

Properties and Microstructure of Polyurethane Resins from Liquefied Wood

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ABSTRACT: In this article, polyurethane resins were synthesized from liquefied benzylated wood and toluene diisocyanate (TDI)–trihydromethylene propane (TMP) prepolymer (as curing agent). The relations of their segmented structure and properties of were investigated. Results indicated that polyurethane resins made from benzylated wood solution have good mechanical and thermal properties. With the increase of curing agent amount from 23.8 to 53.5%, the degree of phase segregation increased, and under experimental conditions in this article, phase transition was de-

tected with a curing agent amount of 69.9%. After this transition, the mechanical properties of polyurethane resins were improved. Thermal history treatment can also influence microstructure and thermal stabilities of polyurethane samples. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 95: 1175–1180, 2005

Key words: thermal properties; structure–property relations; microstructure

INTRODUCTION

Recently, much attention has been paid on how to utilize existing resources economically and how to develop new materials for polyurethane (PU) industry. Many researchers have contributed to preparing PU resins by using waste paper and other cellulosic materials.^{1–2} The use of wood solution as polyols in the PU industry is one of the methods.^{3–4} Based on this technology, early literature mainly concentrated on polyols and phenol with hydroxyls as wood liquefaction reagents.⁵ In previous studies,⁶ our group first employed a novel environmental-friendly liquefying reagent dibasic esters (DBE) without hydroxyl groups and synthesized PU films with good properties. In addition, we have also investigated the reactions between the hydroxyls in benzylated wood solution and three different diisocyanates.⁷ In any case, these works will be potentially valuable for the PU industry.

However, compared to the conventional PUs, the differences of lignocellulosic materials and polyether in structure inevitably lead to differences of PUs obtained in microstructure and other properties. Therefore, systematic studies on the relations between microphase structure and properties of PU with wood cellulosic materials become very important for its industry application. In this article, PU samples with

benzylated wood solution and toluene diisocyanate (TDI)–trihydromethylene propane (TMP) prepolymer were synthesized, and a mixture reagent–DBE and *n*-butyl acetate was employed as wood liquefaction reagent. We also studied the influences of curing agent amount and thermal history on segment structure, phase segregation, and thermal stabilities of PU samples.

EXPERIMENTAL

Materials

The benzylated wood in this study was prepared according to the method described in our previous article.⁸ DBE and TDI–TMP prepolymer (all from Tianjin Beacon Paint and Coatings Co., Ltd., Tianjin, China) and butylacetate (Tianjin Tianhe Reagent Co., Ltd., Tianjin, China) were used.

Liquefaction of benzylated wood

Benzylated wood meal (WPG 75–80%), dibasic esters, butyl acetate, and catalyst (hydrochloric acid) in the ratio of 1 g/2.5 g/0.5 g/0.1 mL were charged into a reactor with stirrer, condenser, and thermometer. The liquefying reaction was conducted at 75–80°C in an oil bath for 2.5–3 h. The resultant product was filtrated.

Synthesis of polyurethane resins

Forty grams of liquefied benzylated wood solution and 0.65 wt % catalyst (dibutyltin dilaurate) were

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charged into a reactor used for wood liquefaction and stirred for 30 min at 50°C. Then, the curing agent TDI-TMP was added. The whole mixture was stirred for 30 min at 50°C and then cooled to ambient temperature.

FTIR analysis

Polyurethane resins from liquefied benzylated wood and TDI-TMP were analyzed by using a Fourier transform infrared (FTIR) spectrometer. FTIR spectra were recorded on a Bio-Bad Exalibur FTS-3000 Fourier transform spectrometer. Transmittance measurements were conducted by using the KBr pellet method.

Differential scanning calorimetry (DSC)

DSC measurements were carried out by using a Netzsch DSC 204 instrument operated at a 10°C/min heating rate from -100 to 300°C and under N₂ atmosphere. A sample weight of ~ 10 mg was used for DSC experiments.

TG and DTA analysis

A thermal gravimetric analyzer (TGA; TA Instruments ZRY-ZP) was used to measure the thermal degradation of the polyurethane resins. Samples with a weight of ~ 10 mg were tested at a heating rate of 10°C/min from 20 to 600°C.

Scanning electron microscopy (SEM) observation

SEM images were observed on a Philips XL-3 scanning microscope. The polyurethane samples were sus-

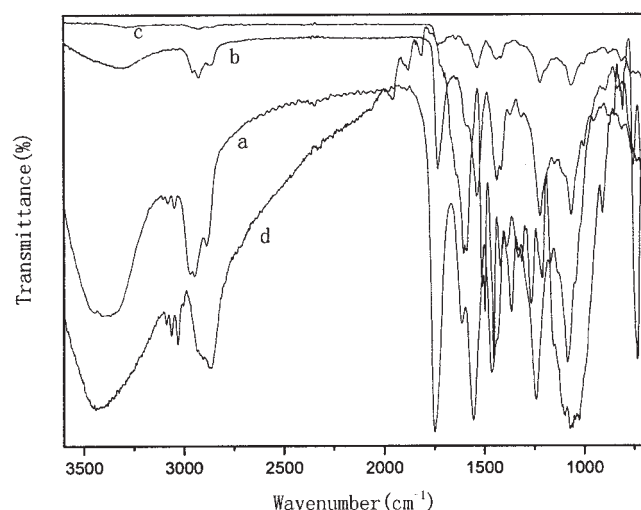


Figure 1 FTIR spectra of benzylated wood and polyurethane samples with different curing agent amounts: (a) 23.8%; (b) 53.5%; (c) 69.9%; (d) benzylated wood powder.

TABLE I
Analysis Data of FTIR Spectra of Benzylated Wood and Polyurethane Resins

| Sample | Absorbing peak/ (cm ⁻¹) |
|-----------------|--|
| Benzylated wood | 3436.493 (γ OH); 3031.152 (γ OH, bonded) |
| PU-a | 3352.392 (γ NH); 1539.425 (δ NH, urethane) |
| PU-b | 3316.363 (γ NH); 1538.369 (δ NH, urethane) |
| PU-c | 3298.579 (γ NH); 1533.875 (δ NH, urethane) |

ended in a bottle in which there was a small amount of ethanol by ultrasonography. The suspension drop was mounted on glass plates and dried for removal of the ethanol and then coated with a thin layer of gold in a vacuum before examination.

PU samples with different curing agent amounts were defined as PU-a (23.5%), PU-b (53.5%), and PU-c (69.9%), respectively. Annealing and quenching treatments were conducted by heating PU samples from ambient temperature to 180°C and kept at this temperature for 30 min. Then, the samples were cooled at a rate of 10°C/min for annealing and rapidly cooled to under zero for quenching.

RESULTS AND DISCUSSION

Segment structure of PU samples

Figure 1 presents the FTIR spectra of benzylated wood and PU samples and Table I shows the results of their analysis. As shown in Figure 1 and Table I, as curing agent, the amount was raised from 23.8 to 69.9%, and the intensity of the characteristic peaks of OH became weak, ultimately disappearing. Also, characteristic peaks of NH were detected in Figure 1, γ NH (3352–3298 cm⁻¹) and δ NH (1540–1530 cm⁻¹). These results imply that the chemical bonds exist between hydroxyl in benzylated wood and NCO in prepolymer. In addition, the characteristic NH groups of these PU samples absorb at a lower frequency and the intensity of characteristic peaks C=O become weak when the curing agent amount is higher. More hard segments were introduced into PU, which resulted in more hydrogen bonds being formed.

Microphase structure of PU samples

Figure 2 shows SEM photos of PU films with different curing agent amounts. As shown in Figure 2, some microparticles were found at the surface of PU samples with curing agent amounts of 23.8 and 53.5%, and the sample with curing agent amount of 53.5% was even more severe. This may be ascribed to the incompatibility of the segments resulting in phase segregation. When the curing agent amount

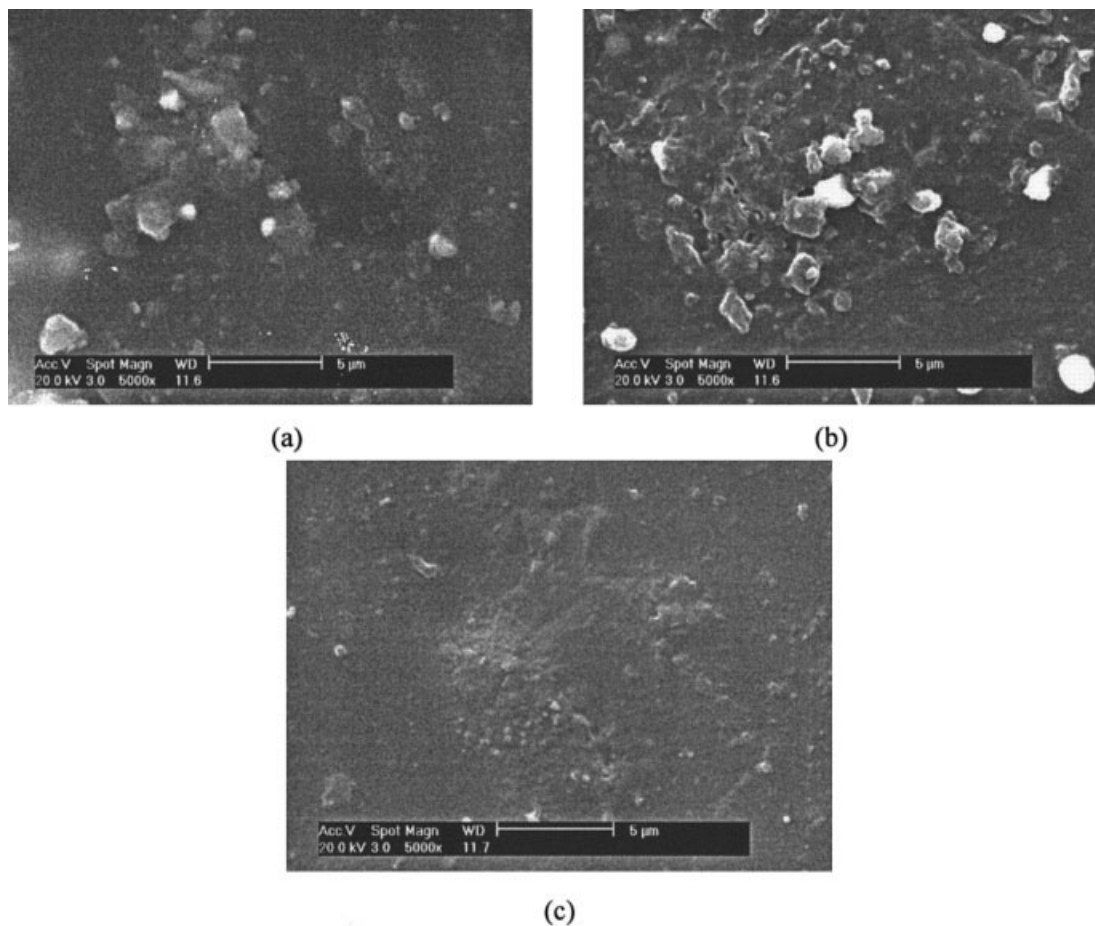


Figure 2 SEM photos of polyurethane films with different curing agent amounts: (a) 23.8%; (b) 53.5%; (c) 69.9%.

increased to 69.9%, however, the surface became more homogeneous and almost a rich phase domain was detected. It is well known in the PU system that an increase in curing agent amount and, thereby, an increased hard segment content and the polar groups confer increased molecular interactions in hard segments. Accordingly, the interactions between soft segment and hard segment became weak and phase segregation occurred. Under experimental conditions, when the hard segment content increased to 69.9%, phase transition was detected, as shown in Figure 2. The morphology of samples has a decisive influence on the physical properties; therefore, after phase transition, the mechanical

properties were greatly improved, as shown in Table II.

Glass transition of PU samples

Figure 3 shows the DSC curves of PU samples with different curing agent amounts. As shown in Figure 3, no obvious glass transitions for each soft and hard segment in PU were detected. Here, we defined top temperature of the transition (0–100°C) as glass transition temperature (T_g) of PU. From Figure 3, we can see that, with the curing agent amount increased from 23.8 to 69.9%, the T_g increased from 53.5 to 77°C. More

TABLE II
Mechanical Properties of PU Samples with Different Curing Agent Amount

| Curing agent amount (%) | Surface drying time (h) | Actual drying time (days) | Pencil hardness | Adhesion (rating) | Resistance to 10% NaOH (24 h) | Resistance to 10% H ₂ SO ₄ (24 h) |
|-------------------------|-------------------------|---------------------------|-----------------|-------------------|-------------------------------|---|
| 23.8 | <24 | <3 | 2H | ≥II | Foamed | Foamed |
| 53.5 | <12 | <2 | 3H | I | Stain | Stain |
| 69.6 | <2 | <1 | 4H | ≥I | No obvious change | No obvious change |

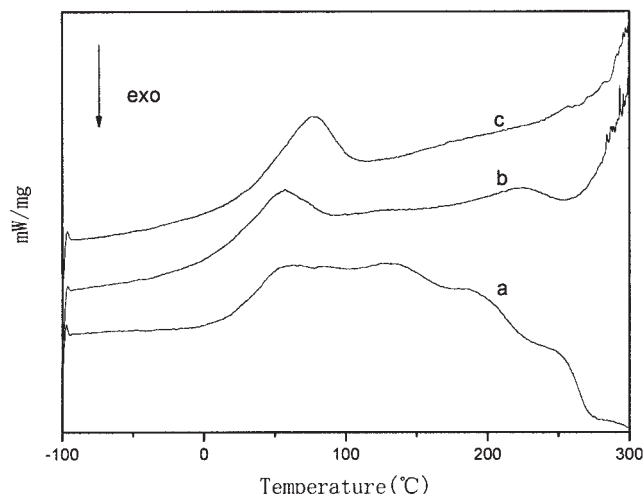


Figure 3 DSC of polyurethane with different curing agent amounts: (a) 23.8%; (b) 53.5%; (c) 69.9%.

TDI-TMP prepolymers acting as hard segments were introduced into PU, which led to the increase of T_g .

Thermal stabilities of PU samples

Figures 4 and 5 show the DTA and TG curves of PU samples with different curing agent amounts. As shown in Figure 4, the decomposition of PU samples proceeds in about two stages. The first part of the degradation correlates with the urethane segments, while the second peak correlates with wood components. From Figures 4 and 5, the onset degradation temperature of PU samples synthesized from wood solution (286–310°C) are all higher than 250°C. These results indicated that PUs from wood solution have

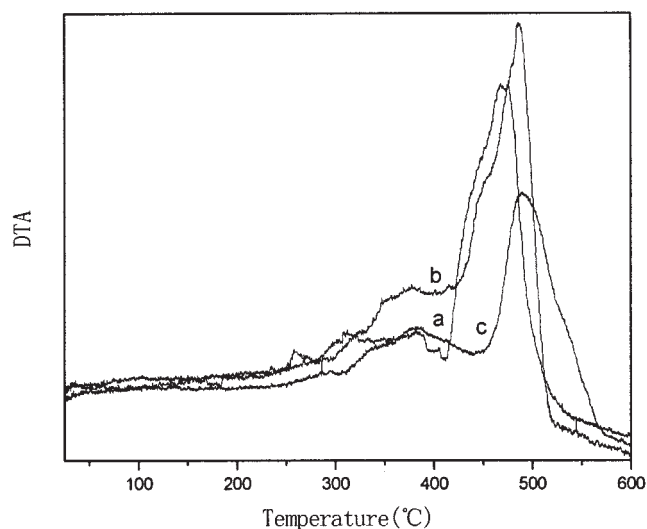


Figure 4 DTA of polyurethane with different curing agent amounts: (a) 23.8%; (b) 53.5%; (c) 69.9%.

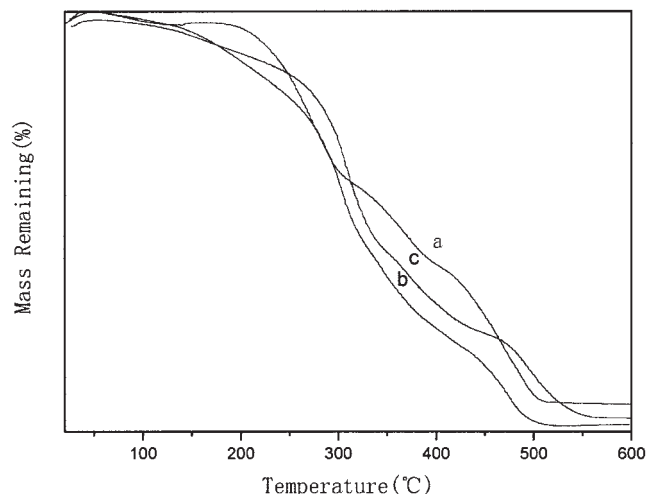


Figure 5 TG curves of polyurethane with different curing agent amounts: (a) 23.8%; (b) 53.5%; (c) 69.9%.

better thermal stabilities than the conventional ones.⁹ Wood is a polyol that can produce a complicated and crosslinked network of the PU because of its comparatively high functionality. With the increase of curing agent amount, the onset degradation temperature of PU samples increases.

Thermal history on segment structure of PU samples

Figure 6 shows FTIR spectra of PU samples undergoing different thermal histories and Table III represents the results of their analysis. As shown in Figure 6 and Table III, after annealing and quenching treatment, the absorption frequency of γNH and $\gamma\text{C=O}$ all changed. In PU, urethanes have strong polarity; they can form

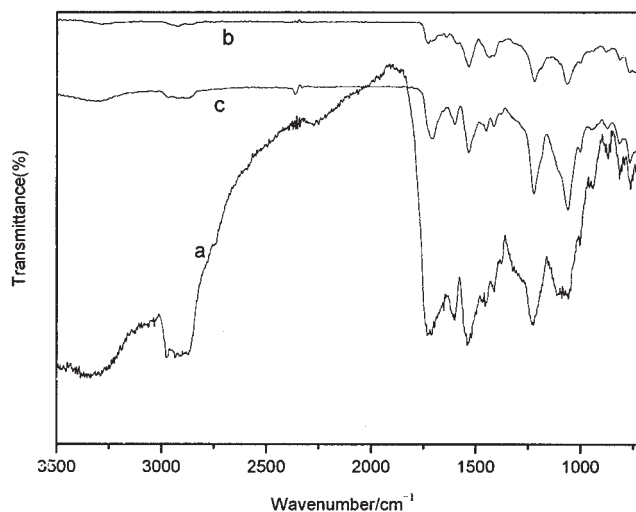


Figure 6 FTIR spectra of PU samples under different thermal histories: (a) anneal; (b) ambient; (c) quench.

TABLE III
Analysis Data of FTIR Spectra of Polyurethane under Different Thermal History

| Sample | Absorbing peak/cm ⁻¹ |
|--------|---|
| PU-a | 3385.064 (γ NH); 1725.505 (γ C=O, free); 1714.286 (γ C=O, hydrogen bonded); 1540.296 (δ NH, urethane) |
| PU-b | 3298.579 (γ NH); 1728.145 (γ C=O, free); 1702.034 (γ C=O, hydrogen bonded); 1533.875 (δ NH, urethane) |
| PU-c | 3314.732 (γ NH); 1705.029 (γ C=O, hydrogen bonded); 1534.878 (δ NH, urethane) |

hydrogen bonds with their C=O and also with —O— in soft segments. The former is a function of phase segregation; the latter is phase mixing. At a higher temperature of 180°C, the molecular PU absorbed enough heat capacity to destroy hydrogen bonds of hard segments. Therefore, PU molecules had enough capacity to move; thus, the molecules' interaction became weak. The peaks of γ NH and γ C=O all shifted to higher frequency as expected. In the process of annealing, however, PU molecules in amorphous state at a higher temperature had sufficient time to relax and rearrange when cooled slowly. Because of the high polarity of urethane, NH (3385.064 cm⁻¹) easily formed hydrogen bonds with C=O and —O—. During quenching treatment, almost all mixed phases in the PU frozen state had to stay amorphous once cooled quickly. In this case, NH in urethanes surrounded by a large amount of —O— may have a tendency to form hydrogen bonds with OH of wood solution. As shown in Figure 6 and Table III, it was observed at 3314.732 cm⁻¹ that the peak might be assigned to the N—H stretching vibration associated with the N—H—O— hydrogen bond.¹⁰

Thermal history on thermal stability of PU samples

Figures 7 and 8 show TG and DTA curves of PU samples undergoing different thermal histories and

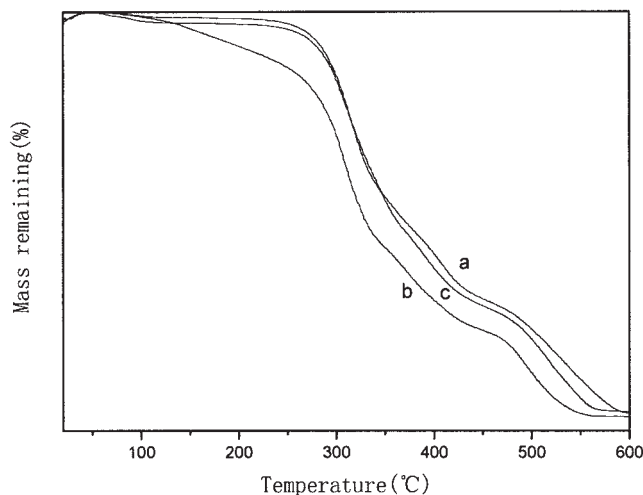


Figure 7 TG curves of PU samples under different thermal histories: (a) anneal; (b) ambient; (c) quench.

Table III represents results of their analysis. As shown in Figure 7, the decomposition of PU samples proceeds in two stages. The first part of the degradation correlates with the urethane segments, whereas the second peak correlates with the degradation of wood components. Qualitative characterization of the degradation process is illustrated by the onset and maximum peak temperature of the first step, T_{1on} and T_{1max} , along with the same for the second step, T_{2on} and T_{2max} . Table IV summarizes T_{1on} , T_{1max} , T_{2on} , and T_{2max} of PU samples undergoing annealing, ambient treating, and quenching treatment, respectively. From Table IV, it is very obvious that the onset degradation temperatures (>300°C) of all PU samples are higher than conventional ones (<250°C).⁹ Different thermal treatment PU samples undergoing treatment have different influences on thermal stabilities. After annealing and quenching treatment, the thermal stabilities of PU samples were all improved, as shown in Table IV data.

CONCLUSION

In the present work, PU samples were synthesized from benzylated wood solution by using DBE and butyl acetate as liquefying reagent and TDI-TMP prepolymer (curing agent).

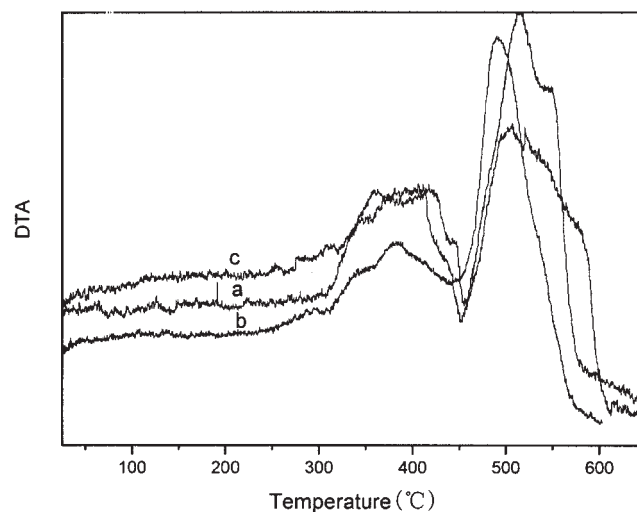


Figure 8 DTA curves of PU samples under different thermal histories: (a) anneal; (b) ambient; (c) quench.

TABLE IV
Analysis Data of DTA of Polyurethane with Different Heat Treatments

| Sample No. | $T_{1\text{ on}}$ (°C) | $T_{1\text{ max}}$ (°C) | $T_{2\text{ on}}$ (°C) | $T_{2\text{ max}}$ (°C) |
|------------|------------------------|-------------------------|------------------------|-------------------------|
| 1 | 306 | 413 | 487 | 506 |
| 2 | 310 | 381 | 482 | 489 |
| 3 | 303 | 406 | 501 | 515 |

By FTIR, DSC, SEM, DTA, and TG analysis, we investigated the relations between the segment structure and properties of PU samples. Results indicated that as curing agent amount increased, the urethanes characteristic peaks —NH shifted to lower frequency; T_g of PU samples were increased, and the thermal and mechanical stabilities were also improved. When the curing agent amount increased from 23.8 to 53.5%, the degree of phase segregation increased, and under the experimental conditions, phase transition was detected with a curing agent amount of 69.9%. Also, this film has the best mechanical properties. In addition, thermal history, including annealing and quenching, all change the segment structure of PU samples. After

these treatments, the thermal stabilities of PU samples were improved.

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