Studies on Moisture-Sensitive Shape Memory Behavior of IPDI –BINA Based Polyurethane

Hongming Yuan, Shaojun Chen, Shiguo Chen, and Zaochuan Ge

***Abstract*—Shape memory polyurethane is attractive in recent years because of its wide applications in many fields. In order to study the moisture-sensitive shape memory effect of pyridine containing shape memory polyurethane, in this work, moisture absorption and moisture-sensitive shape memory behavior of pyridine containing SMPU synthesized from BINA and IPDI are investigated systematically. The results show that IPDI-BINA SMPU shows moisture absorption and the moisture absorption affects significantly the thermal and DMA properties. Finally, shape recovery process under moisture condition demonstrates that IPDI-BINA SMPU show moisture-sensitive shape memory effect that it can recover the origin shape under the moistures condition.**

***Index Terms*—Shape memory, polyurethane, moisture sensitive, diisocyanates**.

I. Introduction

Shape memory polymers (SMPs) are attractive smart materials that can recover to its origin shape by applying extra stimuli like heat, light, water, moisture etc [1], [2]. Most studies of SMPs focus on the thermal-induces SMPs because of their wide possible applications in microelectromechanical systems, actuators, for self healing and health monitoring purposes, and in bio-medical devices last decades [3]. For the thermal-induced SMPs, the shape memory effect is achieved by heating the temperature above transition temperature (T_{trans}) of SMPs, which can be glass transition temperature (T_g), crystal melting temperature (T_m) and other phase transition temperature [4]. Thus, the deformed shape can only be fixed below T_{trans} and they can only be recovered at a higher temperature with extra heat energy. However, in some fields like texture industry or biomedical field, the application temperature is limited to a narrow range of temperature like 37℃, or room temperature. Therefore, it is necessary to develop some new SMPs which can recover their temporary shapes without heating. Moistures-sensitive SMP becomes a good candidate for smart biomedical materials because it can exhibit shape memory effect at room temperature by moisture or water absorption.

Since water-driven SMPs are firstly reported in 2005, there are many investigations about the moisture-sensitive SMPs in recent year. For example, Yu et al [5]，have studied the effect of moisture absorption on the SMPU foam synthesized from1,6-hexanediisocyantes; It demonstrates that water absorption significantly decreased the T_g of the foam. In our previous work [6], [7], we had reported one kind of supramolecular polyurethane containing pyridine moieties. In addition to the thermal-induced shape memory effect, they are also found to show moisture-sensitive shape memory effect. In this system, the polyurethane is mainly composed of N, N -bis (2-hydroxyethyl) isonicotinamid （BINA ）and isophorone diisocyanate（IPDI）. Though the BINA plays an important role in the moisture-sensitive shape memory effect, the inherent mechanism of moisture-sensitive SME is still unclear. This result attracts researchers to further investigate the moisture-sensitive behavior of IPDI-BINA polyurethane containing pyridine moieties.

In this communication, IPDI-BINA polyurethane is synthesized from the BINA and IPDI. The moisture absorptions of IPDI-BINA polyurethane are investigated with TGA. The influence of moisture absorption on the thermal-properties and dynamical mechanical properties is then investigated systematically with DSC and DMA, respectively. Finally, the moisture-sensitive shape memory behaviors of IPDI-BINA polyurethane are studied under moisture condition.

II. Experimental Part

A. Preparation

N, N -bis (2-hydroxyethyl) isonicotinamid (BINA), Dimethylformamide (DMF), isophorone diisocyanate (IPDI) were bought from aladdin-reagent (Shanghai) Co. Ltd. The IPDI-SMPUs were prepared with BINA and IPDI in DMF solution at 1:1.05 molar ratios of groups OH/NCO according to the synthesis procedure described in our previous literature [6], [7]

B. Characterizations

DSC curves of samples were determined by using a TA Q200 instrument having nitrogen as the purged gas. Indium and zinc standards were used for calibration. The TG curves were recorded on a computer-controlled TA Instrument TG Q50 system, under the following operational conditions: heating rate was 10℃/min, Dynamic mechanical analysis curves were determined by using a TA Instrument DMA Q800 at 1.0 Hz.

III. Results and Discussions

Before TGA test, an IPDI-BINA polyurethane sample, coded as IPDI-BINA-b, was conditioned at moisture condition of *RH*=85% and *T*=30 for more than 10 hours. For

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comparison, another sample, coded as IPDI-BINA-a, were dried completely in the vacuum oven at 80℃ for 24h. Fig. 1 present the TG and DTG curve of samples IPDI-SMPU-a and IPDI-SMPU-b. It is found that within the temperature range of 40-100℃, IPDI-BINA systems have 4.4wt% weight loss. It indicates that the IPDI-BINA show good moisture absorption properties [6], [7]. At the same time, it is found in DTG curve that the sample IPDI-BINA-a display three stages of weight loss, e.g. at 197.00 ℃, 263.70 ℃ and 327.30 ℃,respectively. The first one may be related to decomposition of urethane bonds in which the polyurethane is decomposed to IPDI unit and BINA unit [8]-[10]. Whereas the second one may be the decomposition of BINA unit, the last one corresponds to the decomposition of IPDI unit. However, on the DTG curve of sample IPDI-SMPU-b. It is found that there are four stages of weight loss, the DTG peak temperature is at 100.41 ℃ , 259.76 ℃, 316.06 ℃ and 355.51 ℃, respectively. In this sample conditioned at moisture condition, the first DTG peak is correspond to the evaporation of the water, the other three peaks is similar to the sample IPDI-SMPU-a. Comparatively, it is also found that the maximum decomposition temperatures of sample IPDI-BINA-b is higher than that of sample IPDI-BINA-a., and the gap becomes smaller and smaller. It implies that the water/water moisture affect the thermal stability and structure of IPDI-BINA system.

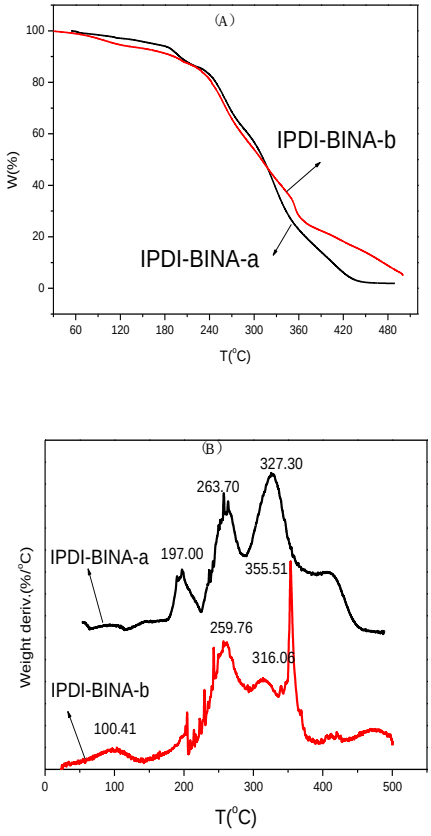

Fig. 1. TG (A) and DTG (B) curve of IPDI-SMPU

DSC curve of sample IPDI-SMPU- b is showed in Fig. 2. On the first heating, it is observed that the T_g of IPDI-BINA-b is very low at 14.52 ℃, and there is an obvious wide endothermic peak between 60 and 120℃, centered at 100℃.

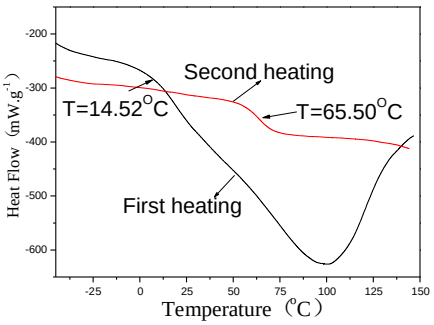

Fig. 2. DSC curves of IPDI-BINA

On the second heating, no endothermic peak can be determined in addition to the glass transition at 65.5℃.As compared with the first heating curves, it is also found that the T_g on the second heating curve shifts to higher temperature range significantly because the sample are dried at high temperature. On the contrary, it is thus confirmed that the moisture absorption greatly influence the motion of polymer chain, showing on the thermal-properties.

According to the above discussion, the moisture absorption has a big influence on the transition temperature of IPDI-BINA SMPU. It indicates that the Tg can be reduced to below 14.2℃ under the moisture condition of RH=8% and T=30℃. Therefore, the dynamical mechanical properties of IPDI-BINA polyurethane should be responsive to both temperature and moisture condition times. For a comparison study, the storage modulus change as well as the loss modulus change upon heating and upon moisture condition time is presented in Fig. 3.

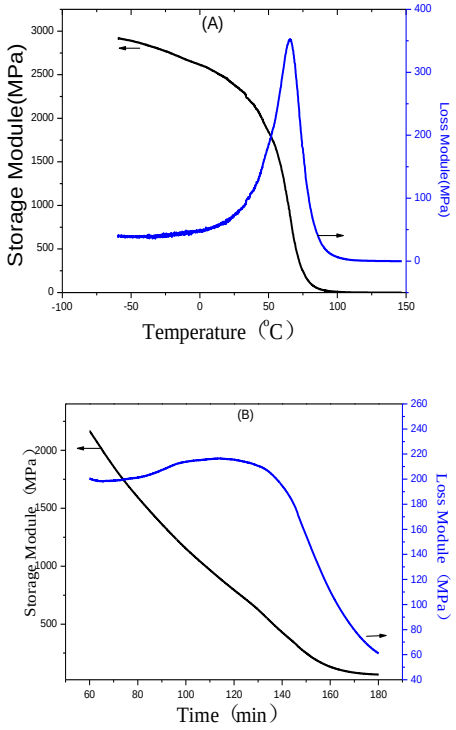

Fig. 3. DMA curve of IPDI-SMPU upon heating (A) and moisture conditioning at *RH*=85% and *T*=30℃ (B)

It is observed in Fig. 3(A) that the storage module of IPDI-BINA polyurethane decreases significantly within the temperature range of 0℃ to 101.0℃, and the loss module

reach its maxima value at 66.0℃, which is correspond to the T_g of IPDI-BINA as discussed in the DSC result. This result implies that the IPDI-BINA polyurethane can be deformed easily above *Tg* and fixed below *Tg*. Similarly, under the moisture condition, it is also found in Fig 3B that the storage modulus is higher than 2.4GPa after conditioning for 1h (before the test), as the conditioning time goes by, the modulus decreases significantly within the conditioning time of 60-170mins, and it then tends to be only 80MPa after 170mins. That is, the reduced modulus ratio is higher than 30. It means that the modulus gets soft after conditioning 170mins. It implies that moisture absorption reduces the modulus of IPDI-BINA polyurethane. From the loss modulus change curves, it is also found that the loss modules decrease slightly before 120mins, and it decreases significantly after 140mins. It thus confirmed that the modulus decreasing process is accompanied by the moisture absorption process.

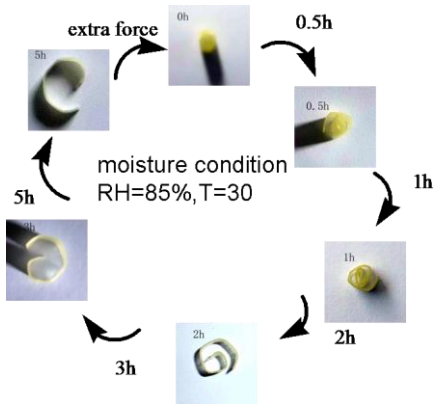

Fig. 4. Moisture-sensitive shape recovery process of IPDI-BINA at *RH*=85% and *T*=30℃

Fig. 4 presents a moisture-sensitive shape recovery process of IPDI-BINA film under the conditions of *RH*=85%, *T*=30℃. As shown in Fig. 4, the test film is coiled tightly before putting on moisture condition. After conditioning for 0.5h or 1h, the coiled film is relaxed. After 2h, the coiled film is open, and it finishes the shape recovery process after conditioning for 5 hours. The film also recovers to its open state. The shape recovery process is very similar to the open process of flower made of HDI-BINA series moisture-sensitive shape memory polyurethane film as reported in previous literature [6], [7] . It is thus confirmed that the IPDI-BINA system can also show moisture-sensitive shape memory.

IV. Conclusion

In this communication, the moisture-sensitive properties of IPDI-BINA SMPU are investigated system. The preliminary results show that the moisture absorption have influenced significantly the glass transition, and it can reduce more than 50℃to below room temperature. Moreover, DMA analysis shows that the modulus reduces more than 30 times due to the greater moisture absorption in the IPDI-BINA system. Thus, similar to the HDI-BINA system, the IPDI-BINA system is found to show moisture-sensitive shape memory effect.

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