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RESEARCH ARTICLE

Preparation and properties of adjacency crosslinked polyurethane–urea elastomers

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ABSTRACT: Adjacency crosslinked polyurethane–urea (PUU) elastomers with different crosslinking density were prepared by using hydroxyl-terminated liquid butadiene-nitrile (HTBN), toluene diisocyanate (TDI) and chain extender 3,5-dimethyl thio-toluene diamine (DMTDA) as raw materials, dicumyl peroxide (DCP) as initiator, and N,N'-m-phenylene dimaleimide (HVA-2) as the crosslinking agent. The influences of the crosslinking density and temperature on the structure and properties of such elastomers were investigated. The crosslinking density of PUU elastomer was tested by the NMR method. It is found that when the content of HVA-2 is 1.5%, the mechanical properties of polyurethane elastomer achieve optimal performance. By testing thermal performance of PUU, compared with linear PUU, the thermal stability of the elastomers has a marked improvement. With the addition of HVA-2, the loss factor tan*δ* decreases. FT-IR spectral studies of PUU elastomer at various temperatures were performed. From this study, heat-resistance polyurethane could be prepared, and the properties of PUU at high temperature could be improved obviously.

KEYWORDS: HTBN, PUU, crosslinking, HVA-2, thermal property, FT-IR

1 Introduction

Traditional linear polyurethane–urea (PUU) polymers show superior mechanical properties owing to their unique characters of internal structures. It is known that mechanical properties of PUU elastomers decreased sharply with the increase of temperature, which limited the application of PUU elastomers in high-temperature surroundings. Over the years through the application of basic research on PUU elastomers, it is found that the temperature not exceed 80°C for long-term use of polyurethane elastomers, and the short-term use temperature more than 120°C has rarely been reported [1]. The excellent performance of the PUU elastomers at room temperature would be degenerative in high-temperature surroundings, which restricts the application of this kind of materials.

The applicability of bismaleimides is widely, and N,N'-m-phenylene dimaleimide (HVA-2) is often used as a compatibilizer in blends. The dimaleimide crosslinking is very stable upon the exposure of the blend to increased temperatures, which makes it an attractive material for the dynamic crosslinking of various blends [2–3]. Hassan et al. [2] investigated the effect of HVA-2 on the morphologies and mechanical properties of polypropylene/natural rubber/linear low density polyethylene blends. In a series of publications Inoue and Suzuki [4–5] investigated polypropylene/ethylene propylene diene elastomer/HVA-2 blends.

In order to improve the thermal resistance of PUU

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elastomers, people carried out the research on the structure and properties of crosslinking polyether PUU elastomer [6–9], trimethylolpropane as a crosslinker. Hydroxy terminated liquid nitrile rubber as soft segment material to modify the structure and properties of polyurethane, the research on thermal performance of the dimaleimide adjacency crosslinked PUU elastomers was also carried out [10]. In our recent work, a series of adjacency crosslinked PUU elastomers were prepared, which based on soft segment of polybutadiene-acrylonitrile copolymer glycol (HTBN), hard segment of toluene diisocyanate (TDI) and dimethyl thio toluene diamine (DMTDA), herein, dicumyl peroxide (DCP) and HVA-2 as cross-linking agent. In this work, on the basis of the past study, we further investigated thermal properties of adjacency crosslinked PUU elastomers, and the Fourier-transform infrared (FT-IR) [11–14] spectroscopy was used to study the hydrogen bonding behaviors of PUU elastomers.

2 Experimental

2.1 Materials

Hydroxyl-terminated polybutadiene acrylonitrile (HTBN), Industrial Product, with hydroxyl value of 0.6054 mmol $\cdot g^{-1}$ and cyano content of 15%, was produced by Zibo Qilong Chemical Corporation, China.

TDI, 2,6/2,4 molar ratio of 80/20, a colorless liquid with low viscosity and molar mass of 174 $g \cdot mol^{-1}$, was produced by Bayer Company AR, Germany.

3,5-dimethyl thio toluene diamine (DMTDA), an amber liquid (0.05 $m \cdot Pa \cdot s$ at 35°C) with molar ratio of 80 to 20 for the mixture of 2,4- and 2,6-isomers of 3,5-dithiomethyl toluene diamine and the equivalent value of 107, Industrial Products, was manufactured by Xin Long Chemical Industry Co., Ltd., Shandong Zibo, China.

HVA-2 was produced by Xianyang Sanjingkegongmao Co., Ltd., China.

DCP, Industrial Product, was produced by Guangzhou Changsheng Technology Co., Ltd., China.

2.2 Preparation of PUU elastomers

The desired amounts of HVA-2 and hydroxyl-terminated polybutadiene acrylonitrile were put into a three-neck flask. The temperature was raised to 100°C–110°C, vacuum removing the moisture in the mixture for 1.5 h. After cooling down to 70°C by nature, the desired amount of TDI was added, maintaining the reaction temperature at 80°C–85°C, and keeping reaction for 2 h. After vacuum degassing, the polyurethane composited prepolymer was made. The DMTDA chain extender and DCP were mixed together with prepolymer at 70°C. The mixture was stirred quickly and poured into the 120°C mold, which was placed at 120°C vulcanizing machine in advance and pressure curing for 1.5 h. The PUU elastomers were prepared. Post-cure process was 120°C×8 h and 150°C×1 h.

During the post-cure process, radical reactions occurred, as shown in Scheme 1.

2.3 Measurements and characterization

Crosslinking density analysis: AC-500 NMR crosslinking density instrument produced by Bruker Company.

Tensile testing machine, AL-7000M, was produced by High-Tech Detection Instrument Co., Ltd. (Taiwan, China), at the rate of 500 mm/min.

Test tensile properties and permanent deformation of the materials in accordance with GB528-1992, tear strength of the material accordance with GB 529-1991, and Shore A hardness of the material in accordance with GB/T 532-1992.

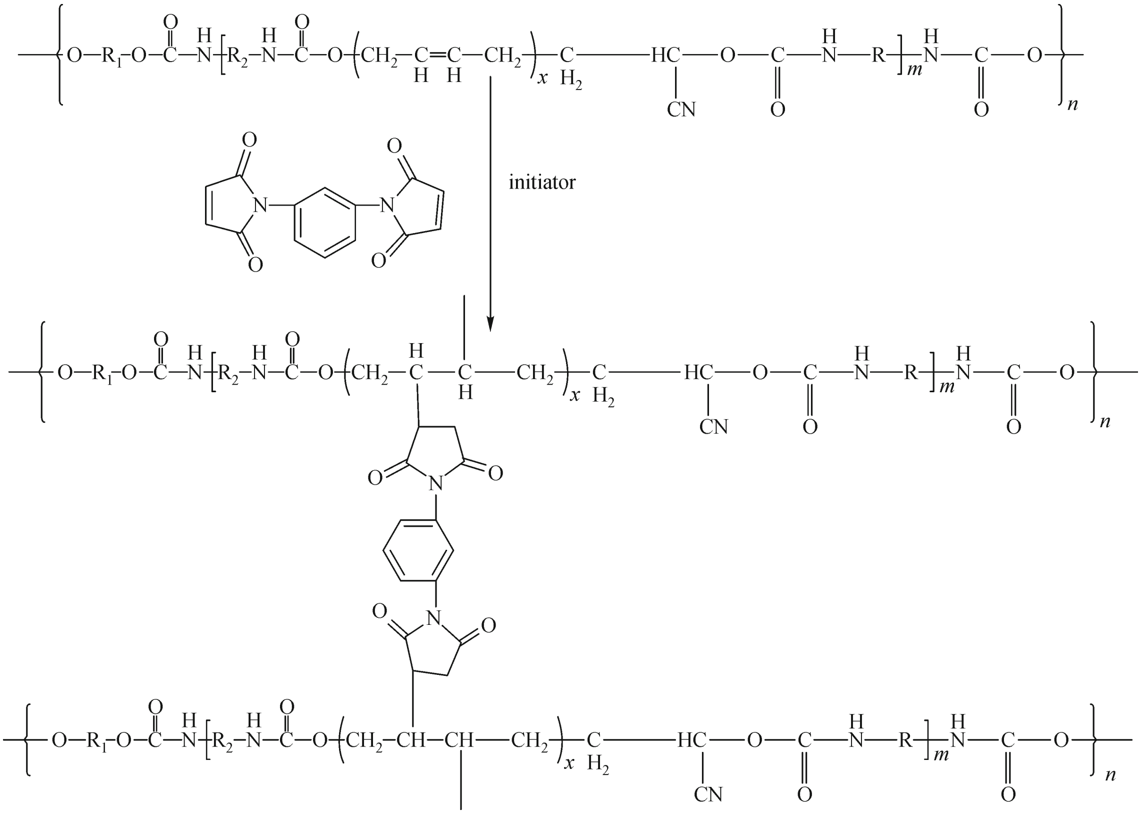
High-temperature tensile properties testing: Taiwan Yukon TS-1000 electronic tensile machine tests mechanical properties of good ruled dumbbell-shaped specimens at 30°C, 50°C, 80°C, 100°C, 120°C, 150°C.

Differential scanning calorimetry (DSC) analysis: the STA 449 C DSC instrument produced by Germany Netzsch-Gerate Ball Company was used to test the material glass transition temperature (T_g) [15], scanning range from −100°C to 200°C, heating rate of 10°C/min, nitrogen protection.

Dynamic mechanical thermal analysis (DMA) Model DMA242, was produced by Germany NETZSCH. Test temperature range is from −100°C to 120°C, thermal heating rate is 10°C/min, and the test frequency is 1 Hz.

Thermal gravimetric analysis (TGA) [16–17] was performed using a STA449C TGA (Germany Netzsch-Gerate Ball Company) instrument to test thermal stability of PUU composites. Samples were heated from 25°C to 600°C at a heating rate of $10°C \cdot min^{-1}$ under nitrogen atmosphere.

VERTEX70 Fourier transform infrared spectrometer (Bruker, Germany) was employed to characterize the PUU



Scheme 1 The reaction principle for the adjacency crosslinked PUU.

samples with the wavenumber ranging from 500 to 4000 cm^{-1}, and the resolution 2 cm^{-1}.

3 Result and discussion

3.1 Crosslinking density analysis

After curing, the elastomer micro-molecular structure changes from linear two-dimensional to three-dimensional network. In general, the crosslinking density of the elastomer molecules can be characterized by the network chain length (average molar mass) of two crosslinking points. The chain length of two crosslinking points in the network would have an impact on the movement of molecules, so the crosslinking density can be studied by analyzing the motion of polymer chains [18]. The method of nuclear magnetic resonance (NMR) [17–19] measuring the crosslinking density is based on the above principle. It can provide more comprehensive information about the micro-network structure [20–23], and has a short test time, small error, and good reproducibility. The studies by Parker et al. [24] have shown that the motion dynamics of polymer chains have a high sensitivity with NMR transverse relaxation process in a wide temperature range, and construct the relationship between NMR relaxation parameters and the curing structure. T_{21} is transverse relaxation time a hydrogen proton in a magnetic field, and it has relationship with part of high-frequency motion and fast motion in the crosslinked network such as the uncrosslinked molecules, small molecules, and the motion of the end of free chains [18]; as proton transverse relaxation time of elastomer crosslinking chain segments, T_{21} can be used to reflect the crosslinking density of elastomers.

From Table 1, it can be seen that with the increase of the content of HVA-2, transverse relaxation time T_{21} decreases. Transverse relaxation time is inversely proportional to the

Table 1 The mechanical properties and crosslinking density of PUU with various HVA-2 contents

Sample	HVA-2 content /wt.%	σ /MPa	ε /%	Hardness (Shore A)	Tear strength /(kN·m^{-1})	T_{21} /ms
No. 1	0	20.77	414.25	95	82.45	0.62
No. 2	1.5	24.40	330.50	96	76.15	0.48
No. 3	3	20.41	168.50	97	77.72	0.45

Note: σ, tensile strength; ε, elongation at break.

crosslinking density, so the crosslinking density is increased, verifying the completion of the adjacency crosslinking qualitatively.

3.2 Mechanical properties of PUU material

The tensile strength and elongation at break of PUU with various HVA-2 contents are also shown in Table 1. What can be seen from the table is that with the increase of HVA-2, tensile strength of PUU elastomer increases at first and then decreases, while elongation at break presents overall downward trend, and when the content of HVA-2 is about 1.5%, the tensile strength achieve maximum. This may be accounted by as the addition of HVA-2, the original linear molecules transform into adjacency crosslinked ones, so the tensile strength increases with the increase of the crosslinking degree. But with continue addition of HVA-2, molecular orientation will be destroyed, resulting in the phenomenon that the tensile strength reduces. On the other hand, with the increase of the crosslinking degree, the elasticity of the material decreases, plastic increases, therefore the elongation at break will decline.

Table 1 also shows that the hardness and tear strength of PUU change with the HVA-2 content. It can be seen from the table that with the addition of HVA-2, the hardness of material is increased slightly. HVA-2 itself is a hard segment, but the amount of crosslinking is not high and the hard segment does not have a visible impact, so there is little effect on hardness of PUU materials. The tear strength of PUU material does not show obvious law with the increase of HVA-2, maybe because HVA-2 makes the original linear molecules loose, and breaks molecular orientation effect, the material exhibits a decrease in tearing strength.

3.3 The thermal properties testing

3.3.1 DSC analysis

DSC curves of the PUU materials with different content of HVA-2 are shown in Fig. 1. The T_g values are listed in Table 2. It is revealed from Fig. 1 that the glass transition temperature (T_g) of PUU material increased slightly with the increase of HVA-2, this illustrates that HVA-2 has a certain impact on the glass transition temperature of PUU material, but not great. The glass transition temperature is a reflection of polymer microstructure, and its level has a great relationship with the flexibility of polymer chain segment. The glass transition temperature of material is increased with the addition of HVA-2. Because with the addition of HVA-2 the original linear molecules are transformed into the crosslinked ones, these interactions enhance the rigidity of the soft segments and limit the movement of the soft segments, thereby reducing the chain flexibility of the PUU elastomer. However, the crosslinking degree is not too high, so its addition does not make the glass transition temperature significantly improved.

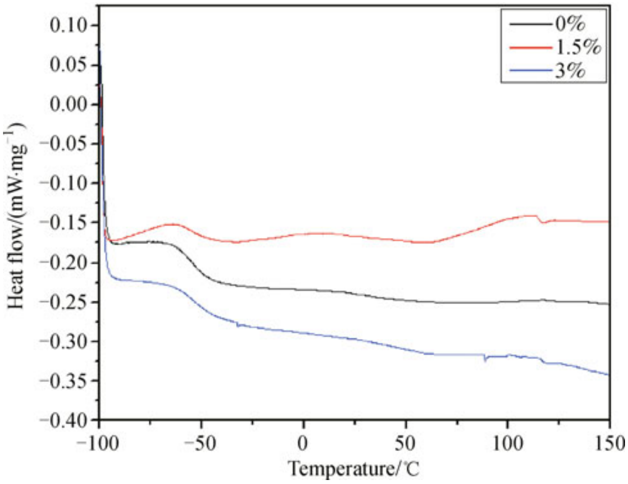


Fig. 1 DSC curves of PUU composites with different contents of HVA-2.

Table 2 DSC results for PUU with different content of HVA-2

Sample	HVA-2 content /%	$T_{g,\ onset}$ /°C	$T_{g,\ midpoint}$ /°C
No. 1	0	−61.42	−54.33
No. 2	1.5	−59.07	−53.49
No. 3	3	−59.77	−53.03

3.3.2 TGA study

The TGA was carried out to study the thermal stability of the linear PUU and crosslinked PUU. From the TGA curves shown in Fig. 2, it can be seen that the TGA decomposition of the linear or crosslinked PUU is divided into two stages. The first degradation stage (200°C–345°C) is attributed to the urethane bond decomposition weight loss. The second weight loss zone is from 420°C to 480°C, which is attributed to the decomposition of the HTBN molecular main chain. With increasing the content of HVA-2, the fastest decomposition temperature also markedly increases. When the content of HVA-2 is 3% compared with the pure PUU materials, although the initial decomposition temperature is basically same, the thermal decomposition rate of crosslinked PUU materials is

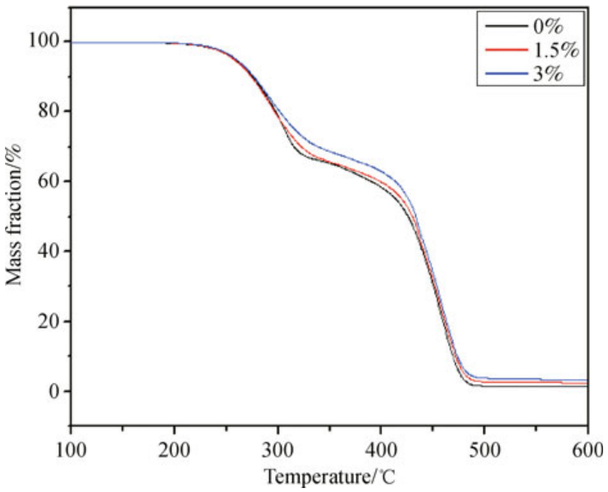


Fig. 2 TGA curves of PUU composites with different contents of HVA-2.

significantly reduced and the quality retention rate is obviously increased, which means that its thermal resistance has been noticeably improved.

The reason maybe is that there are a large number of double bonds in the linear PUU molecules, as the double bonds easily decompose at high temperatures to generate free radicals, which can speed up the decomposition of molecules. With the increase of the crosslinking degree, the number of double bonds in the soft segment of main molecular chain reduces, and consequently thermal resistance of the material is increased.

On the other hand, the stronger the intermolecular interaction is, the greater the random thermal motion of the chain segment is (the chain rigidity is greater), so the high level of the random thermal motion (the temperature meaning the extent of the random thermal motion) is needed to balance, and thus the thermal resistance becomes higher. Due to the addition of crosslinking agent, the soft segment crystallization of the adjacency crosslinked polyurethane molecules will be destroyed, while the hard segment crystal is not affected. In addition the crosslinking bond of soft segments in molecules makes thermal motion been fettered, as a result the thermal resistance of the PUU material is increased.

3.3.3 DMA study

The dynamic thermomechanical behaviors were assessed by the DMA method. It can be seen from Fig. 3 that the PUU composite loss factor tanδ are 0.270, 0.219 and 0.193. With the increase of HVA-2, the loss factor of PUU decreases. Because of the addition of HVA-2, linear molecules are transformed into adjacency crosslinked ones, and with the increase of crosslinking density, the molecular chain movement is restricted, showing the flexibility being reduced, and the storage modulus is reduced accordingly. The loss modulus is also reduced, maybe due to the addition of the crosslinking agent makes the distance between the main molecular chains relatively increased, resulting in relative reduction of the friction between molecules. At the same time, we can conclude that the decrease extent of the loss modulus is greater than the storage modulus. In other words, the impact on elasticity of PUU elastomer is not great by adjacency cross-linking. With the increase of crosslinking degree, the glass transition temperature (T_g) of material moves to high temperature, from -33.7°C to -30.8°C. This also shows that the molecular chain flexibility of the soft segment become smaller in the role of crosslinking agent. This is consistent with the results of DSC testing.

3.3.4 Tensile strength at different temperatures

The curves of the mechanical properties changing with temperature before and after the PUU crosslinked are shown in Fig. 4. It is revealed that the tensile strength and elongation at break of the PUU decrease with temperature increasing. With the temperature increased, the hydrogen bonds between the chains are destroyed gradually, so the mechanical properties such as tensile strength, elongation at break decrease significantly. Figure 4(a) shows that when the temperature is not too high (<100°C), the tensile strength changing with temperature increasing presents linear decreasing trend, while at high temperatures (>100°C), the intensity of decreasing slows down. It also can be seen that when the temperature is high, the mechanical property retention rate of crosslinked PUU elastomer is higher than that of linear PUU. The tensile strength of crosslinked elastomer at 150°C is 7.3 MPa, while that of the elastomer without crosslinking is only 4.7 MPa. The mechanical properties of the PUU elastomer have a strong dependence on temperature. With increasing temperature, the material internal hydrogen bonds are gradually dissociated, microcrystalline orderly structural of hard segment is damaged, the physical crosslink density of PUU is decreased, and the miscibility ability between hard and soft phase is increased, that is, the degree of microphase separation reduced, so its tensile strength gradually decreased. When the temperature reaches 100°C, the microcrystalline of hard segment is extensively damaged, and when the temperature continue increasing, the downward trend of the tensile strength become slow, since mechanical properties mainly depend on the morphology of the soft segment. In addition, with the temperature increase, the entropy elasticity of the material

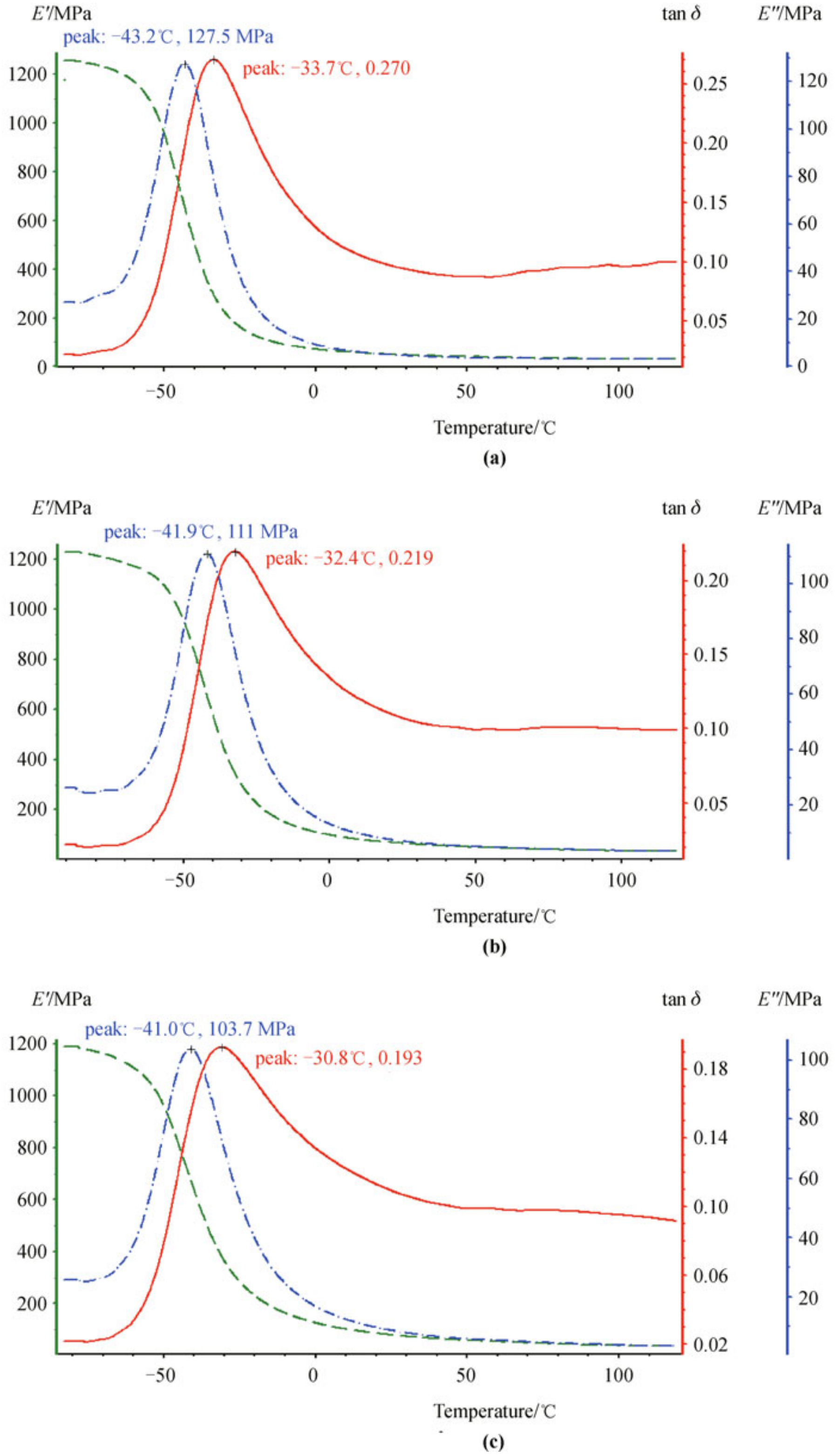


Fig. 3 DMA curves of PUU composites with the HVA-2 content of **(a)** 0%, **(b)** 1.5%, and **(c)** 3%.

soft segment increases, showing the lower elongation at break [25].

From Figs. 4(a) and 4(b), it can be seen that with increasing temperature, the retention rate of mechanical properties of adjacency crosslinked PUU has been markedly improved. We can conclude that the adjacency crosslinked PUU exhibits outstanding comprehensive mechanical properties in high temperature.

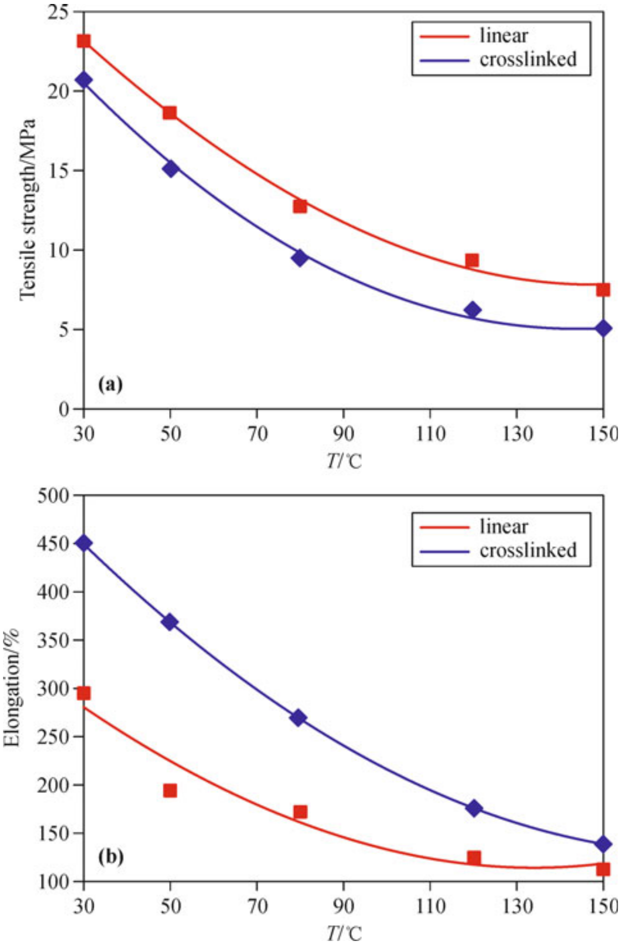


Fig. 4 Temperature dependence of **(a)** tensile strength and **(b)** elongation of both linear PUU composites and adjacency crosslinked PUU composites.

3.4 Temperature-dependent FT-IR analysis

Figures 5(a) and 5(b) show the temperature-dependency of FT-IR spectra for the linear and crosslinked PUU elastomer material in the region of 600–3600 cm^{-1}. In dynamic temperature-dependent infrared spectra, we only observe the changes of band's peak position and peak intensity, but no new absorption peak, indicating that intermolecular forces of PUU reduce with increasing temperature and aggregation structure of the material has changed without thermal degradation.

Almost all of the infrared research [26–29] on PU has been focused on two principal vibrational regions: the N–H stretching vibration (3200–3500 cm^{-1}), and the C = O stretching vibration (1700–1730 cm^{-1}). Because mechanical properties are mainly influenced by hydrogen bonds, our attention was mainly focused on N–H vibrational regions, which consist of not only the N–H stretching vibration at about 3282 cm^{-1} but also the N–H bending vibration at about 1543 cm^{-1}.

Spectra of the N–H stretching and in-plane bending regions of the linear and crosslinked PUU, displayed on the absorbance scale and recorded as a function of increasing temperature, are shown in Fig. 6. It can be clearly seen that the peak wavenumber varies with temperature. The strong absorption peaks at 3300 cm^{-1} is attributed to the hydrogen-bonded N–H stretching vibration, while the weak absorption peak at 3450 cm^{-1} is attributed to the "free" N–H stretching vibration [30]. As seen from Fig. 6(a), strong absorption peaks at 3282 cm^{-1} suggest the N–H bond before and after crosslinking exists in the form of hydrogen-bonded N–H which is hydrogen bonded with C = O (and also C–O–C). With increasing temperature, the peak maximum of the hydrogen-bonded N–H band shift to higher wavenumber (3282–3305 cm^{-1} from 30°C to 250°C) because the molecule movement at room temperature is suppressed, and the increasing temperature decreases the hydrogen-bond effects. The significant decrease of the integrated absorbance of the hydrogen-bonded N–H band with increasing temperature was perforce due to the variation of the hydrogen bond strength, or (which is exactly the same) the variation of the integrated absorption coefficient with the shift of the bonded N–H band maximum [30]. The infrared absorption of 1543 cm^{-1} is attributed to hydrogen-bonded N–H in-plane bending vibration between the N–H and C = O groups [31]. It can be seen from Figs. 6(b) and 6(d) that with increasing temperature, the bending vibration peak of hydrogen-bonded N–H moves to lower wavenumber, which is just opposite to the trend of its stretching vibration. The reason may be that with the increasing temperature, hydrogen bond is destroyed, the molecular thermal motion become stronger, thus the original bending vibration restricted by hydrogen bonds becomes free, resulting in bending absorption band moves to higher frequency.

To get the law of the band movement, wavenumber and temperature are used to plot.

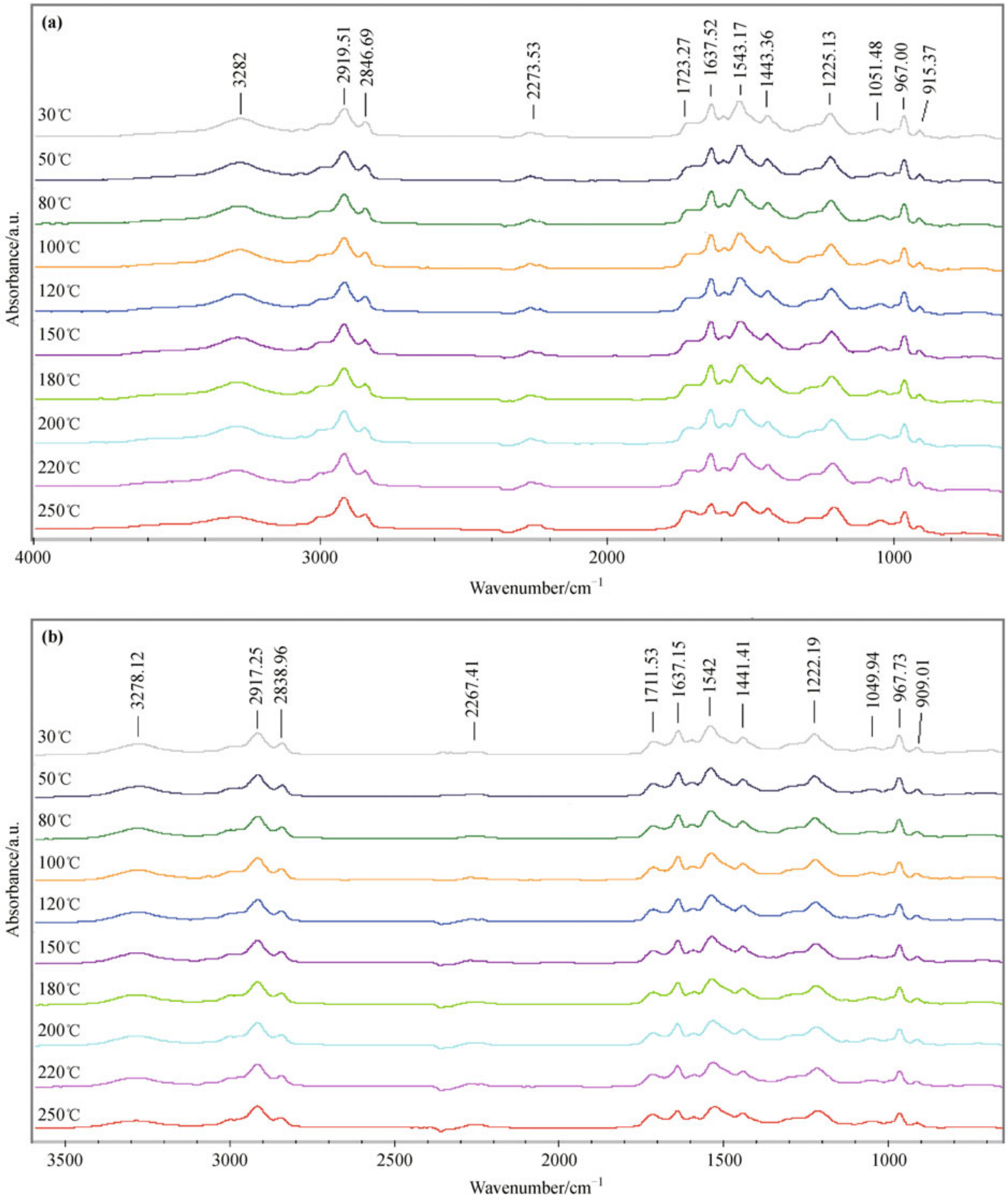


Fig. 5 FT-IR spectra of **(a)** linear PUU composites (with the HVA-2 content of 0%) and **(b)** crosslinked PUU composites (with the HVA-2 content of 1.5%) at different temperatures.

From Fig. 7(a) it can be seen that in different temperature ranges, the characteristic of the wavenumber is not the same, as the temperature increases, change of the wavenumber shows slowly at first and then fast. The change of the wavenumber is obvious after 150°C, and the shape of absorption peak becomes broad. This can be explained by the weakness of the average hydrogen bond strength [32], the effect of the hydrogen bonding is weakened after the heating of the hard segment region, the microcrystalline of hard segment dissociates, the

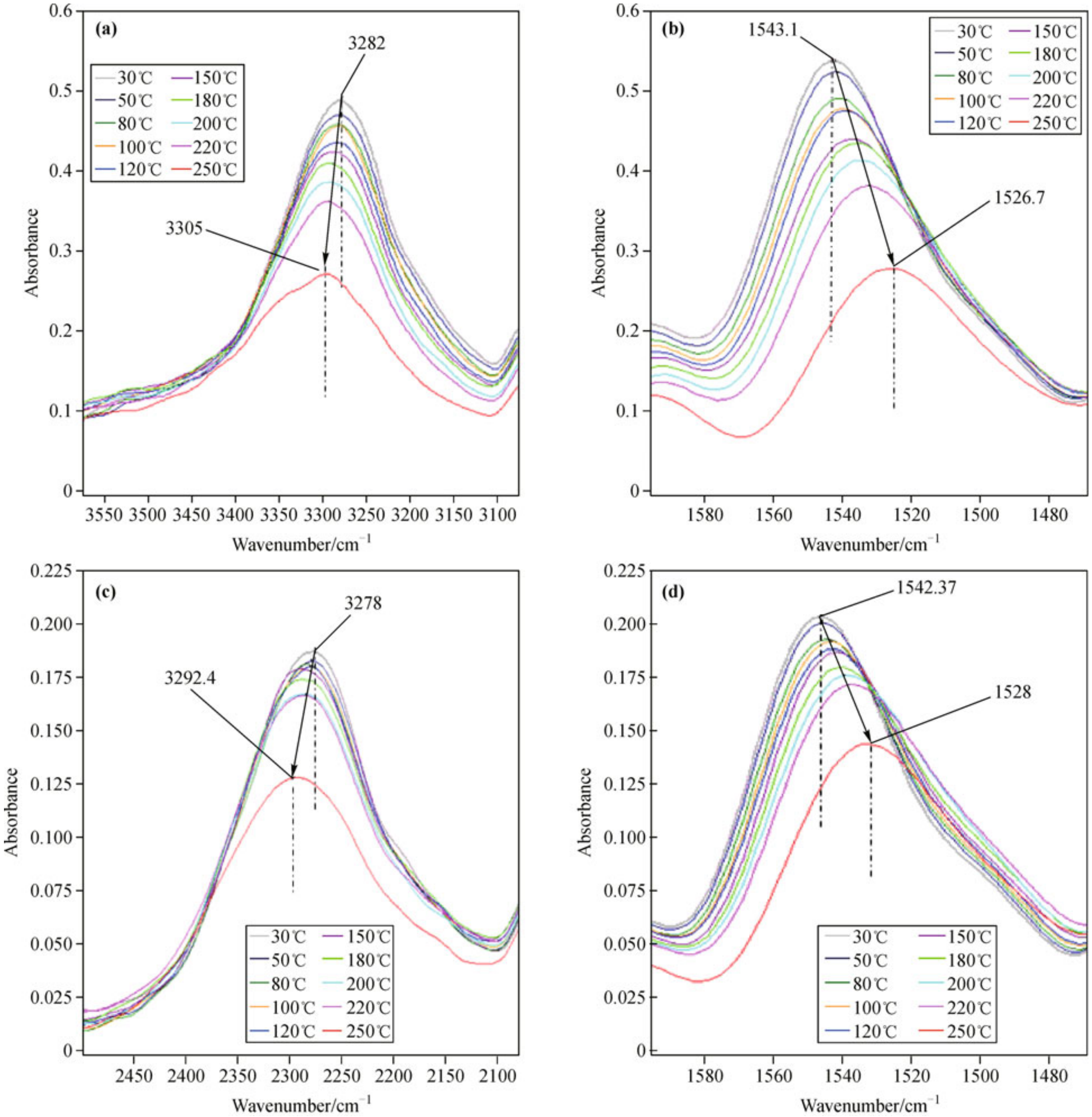


Fig. 6 FT-IR spectra of **(a)(b)** linear PUU composites (with the HVA-2 content of 0%) and **(c)(d)** crosslinked PUU composites (with the HVA-2 content of 1.5%) at different temperatures.

orderly ureido gradually transform into a less degree of order or free ureido; above 150°C, wide range dissociation of hydrogen bonds in hard segment microcrystalline occurs.

Comparing the two graphs of Figs. 7(a) and 7(b), it can be seen that the stretching vibration band of N–H of uncrosslinked PUU moves to higher wavenumber about 23 cm^{-1}, while the N–H stretching vibration band of the crosslinked PUU only moves about 13 cm^{-1}; the N–H bending vibration band of uncrosslinked PUU moves about 16 cm^{-1}, while the crosslinked moves about 14 cm^{-1}. The data shows that the N–H stretching and bending vibration bands of the crosslinked PUU shift smaller than linear PUU. And the change of the N–H stretching is obvious, whereas the N–H bending rarely changes. The reason maybe is that crosslinking makes the originally relatively free molecular chain fettered, the range of the N–H stretching and bending vibration band of the crosslinked PUU decreases to a certain degree. And the bending vibration relative to stretching vibration is mainly affected

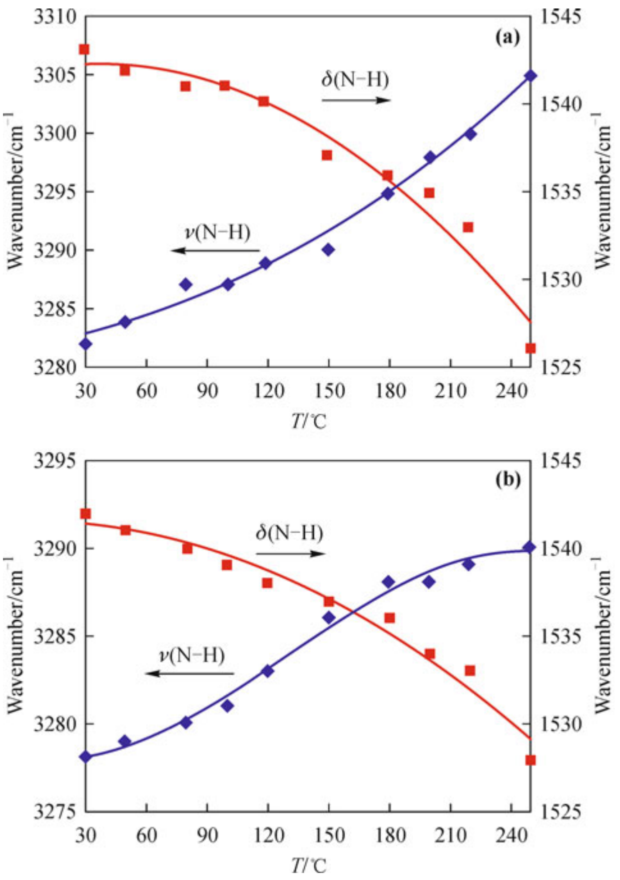


Fig. 7 Temperature dependence of ν(N–H) (the stretching vibration) and δ(N–H) (the bending vibration) band sites of **(a)** linear PUU composites and **(b)** crosslinked PUU composites.

by the temperature, in other words, the bending vibration can rarely be affected by the crosslinking. From Fig. 7, it is found that the wavenumber of stretching vibration in linear PUU is nearly linear growth, while when the temperature is above 100°C, the trend in crosslinked PUU become gradual. On the other hand, this can explain the crosslinked PUU has high retention rate of mechanical properties at high temperature.

4 Conclusions

NMR studies revealed that the transverse relaxation time T_{21} of the crosslinking density of PUU decreased with the increase of the HVA-2 content. Mechanical properties testing showed that when the HVA-2 content was 1.5%, the tensile strength of crosslinked PUU arrived 24.4 MPa. TGA, DSC and DMA studies revealed that the heat resistance of the crosslinked PUU was significantly improved, the glass transition temperature was increased, and the loss factor tanδ was reduced respectively. Tensile strength testing at different temperatures showed that, when temperature was increased, the retention rate of mechanical properties of PUU improved markedly because of the adjacency crosslinking. Temperature-dependent FT-IR testing suggested that when the temperature was increased, the movement of the crosslinked PUU wavenumber was less evident than linear PUU, in other words, the hydrogen bonding effect of crosslinked PUU was stronger than that of linear one. The results of this study will have a great impact on broadening the practical use and applications of PUU materials.

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