not only thermal-induced shape memory effects[14] but also moisture-sensitive shape memory effects.[16] In the previous studies,[17,18] we had studied the effect of MDI–BDO hard segment, BINA content on the structure and properties of the BINA–SMPUs, including shape memory properties and moisture absorption. However, the previous BINA–SMPUs are mainly synthesized from HDI diisocyanate, there is only a preliminary result about the moisture-sensitive shape memory behaviors of IPDI–BINA-based polyurethane.[19] Up to date, there is no report about the effect of diisocyanate structure on the pyridine-containing SMPUs based on BINA.

Therefore, in this study, four kinds of pyridine-containing SMPUs are synthesized from BINA with four different diisocyanates: HDI, IPDI, MDI, and tolylene diisocyanate (TDI). The samples are coded as BINA–HDI, BINA–IPDI, BINA–MDI, and BINA–TDI, respectively. The influences of diisocyanate on the BINA–SMPUs are investigated systematically from the thermal

properties, thermal stability, dynamical mechanical properties, moisture absorption properties, and shape memory properties.

EXPERIMENTAL

Preparation
BINA was bought from Jiaxing Carry Bio-Chem Technology Co. HDI, MDI, IPDI, TDI, and Dimethylformamide (DMF, HPLC) were bought from Aladdin-reagent (Shanghai) Co. The BINA–SMPUs were prepared with BINA and HDI, or MDI, or IPDI, or TDI in DMF solution at 1 : 1.05 molar ratio of group OH/NCO according to the synthesis procedure described in our previous literature.[14] The composition of BINA–SMPUs is presented in Table I. The molecular structures of BINA–SMPU systems like HDI–BINA, IPDI–BINA, TDI–BINA, and MDI–BINA are presented in Scheme 1.

Characterization
FTIR Analysis. FTIR spectra were recorded with a Nicolet 760 FTIR spectrometer. Ten scans at 4 cm^{-1} resolution were signal averaged and stored as data files for further analysis, and smooth polymer film with a thickness of 0.2 mm were scanned by the FTIR attenuated total reflection method.

^{1}H-NMR Analysis. The ^{1}H-NMR spectra were recorded at 25°C on the varian VXR500 spectrometer at 500 MHz using TMS as an internal standard. DMF-d$_7$ was used as a solvent.

Differential Scanning Calorimetry. Differential Scanning Calorimetry (DSC) curves of samples were determined by a TA Q200 instrument using nitrogen as the purged gas. Indium and zinc standards were used for calibration. Samples were first heated up from −60 to 200°C at a heating rate of 10°C/min and kept at 200°C for 1 min, subsequently, cooled to −60°C at a cooling rate of 10°C/min, and finally, the second heating scan from −60 to 250°C was performed again.

Dynamical Mechanical Properties. Dynamical mechanical analysis (DMA) curves were determined by a TA Instrument DMA Q800 at 1.0 Hz with a scanning rate of 3°C/min in tension mode.

Thermogravimetric Analysis. The TG curves were recorded on a computer-controlled TA Instrument TG Q50 system at a heating rate of 10°C/min, under nitrogen atmosphere.

Moisture Absorption. The moisture absorption was determined by weighing the specimens on a balance according to the procedure described in the literature.[19] Before testing, the specimens
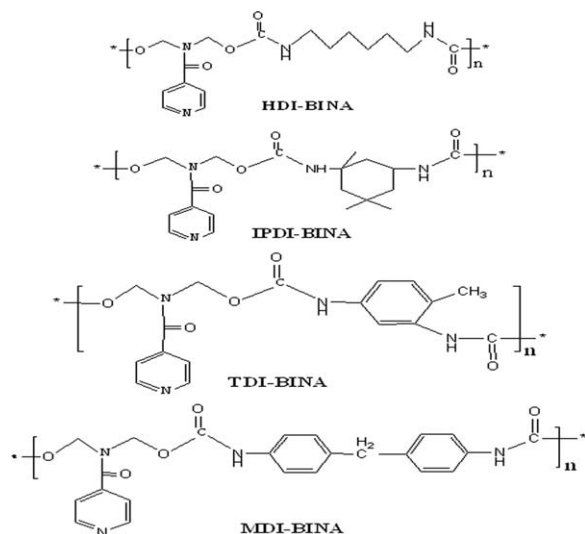
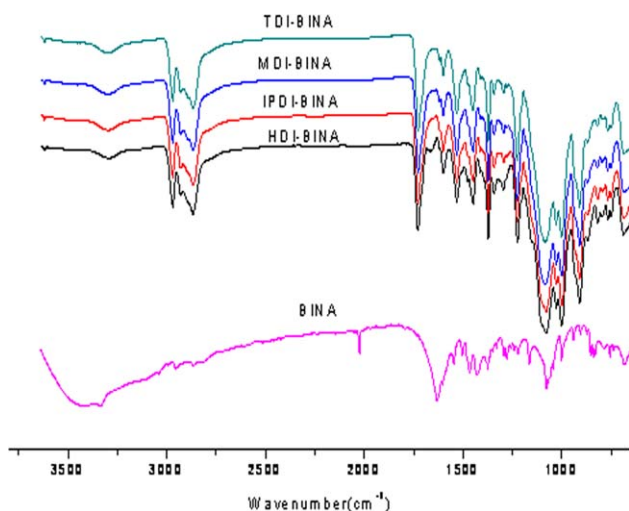**Scheme 1.** Structure of BINA–SMPU systems.

Figure 1. FTIR spectra of BINA–SMPUs with various diisocyanates and pure BINA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

with a thickness of 1.0 mm were dried completely. The specimen was then put on the moisture condition with a certain RH and a certain temperature. The moisture absorption in percentage at a certain time (M_t) is calculated by the following equation:

$$M_t = \left[\frac{W_t - W_d}{W_d}\right] \times 100\%$$

where W_d and W_t refer to the weight of the dry specimen and the wet specimen, respectively.

Characterization of Shape Memory Behavior. Thermal-induced shape memory behavior was done using a mechanical tensile testing apparatus (SANS, China) with a temperature-controlled chamber and a personal computer. First, the sample film with 5-mm width, 20-mm length, and 0.5-mm thickness was heated to T_{high}, 60°C within 600 s. Then, the sample was stretched to ε_m, 100% elongation at T_{high} with 10 mm/min stretching rate. Second, cool air was introduced to the chamber for cooling sample film with constant strain, ε_m, 100% elongation, to T_{low}, 20°C, within 900 s. Thereafter, the strain was released from ε_m to 0 and the recurrent heating to 80°C for 600 s began. That is, one cycle among all cyclic tensile tests and the cycle will be repeated for assessing the shape memory effect. Thus, the shape fixity and shape recovery can be calculated according to the method described in the previous literature.[17]

Moisture-sensitive shape memory behavior was investigated according to the procedure described in the literature.[20] Before testing, the sample was dried completely at 80°C vacuum oven and a rectangle uncoiling specimen was cut from this dried sample. A temporary shape of coiled film was first prepared by deformation at 80°C and subsequent fixation at room temperature. The temporary shape was then put on the moisture-temperature controlled oven, and the shapes at any immersing time were recorded for analysis.

RESULTS AND DISCUSSIONS

Analysis of Molecular Structure

The molecular structures of BINA–SMPUs are first investigated with FTIR and NMR. Figures 1 and 2 show the FTIR and ^{1}H-NMR spectra of BINA–SMPUs with various diisocyanates and pure BINA. FTIR spectra demonstrate that all designed BINA–SMPUs are synthesized successfully. Because there are frequencies at about 3283–3291 and 1727–1728 cm^{-1}, which are assigned to the stretching vibration of N—H and stretching vibration of C=O presented in urethane groups, respectively. There are also some frequencies of pyridine ring at about 1598–1600, 1475, 1077, 1028, and 1000 cm^{-1}.[15] There is nearly no difference observed in the FTIR spectra of BINA–SMPUs with varying diisocyanates, whereas ^{1}H-NMR spectra provides more detail information of hydrogen proton structures to the synthesized BINA–SMPUs. As shown in Figure 2, there are typical hydrogen proton structures of HDI unit at 1.21 and 1.34 ppm for HDI–BINA copolymers; there are multipeaks from 7.28 to 7.38 ppm exhibiting the hydrogen proton structures of TDI unit for TDI–BINA copolymers; there are weak multiple peaks from 0.8 to 1.0 ppm showing the hydrogen proton structure of IPDI units for IPDI–BINA copolymers; and MDI–BINA copolymer also shows the typical hydrogen proton structures of MDI unit from 7.22 to 7.44 ppm. It is thus confirm that the synthesized polyurethanes contain the designed repeated units, for example, -HDI–BINA-, -MDI–BINA-, -IPDI–BINA- and -TDI–BINA-. That is, the synthesized BINA–SMPUs are pyridine-containing polyurethanes based on only different diisocyanate units. Similar to the HDI–BINA system reported in the previous literature,[14] MDI–BINA, IPDI–BINA, and TDI–BINA systems are also expected to form supramolecular networks. Because the N of pyridine ring is a well-known H-acceptor and H of N—H is the best H-donor for hydrogen bonding in these polyurethanes. It was verified that the hydrogen bondings between pyridine rings with N—H were formed below 60°C[15]; whereas the hydrogen bondings between N—H and C=O of urethane groups did not dissociated until 120°C.[11] Thus, in the supramolecular networks
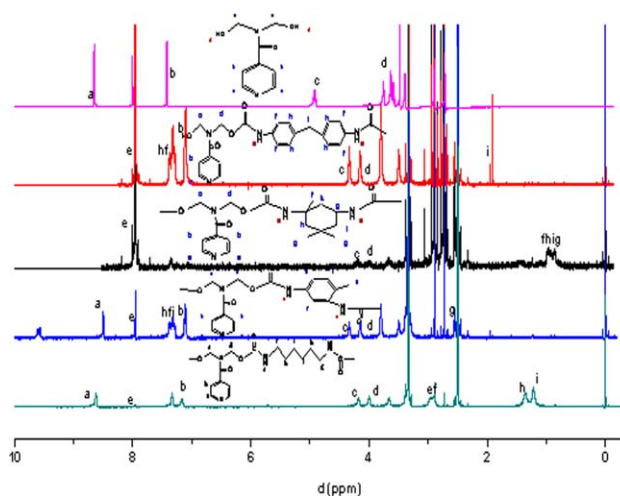

Figure 2. ^{1}H-NMR spectra of BINA–SMPUs with various diisocyanates and pure BINA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
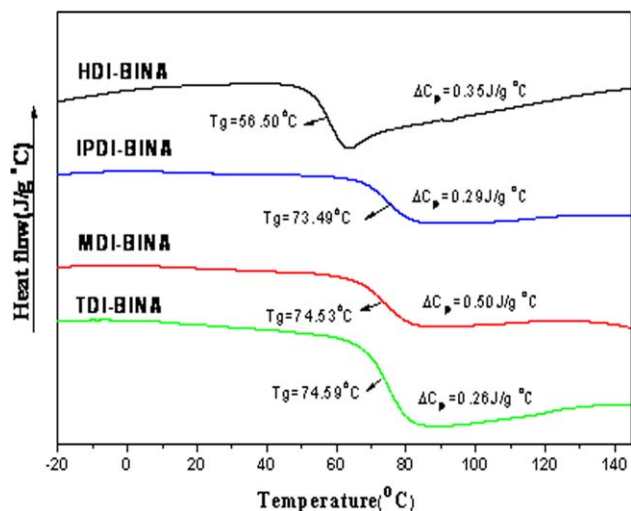
Figure 3. The second heating DSC curves of BINA–SMPUs with various diisocyanates. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of BINA–SMPUs, the strong hydrogen bondings between N of pyridine ring and N—H of urethane groups can serve as molecular switch, whereas the strong hydrogen bondings between N—H and C=O of urethane groups form physical netpoints.

Thermal Properties

Figure 3 presents the second DSC heating curves of BINA–SMPUs with various diisocyanates. Thermal properties of BINA–SMPUs are mainly investigated from the thermal transition. The thermal properties of BINA–SMPUs are summarized in Table I. DSC curves show that all BINA–SMPUs have obvious glass transition temperature (T_g) at about 56.50°C for HDI–BINA, 73.49°C for IPDI–BINA, 74.53°C for MDI–BINA, and 74.59°C for TDI–BINA. It implies that amorphous phase serving as reversible phase of SMPUs is formed in all BINA–SMPUs.[21] Comparatively, the MDI–BINA and TDI–BINA systems show higher T_g because their polymer chains are composed of rigid benzene ring structure, whereas the HDI–BINA system has lower T_g as the polymer chain is aliphatic chain. In addition, as compared with common segmented SMPUs, the step change of specific heat (ΔC_p) during the glass transition is much higher in all BINA–SMPU systems, for example, 0.35 J/g°C for HDI–BINA, 0.29 J/g°C for IPDI–BINA, 0.50 J/g°C for MDI–BINA, and 0.26 J/g°C for TDI–BINA. It is well-known that the magnitude of the step change in the ΔC_p origins from the segmental motion. Comparatively, the MDI–BINA system shows the biggest ΔC_p. One possible reason is that the MDI–BINA system has more rigid structure influencing the motion of polymer chain during the glass transition process. Another possible reason is that there are more stronger molecular interactions including hydrogen bonding presented in both urethane groups and pyridine ring as more repeat units are formed as discussed above.[17] Similarly, HDI–BINA shows higher ΔC_p value than that of IPDI–BINA and TDI–BINA, because the molecular interactions are also stronger in the HDI–BINA system due to its more regular structure comparing to IPDI–BINA and TDI–BINA systems.

Thermal Stability

Figure 4 shows the Thermogravimetric Analysis (TGA) curves of BINA–SMPUs with various diisocyanates. The effect of diisocyanate on the thermal stability of BINA–SMPUs is reflected on the TGA curves. Decomposition temperatures are summarized in Table I. It is observed that the onset decomposition temperature (T_i) is lower in the MDI–BINA, for example, 133°C, whereas it is much higher in the HDI–BINA, for example, 218°C. The T_i of IPDI–BINA is also higher than that of TDI–BINA. However, TDI–BINA and MDI–BINA systems show higher end decomposition temperature (T_e). Moreover, the T_e of BINA–SMPUs is generally much higher than that of common segmented polyurethanes. In an earlier communication,[22] it was reported that the lower temperature degradation of polyurethane was ascribed to the degradation of urethane, whereas the higher temperature degradation of BINA–SMPUs was resulted from the decomposed monomers like BINA, MDI (or IPDI, or TDI, or HDI) units. This observation is very consistent with the previous report that alkyl isocyanate produces more thermo-stability as compared to the aromatic diisocyanate in the polyurethane.[23] Because the aromatic diisocyanates like TDI and MDI contain benzene ring with conjugated electronic structure, and this conjugated electronic structure reduces the thermal stability of linked urethane group in TDI–BINA and MDI–BINA systems; whereas alkyl isocyanates like HDI and IPDI have no conjugated electronic structure, and the linked urethane groups show more thermo-stability in HDI–BINA and IPDI–BINA systems.

Dynamical Mechanical Properties

DMA curves of BINA–SMPUs with various diisocyanates are presented in Figure 5. DMA curves also provide another proof to the changing tendency of glass transition of BINA–SMPUs. Significant modulus loss is observed during the glass transition. Loss modulus graph demonstrates that the HDI–BINA system shows the lowest T_g while MDI–BINA system has the highest T_g as shown in Figure 5(B). This observation is consistent with the
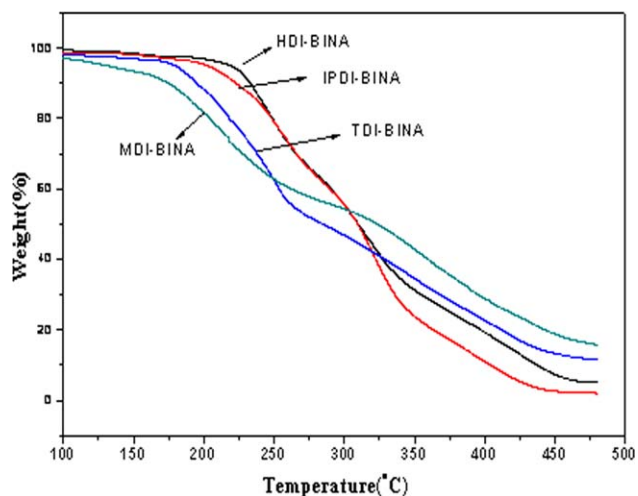

Figure 4. TGA curves of BINA–SMPUs with various diisocyanates. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
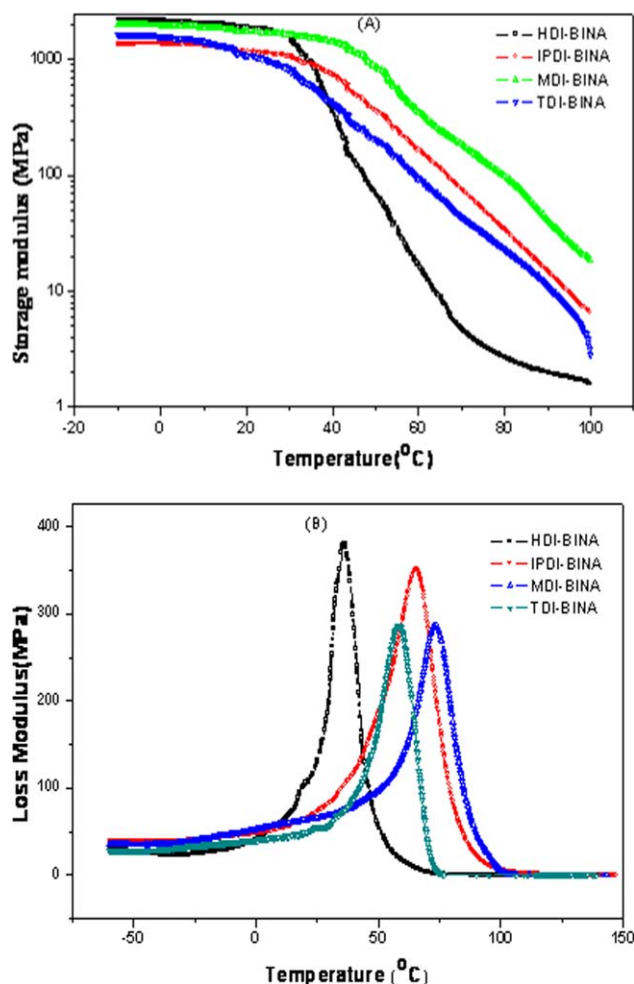
Figure 5. DMA plots (A: storage modulus graph and B: Loss modulus graph) of BINA–SMPUs with various diisocyanates. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

DSC results. Similar to the HDI–BINA system, the storage modulus at glass state is higher than 1.5 GPa in IPDI–BINA, MDI–BINA, and TDI–BINA systems. During the glass transition process, the storage modulus is decreased significantly as the temperature increases. Finally, the modulus at 80°C is only about 2.64 and 15.0 MPa in the HDI–BINA and TDI–BINA systems, respectively. IPDI–BINA and MDI–BINA systems also get very soft above 100°C. Thus, the rubber plateaus cannot be detected because the physical netpoints are mainly formed by the hydrogen bonding among urethane groups, without forming hard phase. However, DMA curves demonstrate that big modulus ratios between glassy modulus (E_g) and rubber modulus (E_r) in the HDI–BINA and the TDI–BINA systems are higher than 100. All BINA–SMPUs can be deformed above T_g or at rubber state and the deformed strain can be fixed at room temperature.[17] Therefore, the BINA–SMPU is expected to be used as shape memory materials.

Moisture Absorption

Moisture absorption properties of BINA–SMPUs were first measured with the weight method. In this method, the specimens were put on the standard temperature humidity chamber with a moisture condition of RH = 90% and T = 30°C. The weight of specimen conditioning for different time was collected with high-precision weighing scales for analysis.[19] Figure 6 presents the moisture absorption curves of BINA–SMPUs with different diisocyanates. It is observed in Figure 6 that the moisture absorption increases quickly within the first 300 min in the HDI–BINA, IPDI–BINA, and TDI–BINA systems. The absorption speed gets slow between 300 and 350 min, and the moisture absorption keeps stable after 400 min. Comparatively, the HDI–BINA system shows the biggest moisture absorption, up to 9.0 wt %, during the moisture conditioning process; and the IPDI–BINA system also has about 7.0 wt % moisture absorption. However, the MDI–BINA system absorbs the moisture slowly, and only about 3.0 wt % moisture absorption is measured after conditioning for more than 450 min. It indicates that the HDI–BINA and IPDI–BINA systems show good moisture absorption properties. The inherent mechanism of moisture absorption in the BINA–SMPUs with different diisocyanates should be further investigated in future studies. However, these differences in the moisture absorption can be explained briefly according to the molecular structure and intermolecular force. As shown in Scheme 1, TDI–BINA and MDI–BINA systems were synthesized from aromatic diisocyanates, TDI and MDI, respectively. They form alternative rigid structures in the polyurethane chain. As discussed above, the TDI or MDI forms rigid chains with less free volume, preventing the moisture, or water to enter into polymer chains.[24] However, the IPDI–BINA and HDI–BINA systems are mainly composed of aliphatic repeat units, forming lots of free volume among the molecular chains, which promotes the moisture transferring or moisture absorption.[25] Thus, the IPDI–BINA and HDI–BINA systems show higher moisture absorption under the same condition. Similarly, MDI contains two rigid benzene rings, whereas TDI has only one benzene ring, the MDI–BINA thus shows lower absorption compared to TDI–BINA.
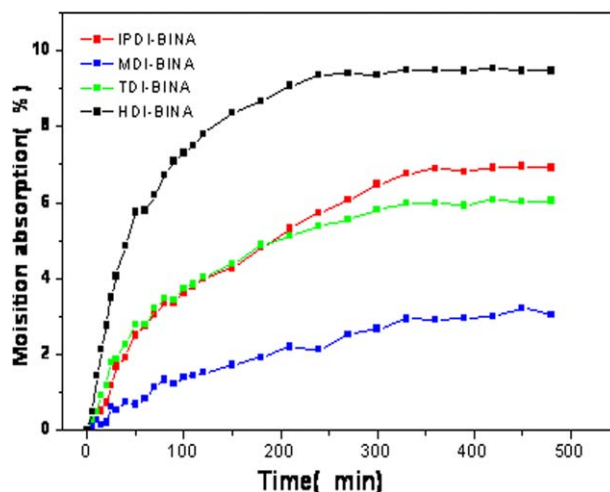

Figure 6. Moisture absorption of BINA–SMPUs with various diisocyanates. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
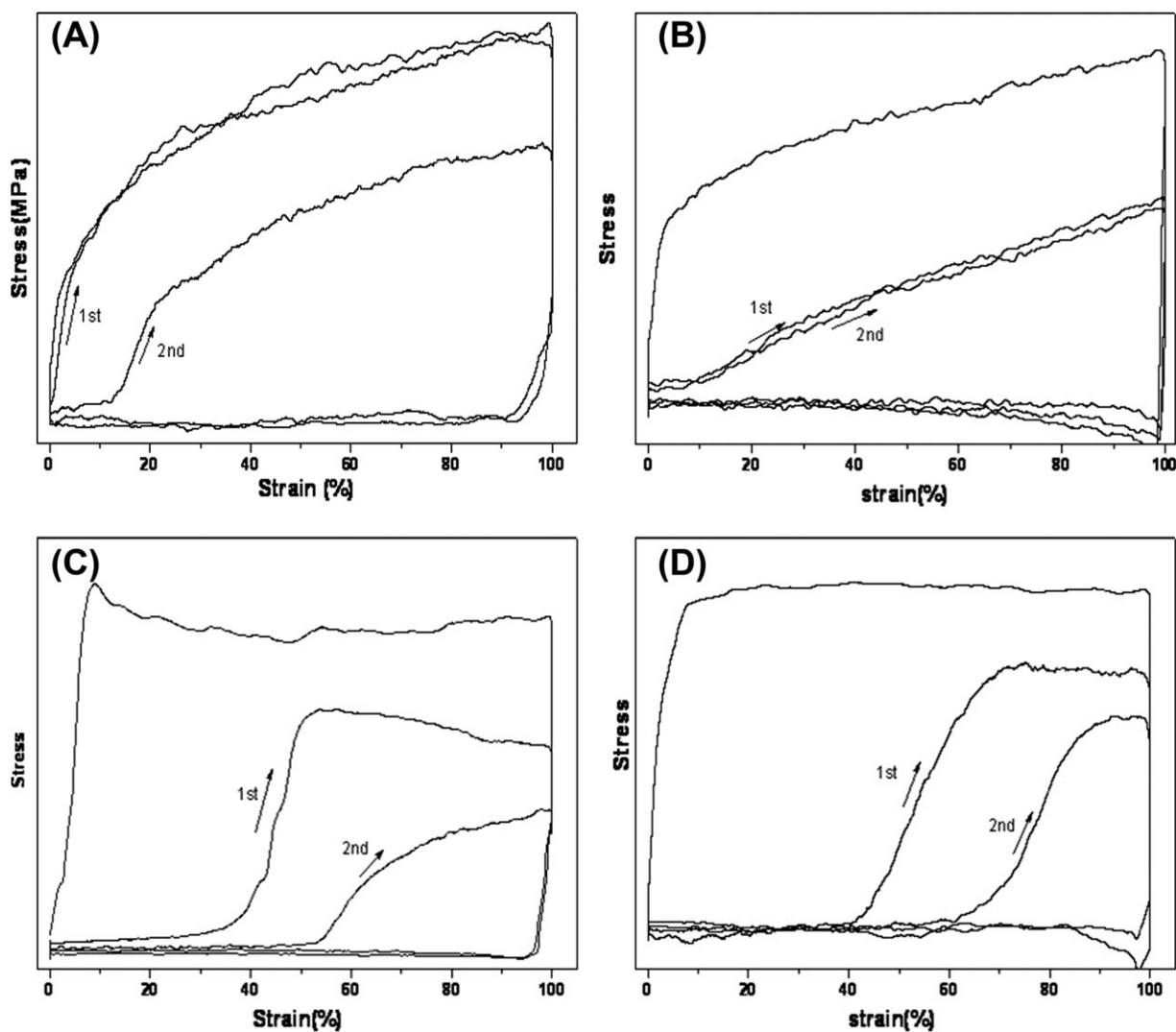
Figure 7. Strain–stress curves of BINA–SMPUs.

Shape Memory Effect

In the previous literatures,[16,26] it was reported that the HDI–BINA system shows not only thermal-induced shape memory effects, but also moisture-sensitive shape memory effects. From the discussion above, it is known that the T_g in all BINA–SMPUs systems is higher than room temperature, and their storage modulus decreases significantly above T_g. Thus, thermal-induced shape memory properties are investigated comparatively with cyclic tensile test in this study. Strain–stress curves of BINA–SMPUs with various diisocyanates are presented in Figure 7. It is found that shape fixity of the HDI–BINA is about 92%, and IPDI–BINA, MDI–BINA, and TDI–BINA systems show higher than 99% shape fixities. With respect to the shape recovery, the IPDI–BINA system shows much stable shape recovery, higher than 92%. However, the shape recovery of the HDI–BINA system decreases from 99% on the first cycle to only 88% on the second cycle. The MDI–BINA and TDI–BINA systems show bad shape recovery on both the first cycle and the

second cycle. One possible reason is that their physical net-points formed by molecular interactions are weak in the MDI–BINA and TDI–BINA systems, whereas IPDI–BINA and HDI–BINA show higher hydrogen bonded molecular interaction as mentioned above. It is thus confirmed that the IPDI–BINA system shows better thermal-induced shape memory effect. Both HDI–BINA and IPDI–BINA systems can be used for thermal-induced shape memory materials.

With respect to the moisture-sensitive shape memory effect, it is known from the moisture absorption properties that the HDI–BINA and IPDI–BINA systems show higher moisture absorption, whereas the MDI–BINA system absorbs moisture slowly. It implies that the HDI–BINA and IPDI–BINA systems can also be used as moisture-sensitive shape memory materials. The moisture-sensitive shape memory behavior of HDI–BINA system was investigated systematically in previous literatures.[19,20] In this work, the moisture-sensitive shape memory behavior of IPDI–BINA system is further explored for a
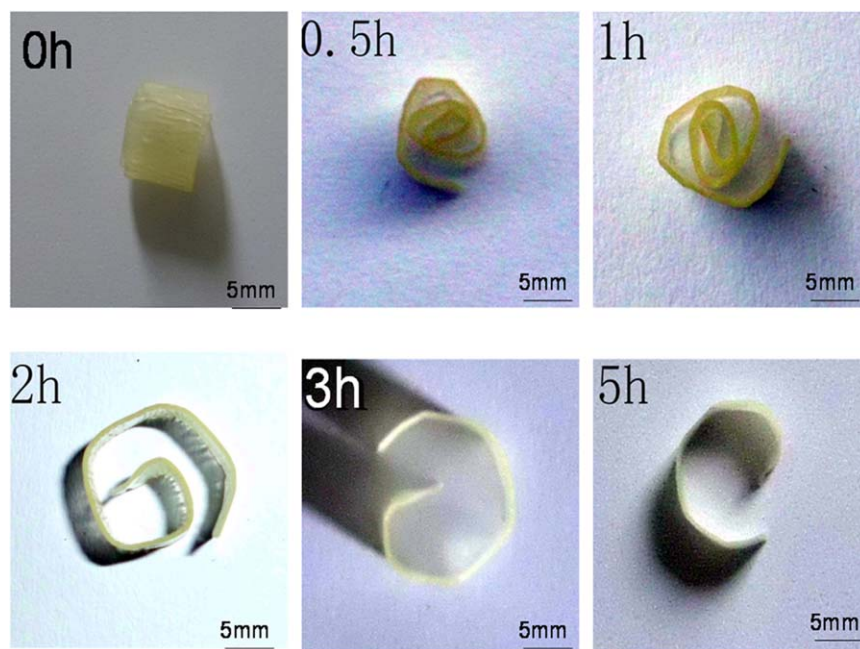
Figure 8. Moisture-sensitive shape recovery process of IPDI–BINA at RH = 90% and $T = 30°C$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

comparative study. Figure 8 presents a moisture-sensitive shape recovery process of IPDI–BINA film conditioning at RH = 90% and $T = 30°C$. Before testing, the sample was dried completely at 80°C vacuum oven and a rectangle uncoiling film was cut from this dried sample. As shown in Figure 8, the test film is coiled tightly before putting on moisture condition. After conditioning for 0.5 and 1 h, the coiled film is relaxed. After 2 h, the coiled film is opened, and it finishes the shape recovery process after conditioning for 5 h. That is, the IPDI–BINA film recovers gradually under the moisture condition. This shape recovery process is very similar to the moisture-sensitive open process of flower made of HDI–BINA film as reported in the previous literature.[20] It is thus confirmed that the IPDI–BINA system also shows moisture-sensitive shape memory properties. However, as compared with the shape recovery process of HDI–BINA elongated film under the moisture condition of RH = 85% and $T = 30°C$,[19] the shape recovery speed of IPDI–BINA coiled film is slow, and it takes more than 5 h to recover its original shapes, whereas the HDI–BINA elongated film recovers its original length within 170 min. The RH of moisture condition in the HDI–BINA system is also lower than that in the IPDI–BINA system. This result suggests that the HDI–BINA system has better response speed and better shape recovery properties. One possible reason is that the more regular structure of HDI–BINA system has formed more stable physical netpoints among the urethane groups. Another reason is that the HDI–BINA system shows a lower T_g and higher moisture absorption comparing with the IPDI–BINA system as discussed above. It is well-known that moisture absorption can reduce the T_g.[27] The moisture-sensitive shape recovery occurs when the T_g of polymer is lower than the ambient temperature.[12] Thus, HDI–BINA system shows a fast recovery.

CONCLUSIONS

In this article, four kinds of BINA–SMPUs are successfully synthesized with BINA and four different diisocyanates: HDI, IPDI, MDI, and TDI. A comparative study is preformed to investigate the effect of diisocyanate structure on thermal properties, thermal stability, dynamic mechanical properties, moisture absorption, and shape memory properties of BINA–SMPUs. Results show that all BINA–SMPU systems have amorphous phase serving as reversible phase; and all BINA–SMPUs can be deformed above T_g and the deformed strain can be fixed at room temperature. Comparatively, the MDI–BINA and TDI–BINA systems show higher T_g. The HDI–BINA and IPDI–BINA systems show better thermal stability. The HDI–BINA and the IPDI–BINA systems show better moisture absorption properties. It is finally found that the HDI–BINA and the IPDI–BINA systems show good thermal-induced shape memory effect and good moisture-sensitive shape memory effect. Particularly, the HDI–BINA system has better response speed and better shape recovery. It is thus proposed that HDI or IPDI are the good diisocyanates for designing BINA–SMPU with shape memory effect.

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