

The Effects of Isocyanate Index on the Properties of Aliphatic Waterborne Polyurethaneureas

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ABSTRACT: The aliphatic waterborne polyurethaneureas (WPU) with different isocyanate index (R) were synthesized by isophorone diisocyanate (IPDI) and polyester glycol via prepolymer mixing method. The effects of the R value on the structure and the properties of the resultant polymers have been analyzed. The polymer with a certain R value ($R = 1.44$) exhibited excellent mechanical properties with both high tensile strength (55 MPa) and high elongation at break (1400%). The water resistance and the thermal stabilities of WPUs have been improved with the increase of R . The results were interpreted in terms of the structures associated with the micro-phase separation. According to differential scanning calorimeter (DSC) anal-

ysis, the microphase separation degree was elevated by increasing R value. FTIR spectrum showed the more R value, the more hydrogen bonded urea groups. No crystallinity was found in X-ray diffraction (XRD) patterns showing the typical amorphous morphologies of IPDI-based WPUs. Thus the primary driving force for microphase separation was the hydrogen bonding between urethane and urea groups, making significant influence on the properties of WPUs, as shown in dynamic mechanical analyzes. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 920–927, 2010

Key words: aliphatic waterborne polyurethaneureas; isocyanate index; properties

INTRODUCTION

To minimize the environmental impact of volatile organic compounds (VOCs), extensive investigations have been conducted on the aqueous dispersions which need no external emulsifiers and which are found their outlets as environmental friendly lacquers.^{1,2} Waterborne Polyurethaneureas have become one of these issues since water is their only solvent, effectively reducing the release of VOCs into the atmosphere during the polymer processing and applications.³ Owing to the excellent properties, such as the fire safety, oil resistance, as well as the resistance to photo-oxidative aging of non-aromatic WPU, waterborne polyurethaneureas are coming to

replacing the solvent-based polyurethaneureas and have been widely used in printing, rubber, paper making, adhesives and other industry, and in everyday life.

The wide applications of WPUs come from the fact that their performance properties can be widely modified by employing various production methods⁴ and by selecting appropriate raw materials, catalysts, and auxiliary compound. At present, MDI and TDI are the principle raw materials to synthesis waterborne polyurethaneureas. The presence of the aromatic radical on the one hand contributes to the high strength and high modulus of the products.⁵ On the other hand, it also leads to the unwanted yellowing of the products. In this circumstance, the aliphatic isocyanates become a priority due to their antioxidation, light-stability, a longer pot life over the aromatic isocyanates.⁶ The wide range of aliphatic polyisocyanates, prepolymers, and adducts on the market today are primarily based on the aliphatic diisocyanate monomers: hexamethylene diisocyanate (HDI), isophorone diisocyanate (IPDI), 4,4'-Dicyclohexylmethane diisocyanate (H_{12} MDI).

IPDI, as aliphatic isocyanate, its anti-photo-degradation in direct sunlight service makes it available to apply in external protection. Second, its low reactivity makes the process under controllable to achieve

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more stable products. Lastly, the cyclo-aliphatic group in IPDI structure makes the steric hindrance increase, decreasing the ability of macromolecular slippage and increasing the modulus of elasticity and the tear and tensile strength of the aliphatic waterborne polyurethaneureas.

As is widely accepted that the thermodynamically incompatible hard and soft segments in segmented polyurethaneureas mix on a molecular level to form a microphase separated structure.⁷ Usually the soft segment derives from the ester or ether polyols, whereas the hard segment derives from the diisocyanate, short extenders as diol or diamine and the hydrophilic extender as DMPA. The final performance of WPU is determined by the structure, which is not only dependent on the type of employed raw materials, but also on the stoichiometry of reaction as well as the process conditions. Xiu et al.⁸ utilized ester-type and ether-type polyols to synthesize PU and discovered that better mechanical properties arose from the ester-type polyol PU. Eliane Ayres et al.⁹ found that phase separation between hard and soft segments of poly (ester-urethane) is more significant than that of poly (ether-urethane). Kim and Kim¹⁰ showed that the mechanical properties of PU were enhanced at higher polyester-type poly(tetramethylene adipate) glycol (PTAd) contents, prepared using IPDI and PTAd/PPG as the hard and soft segments, respectively.

Our work focused on the different stoichiometry, defining the molar ratio of the isocyanates to hydroxyls and the amino groups as the isocyanate index, which has not been reported in literatures yet now, to obtain the better properties of IPDI-based WPU by tailor-make the structural composition, to provide fundamental insights into the structural factors which govern the resultant properties, and to give theoretical guidance for further modification.

In this article, the systematical studies on IPDI-based aliphatic WPU were performed by changing the stoichiometric ratio of isocyanates and hydroxyl plus amino groups (defined as R) simultaneously keeping DMPA (dimethylol propionic acid) content invariable to rule out the influence of the ions, which was greatly different from the traditional synthesis strategy, so that the constitutive elements related to the final properties could be better developed. In addition, the structure-property correlation was also investigated.

EXPERIMENTAL

Materials

Poly(ethylene adipate) glycol (PEA; $\overline{M}_n = 2000$); dimethylol propionic acid (DMPA) as an internal hydrophilic extender (both were supplied by Yantai wanhua Polyurethane Company, Yantai city, China, China) isophorone isocyanate (IPDI, Bayer, Leverkusen, Ger-

TABLE I
The Recipe for Aqueous PU Samples

Sample name	R	IPDI ^a (wt %)	DMPA ^a (wt %)	EDA ^a (wt %)	Hard segment (%)
PU-1	1.16	19.4	5.0	0.71	25
PU-2	1.44	23.5	5.0	1.92	30
PU-3	1.73	27.8	5.0	3.17	35
PU-4	2.05	32.1	5.0	4.45	40

R is the molar ratio of $-\text{NCO}/(-\text{OH})$.

^a Based on the weight of prepolymer.

many). The purity of the diisocyanate was confirmed to be more than 99% by an amine equivalent method. Dibutyltin dilaurate (DBTDL) used as catalyst, triethylamine (TEA) used as neutralization agent and ethylene diamine (EDA) used as chain extender. These reagents were used as received. Deionised water was used as dispersing phase. PEA and DMPA were vacuumed desiccated before used.

Synthesis of the waterborne polyurethane dispersions (PUD) and film preparation

The PUDs were prepared by the prepolymer mixing process. A 500 mL round-bottom, four-necked flask equipped with a mechanical stirrer, thermometer backflow condensation tube and inlet of N_2 was used as a reactor. The polymerization was carried out in a constant temperature oil bath. According to the recipe listed in Table I, the macroglycol PEA was charged into the reactor. IPDI and 0.02 wt % DBTDL catalyst were added into the reactor to react at 80°C for about 2 h with the continuous stirring then DMPA (5 wt % of the total prepolymer weight) was added to react about 3 h until the residual amount of NCO groups reached the desired value by n -dibutylamine titration¹¹ to obtain the prepolymer. After cooled to 50°C, the carboxylic acid in the prepolymer was neutralized by TEA for 30 min to get the ionomer. Before the neutralization, a little acetone was added to decrease the viscosity of the prepolymer. Then the ionomer was dispersed into deionized water at 40°C with vigorous stirring followed by EDA extending the chains. After removing the acetone by vacuum distillation, the stable aqueous polyurethane dispersion with a solid content of about 30% was obtained.

The PU membranes were prepared by casting the WPU polymer aqueous solution on a PTFE plate at 80°C for 4 h in vacuum. The film thickness was constant at about 1 mm, in the shape of strips with 200 mm long by 40 mm wide.

Characterization methods

FTIR-ATR

The chemical structures of the PUD films were analyzed by an infrared spectrophotometer. (NICOLET

500). Measurements were carried out by the attenuated infrared total reflectance (ATR) method.

Particle sizes and distributions of PUD

The particle sizes and distributions of waterborne polyurethane dispersion were measured by a light scattering ultra-fine particle master sizer 2000 analyzer (Master, Britain). The samples were diluted to the required concentration with distilled water before measurement. The estimated solution parameters of the analysis were as follows: material refractive index of 1.59, dispersant refractive index of 1.33, and viscosity of 0.8872 mPa s.

Mechanical properties

The tensile strength and elongation-at break of PUD samples were measured by tensile testing on the dumbbell type films with 120 mm × 6 mm × 1 mm dimensions at 200 mm/min cross-head speed using a DQA503B electron universal tensile machine (Shenzhen SANS, China).

Water resistance experiment

The water resistance properties of PUD films were determined as follows. The films were prepared by tailoring into 20 mm × 20 mm specimens. The weighed samples (W_0) were immersed into distilled water at room temperature for 24 h, followed by wiping off the surface water with a piece of filter paper to determine the weight W_1 . So the absorption water ration W of the films were given by following equation.

$$W = \frac{(W_1 - W_0)}{W_0} \times 100\%$$

Differential scanning calorimetry

The thermal behaviors of the sample films were analyzed by means of a differential scanning calorimeter DSC 200 F3, (NETZSCH, Germany). PUD samples (8–10 mg) were placed in an aluminum pan and the experiments were carried out under nitrogen atmosphere by using a heating rate of 10°C/min, from –60 to 250°C.

X-ray diffraction

The WAXD experiments were performed on a DX-2500 discover X-ray diffractometer (Dan Dong Fang Yuan, China) in the range of $2\theta = 0\text{--}55^\circ$, employing nickel-filtered Cu K-radiation (1.5418 Å) at an operational voltage of 40 kV.

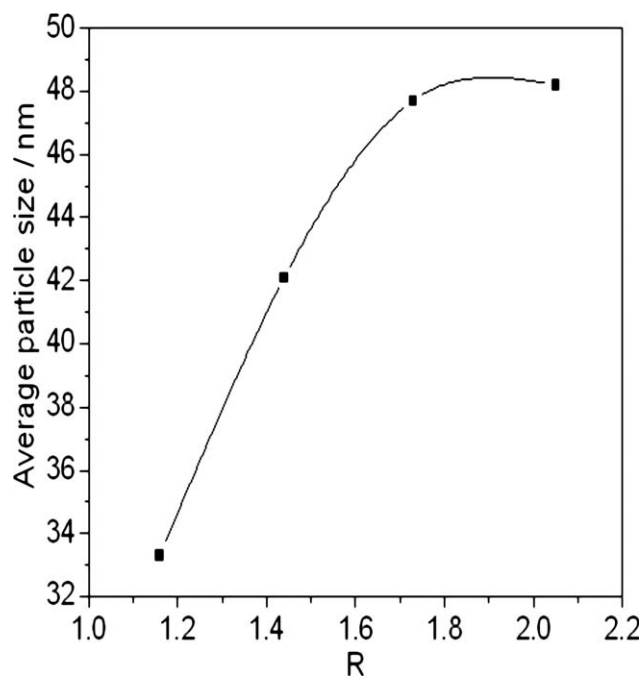


Figure 1 The average particle size of WPUs with different R value.

Dynamic mechanical analysis

The viscoelastic properties of the PUD samples were measured on a viscoelastomer DMA Q800 (TA), with temperature from –80 to 150°C.

RESULTS AND DISCUSSION

Emulsion particle size and particle distribution

As shown in Figure 1, the average emulsion particle size of each sample was smaller than 50 nm, indicating the successful preparation of nano-particle dispersions. With the increase of R value, the average particle size increased linearly first and then leveled off at $R = 1.73$. Figure 2 shows the volume distribution of the latexes, some of which had two continuous peaks, indicating the binary particle distribution. With R value increasing, the peak width of the particle distribution curves became gradually wider, especially in PU-4. It indicates that the increase of R value leads to more particles. These particles can crash and aggregate easily each other resulting in the wider volume distribution.

The mechanical properties

Figure 3 shows the stress-strain behaviors of the aliphatic WPU films with different R values. All of WPU films exhibited positive yields, necking strain hardening, and high elongation at break (over 800%). There exhibited a transition from elastic to plastic behavior from PU-1 to PU-4. The ultimate

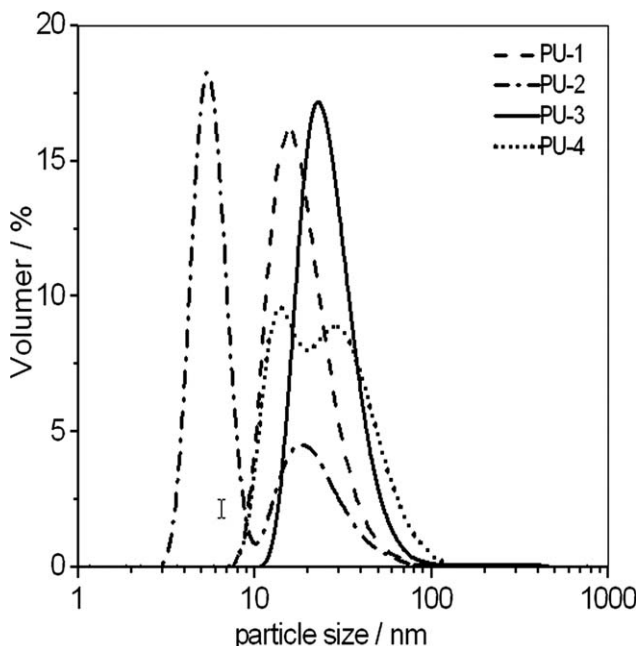


Figure 2 The particle size distribution by volume of PUDs.

strength of PU-2, PU-3, and PU-4 were obviously higher than that of PU-1. The increase of R makes more rigid segments. These rigid segments distribute in the continuous soft segment matrix and form physical crosslinks to effectively reinforce the ultimate strength. Comparatively, the elongation at break reduced from 2250% to 860% indicating that the creation of more urethane, urea groups, and

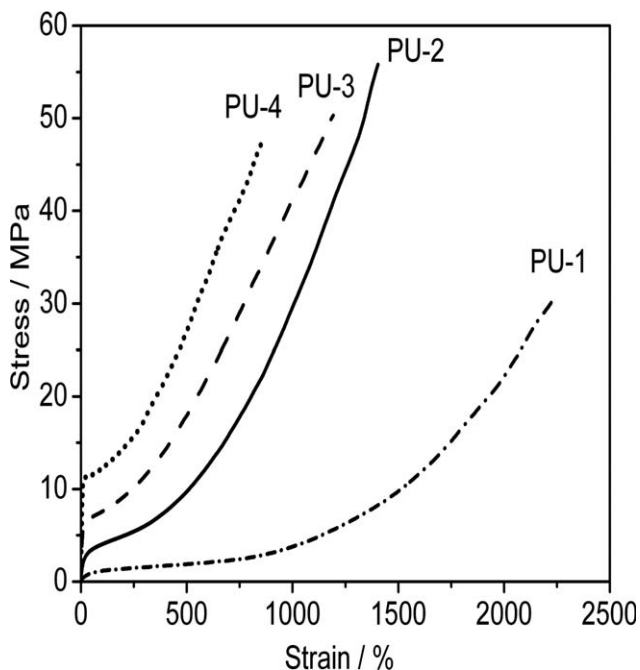


Figure 3 The stress-strain curves of PUD films with different R value.

TABLE II
The Young's Moduli of WPU Films with Different R Value

Sample	R	Young's modulus (MPa)
PU-1	1.16	3.5
PU-2	1.44	27.9
PU-3	1.73	64.1
PU-4	2.05	78.2

hydrogen bonded ureas by more R value limited the PU chains to motion freely. Table II shows Young's moduli of these samples. With the increase of R value, the modulus increased. PU-1 showed the least Young's modulus indicating the very soft and flexible material. While the other samples showed much higher modulus than PU-1, indicating the flexibility of the films decreased greatly when the R value was above 1.16.

Water resistance

The water absorption reflects the water resistant ability of WPU films, which is of great importance for application. It can be seen in Figure 4 that the water absorption of samples heavily depended on the variations of R value. The water absorption decreased distinctly in PU-3 and PU-4 compared with PU-1 and PU-2, indicating the water resistant property was greatly improved when R was above 1.73. It seems that the strong intermolecular links created by more R value have prevented the water

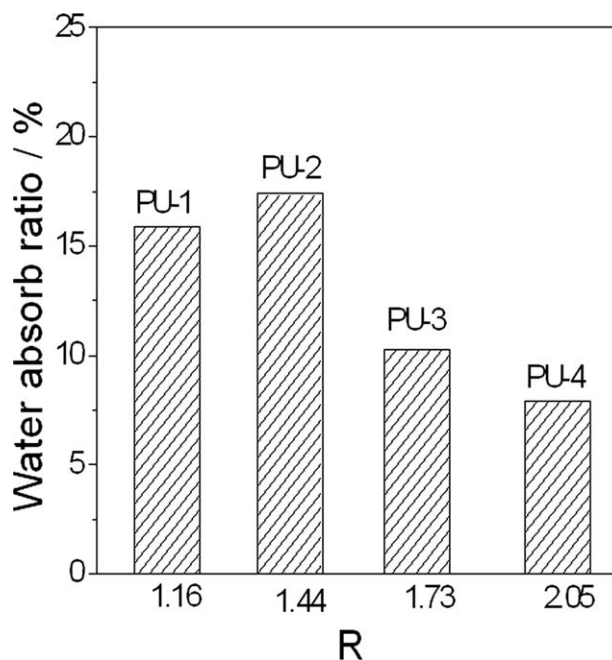


Figure 4 The water absorption of PUD films with different R value.

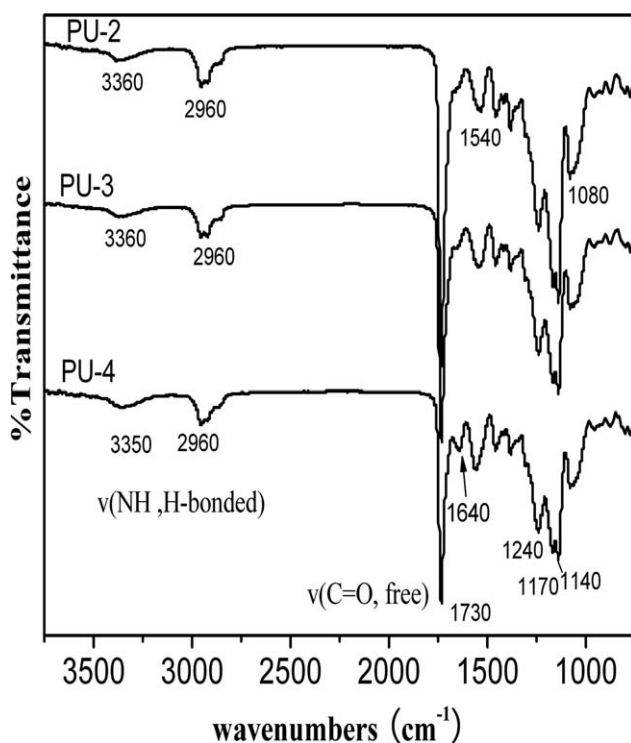


Figure 5 The FTIR spectrum of PUD films.

from diffusing into the area with more rigid hard segments surrounding the soft segments.^{12,13}

In conclusion, comparatively, PU-1 had high water absorption and poor mechanical strength. Besides, PU-1 film was too sticky to characterize the structure and other properties. Therefore PU-2, PU-3, and PU-4 were chosen for further characterization to investigate the structure-property correlation of aliphatic WPU films.

FTIR analysis

Figure 5 shows the IR spectra of WPU with different R values. The WPU chain synthesis reactions were completed by monitoring the complete disappearance of characteristic peaks of NCO groups (at 2270 cm^{-1})¹⁴ as well as the appearance of characteristic absorption peaks at $3350\text{--}3360\text{ cm}^{-1}$ [$\nu(\text{NH})$], 1730 cm^{-1} [$\nu(\text{C}=\text{O})$], 1540 cm^{-1} [$\delta(\text{NH})$], respectively, which are the typical absorption peaks for the spectra of polyurethane.

It has been known that the N—H in urea groups and the carbonyl oxygen in urethane groups can form the hard-hard segment H-bonding as the main intermolecular force between the hard segments.¹⁵ Besides, the N—H in urea groups can also form a little part of hard-soft segment H-bonding with ester oxygen.

The small, broad peaks at $3350\text{--}3360\text{ cm}^{-1}$ indicated the weak N—H hydrogen bondings. Figure 6 is the enlarged FTIR spectrum in the range of $2000\text{--}1000\text{ cm}^{-1}$. Obviously, the absorption in the range of

$1640\text{--}1650\text{ cm}^{-1}$ due to the hydrogen bonded urea $\text{C}=\text{O}$ ¹⁶ slightly shifted to the lower frequency from PU-2 to PU-4 and became stronger at 1640 cm^{-1} in PU-4 indicating the presence of higher number of the hydrogen bonded urea carbonyls.¹⁶ Moreover, the absorption bands between $1530\text{--}1550\text{ cm}^{-1}$ assigned to [$\nu(\text{C}-\text{N}) + \delta(\text{NH})$ amideII] and the bands at 1240 cm^{-1} due to [$\nu(\text{C}-\text{N}) + \delta(\text{NH})$ amideIII]^{17,18} also testified N—H was in the H-bonded state.¹⁹ The small peak at 1170 cm^{-1} was due to coupled C—N and C—O stretching vibration and the peak at 1140 cm^{-1} was due to the asymmetric C—O—C stretching vibration²⁰ from urethane and ester groups. In contrast, the peak intensity ratio of 1240 cm^{-1} to 1140 cm^{-1} gradually increased with the increase of R value, indicating the relative concentration of the hard segments increased.

DSC analysis

Differential Scanning Calorimetric (DSC) study was performed on PU-2, PU-3, and PU-4 films to reveal the structures of the polymers, as illustrated in Figure 7. The glassy transition temperature of the soft segment (T_{g1}) was shifted to lower temperature, indicating that the microphase separation degree is enhanced²¹ by R value increasing. In addition, no clear glass transition points of hard segment in these samples were detected probably due to the relatively less hard segments and consequent lack of hard segment order produced by the less R value. On the other hand, the asymmetrical IPDI structure also prevents from the formation of the highly ordered

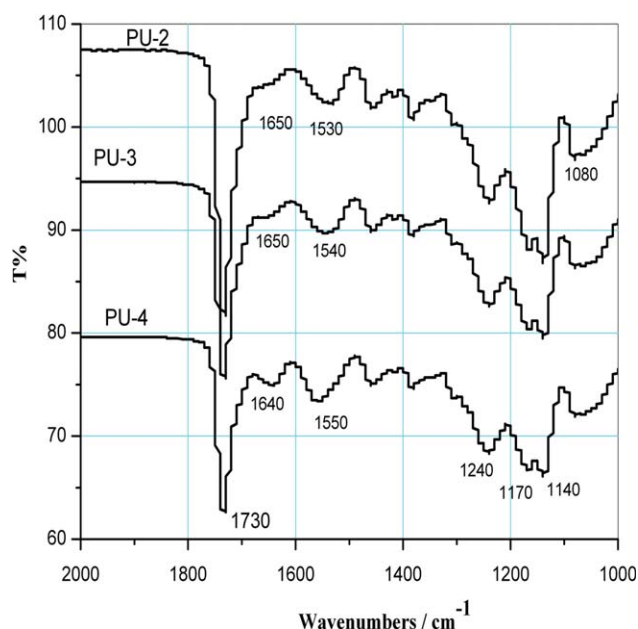


Figure 6 The enlarged FTIR spectrum in the range of $2000\text{--}1000\text{ cm}^{-1}$. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

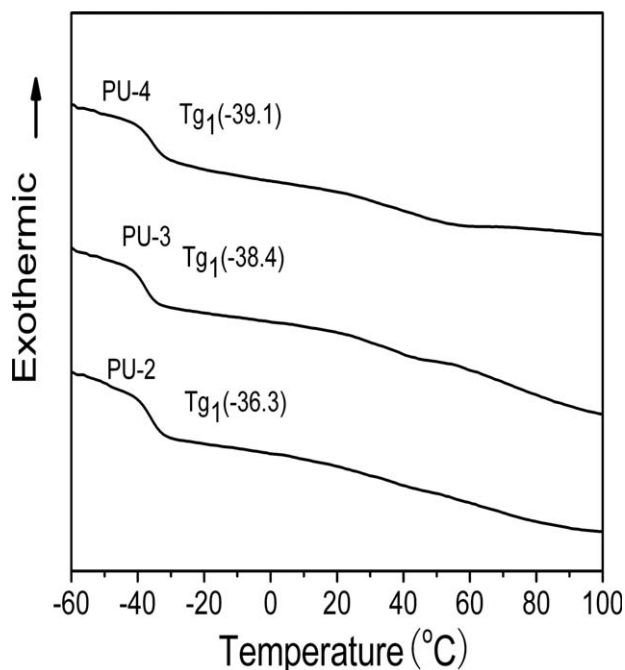


Figure 7 The DSC graphs of WPU films with different R value.

hard segment,²² resulting in the very low heating capacity change above the glass transition of the hard segment,²³ which also accounts for the no evidences of the melting point of the hard segments.

XRD analysis

As shown in Figure 8, the X-ray diffraction (XRD) patterns of PU-2, PU-3, and PU-4 were similar, displaying the typical amorphous morphology. Besides the broad diffraction peak at about $2\theta = 20^\circ$, there were no crystalline peaks emerging in good agreement with the disappearance of the melting temperature in DSC curves.²⁴

It is confirmed that it is the microphase separation rather than the crystallization that determines the mechanical properties, water repellent, and thermal stable properties of the resultant PU structure.

DMA characteristic

Dynamic mechanical analysis (DMA) is utilized to investigate the thermal mechanical properties of WPU films to further understand the structure/property relationships. The storage modulus (E') is a measurement of material stiffness and can be used to provide information regarding the molecular weight of a polymer, degree of cure, and crosslink density.²⁵ The $\tan \delta$ peak corresponds to the glass transition temperature (T_g) of the material designating phase mixed morphology of the segmented

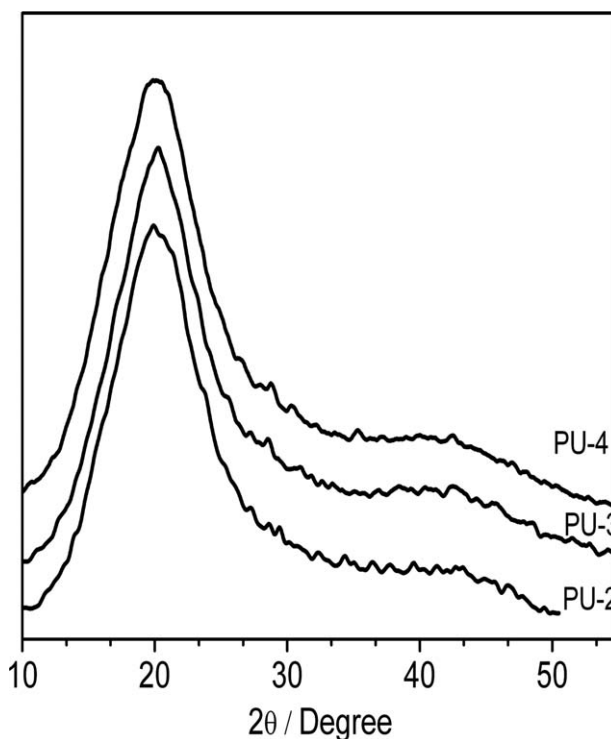


Figure 8 The XRD images of WPU films with different R value.

PU.²⁶ And the loss modulus (E'') value suggests the mobility of the polymer chain associated with the dissipation of energy when the polymer chain is subjected to deformation.²⁷

Figures 9–11 showed the variation of the storage modulus (E'), the loss modulus (E''), and $\tan \delta$ as a

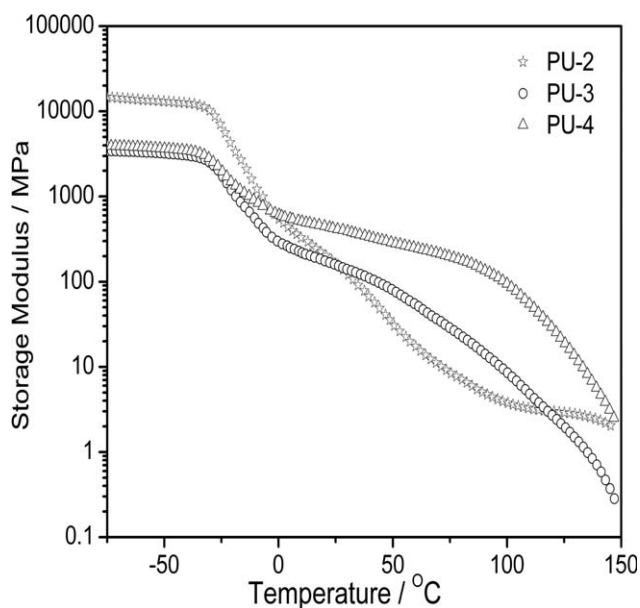


Figure 9 Storage modulus (E') of WPU films with different R value.

function of the temperature, respectively, for WPU films with different R value. As in Figure 9, the rubbery plateau after the initial modulus decrement became gradually wider and the temperature insensitivity increased with R increasing for the range over the hard segment softening temperature was extended by the more urethane and urea groups.²⁸ It was apparent in Figure 11 that the maximum E'' value of PU-2 was predominantly higher than that of the others, due to lack of covalently linked hard segment to restrict the segment motion. Besides, the plateaus in Figure 11 also broadened in response to R increasing.

Figure 10 discloses the microphase separation of these samples. Similar with the DSC results, the T_{g1} of these samples shifted from -15.9°C to -22.0°C in response to the R increasing, confirming again the microphase separation was improved. However, the hard segment glass transition was a little more complicated. The PU-2 sample displayed T_{g2} at ca. 50°C ; while in PU-3, the hard T_{g2} could not be observed but a shoulder peak at ca. 110°C attributed to the possible inter-segmental hydrogen bonding between the soft and urea segments.¹⁸ In PU-4, the high temperature thermal transition disappeared, leaving the $\tan \delta$ value increased infinitely with temperature increasing. From the above information, it can be illustrated that more R value leads to more and stronger hard-hard segment hydrogen bonds, which act as physical cross links, making it difficult for the polymer chain to motion. As a result, a more phase separation can be obtained.

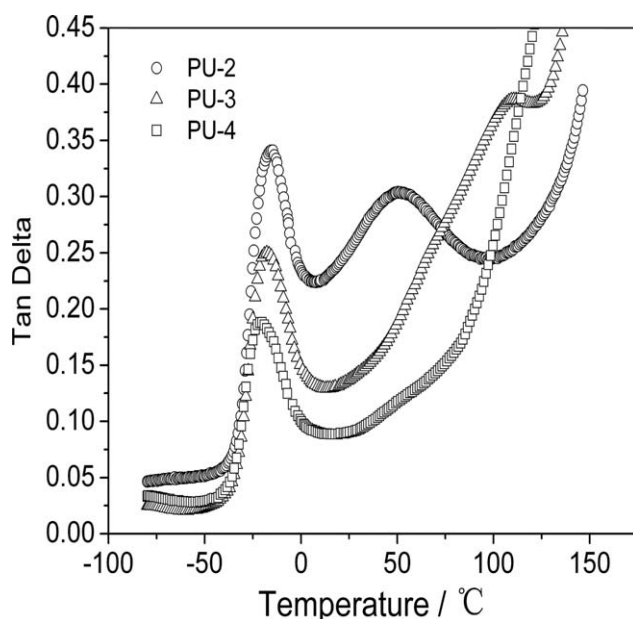


Figure 10 $\tan \delta$ curves of WPU films with different R value.

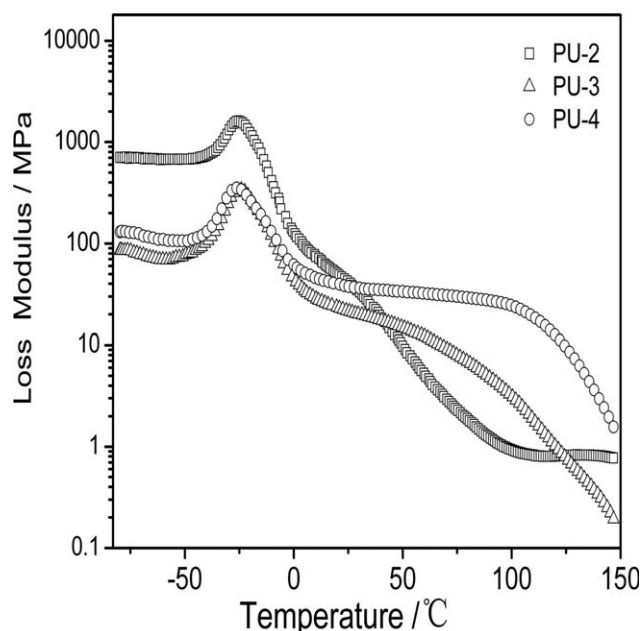


Figure 11 Loss moduli of WPU films with different R value.

CONCLUSIONS

The IPDI-based aliphatic nano-particle WPU dispersions with different isocyanate index (R) were successfully prepared. And the relationships between the structure and the properties were investigated. With the R value increasing, the tensile strength increased to a maximum followed by a small decrement while the elongation at break kept decreasing. The thermal stability also increased by the increase of the R . The water absorptions of PU-3 and PU-4 were obviously lower than that of PU-1 and PU-2, indicating the water resistance was greatly improved when R value was above 1.73. The increase of the R value also resulted in more hydrogen bonds shown in FTIR spectrum. No crystallinity was found by XRD and DSC analyzes showing the typical amorphous morphologies of IPDI-based WPUs. The more hydrogen bonds increased the microphase separation degree in the polymer structure by the analyzes of DSC and DMA. The increased microphase separation was responsible for the improvement on the polymer properties.

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