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Synthesis and Properties of Aliphatic Waterborne Polyurethanes with High Ionic Concentration

Ya Peng,* Guangbin Zhao, Ke Wang, Rongbai Tong, Fei Sun, Fangfang Mei, and Shoutao Lu
School of Material Science and Engineering, XiHua University, Chengdu 610039, P. R. China

(Received April 19, 2011; CL-110328; E-mail: pengyar@mail.xhu.edu.cn)

A series of aliphatic waterborne polyurethane (WPU) dispersions with high ionic concentration were synthesized by prepolymer mixing. The resultant structure–property relationships were investigated. It was revealed that there was a new microphase besides the phase separation between the soft and the hard domains. The new microphase separation found in the hard domains was formed by aggregation of the ionic groups characterized by dynamic mechanical analysis, FTIR characterization, and thermal gravimetric analysis.

Ionic groups introduced into the structure of WPUs play a decisive role in the structure and properties due to the formation of double electric layers, which lead to structural morphology changes of WPUs especially the transformation of microdomains present in the WPU structure with high ionic concentrations. Furthermore, aqueous aliphatic WPUs have attracted much more attentions due to their preferable performances, longer shelf life as well as process maneuverability compared to that of aromatic WPUs.[1] It seems that the absence of benzyl in the WPU structure contributes to the improvement of the resultant properties of WPU films prepared by isophorone isocyanate (IPDI).

The aqueous WPUs with high ionic concentration were synthesized by the following steps: first, after removing moisture, poly(ethylene adipate) glycol reacted with IPDI until the remaining NCO content reaches the theoretical value. Second, 5–8 wt % (of the total prepolymer weight) dimethylolpropionic acid (DMPA) was added to accomplish the prepolymerization. The recipe is shown in Table 1. Then triethylamine (TEA) was added for neutralization following which deionized water was added to disperse with vigorous stirring. Simultaneously, ethylenediamine (EDA) extender was added. Finally, the stable aqueous polyurethane dispersions were obtained.

The increase of DMPA content formed uniform dispersions with particle distribution shown in Figure 1.

The particle sizes and distributions of WPU dispersion were measured by a light scattering ultrafine particle master sizer 2000 analyzer (Master, Britain). The samples were diluted to the required concentration with distilled water before measurement. The particle distribution peaks moved to smaller particle size with increasing DMPA, indicating that the average particle size became smaller and smaller. The maximal number percent of particles of all the samples was below 50 nm, indicating the formation of the nanodispersions. Furthermore, the peak shapes became narrower, indicative that the homogeneity of the dispersions was greatly improved.

The viscosities of the aqueous WPU were measured in a rotational viscometer (NDJ-7, China). Measurements were carried out at 25 °C, using the spindle No. 1 at 75 rpm. In Figure 2, the dispersion viscosity changed greatly responding to the increase of the DMPA content. The hydrophilicity of the polymer was increased by the greater number of ionic groups resulting from the higher DMPA content, which resulted in the increase of the molecular hydration and the decrease of the tangle between the chains. Therefore, the viscosity of the

Table 1. The recipe for the aliphatic WPUs

Sample name	DMPA content /wt %	Hard segment content/wt %	Molar ratio (NCO/OH)[a]
PU1	5.0	35	1.732
PU2	6.0	35	1.540
PU3	7.0	35	1.382
PU4	8.0	35	1.249

[a]NCO/OH: The molar ratio of the isocyanate groups from IPDI to the hydroxy groups from poly(ethylene adipate) glycol and DMPA.

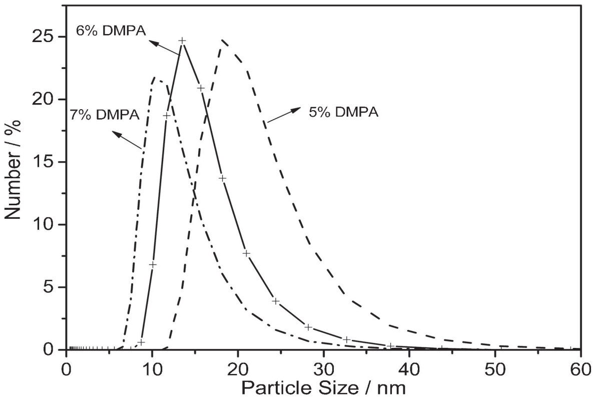

Figure 1. The particle distributions of WPUs with different DMPA content.

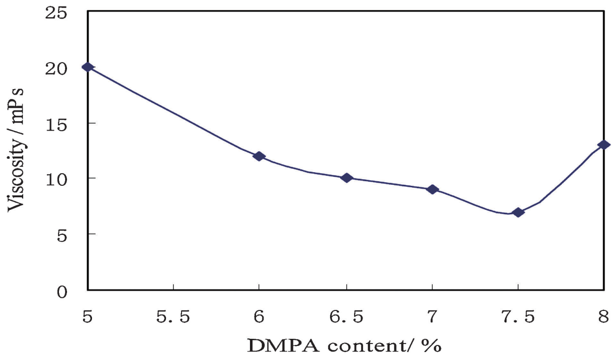

Figure 2. Viscosity of WPU dispersions.

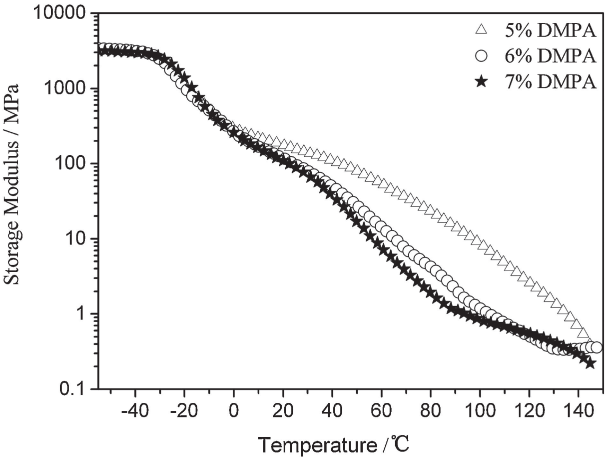

Figure 3. The storage modulus E' of WPU films.

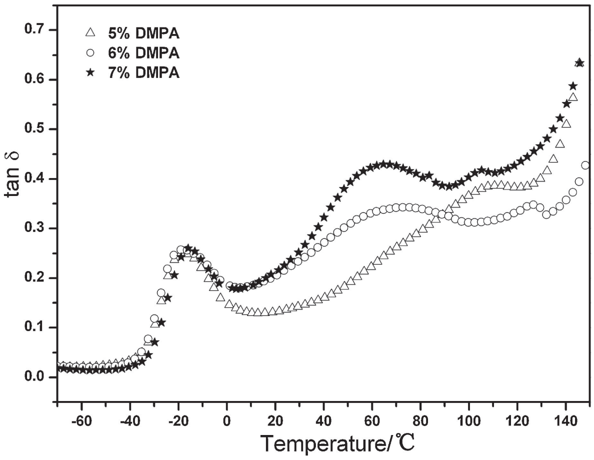

Figure 4. tan δ of WPU films with different DMPA content.

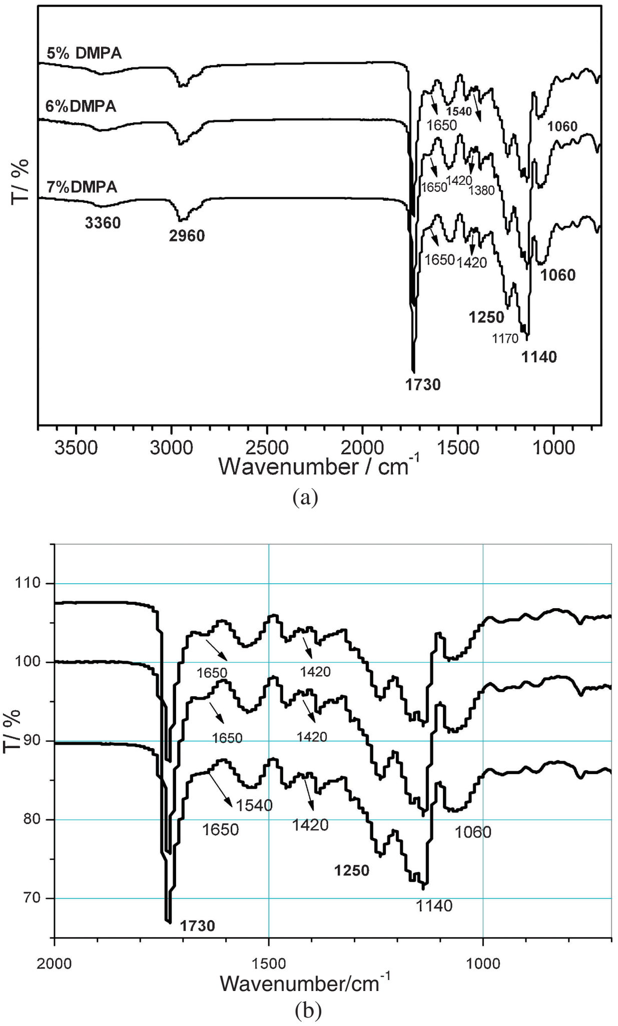

Figure 5. (a) FTIR spectra of WPUs with different DMPA content. (b) The enlarged spectra with 700–2000 $\mathrm{cm^{-1}}$.

dispersion was decreased at first. However, with the number of the ions and counter ions continuously increasing, the electrical viscous effects also increased, leading to the increase of the fluid dynamic volume and the displacement resistance so that the viscosity increased.

The increase of the electrical viscous effects also reflected in viscoelastic properties according to dynamic mechanical analysis. The viscoelastic properties of the polyurethane dispersion (PUD) samples were measured on a viscoelastomer DMA Q800 (TA, USA), with temperature of −80 to 150 °C.

In Figure 3, after the initial rubbery plateau at the range of 28–35 °C, the storage modulus of all the samples began to decrease. When DMPA content was above 6%, in the storage modulus appeared another short plateau above 100 °C in both samples. The new plateaus may result from the more ionic groups.

In Figure 4, the samples displayed a similar glassy transition attributed to the soft segments at about −20 °C, indicating that the ionic concentration did not show much influence on the soft segments. However, the increased ionic concentration as the result of the increase of DMPA content leads to clearly different glassy transition of the hard segments. When DMPA content was 5%, the hard segment displayed a glassy transition at about 110.7 °C. While DMPA increased to 6%, the hard glassy transition shifted to the higher temperature of 126.4 °C. Moreover, at about 70 °C, a moderate tan δ peak occurred, which became more evident when DMPA content was as high as 7%.

The mediate tan δ peak distinct from that of the soft segment and hard segment revealed that a new mediate domain was formed due to the more ionic groups introduced into the polymer structure. These ionic and counter ionic groups tended to aggregate to form a tiny sphere to form the crosslinks interacted by Coulombic forces.[2] The new crosslinked domain alleviated the loss of the storage modulus accounting for the short plateaus in Figure 3.

The microstructure of aliphatic WPU can be explored by FTIR characterization with a NICOLET 500 FTIR spectrometer (NICOLET, USA). Measurements were carried out by attenuated infrared total reflectance (ATR).

As shown in Figure 5, clearly the successful synthesis of WPUs was shown by the disappearance of a characteristic NCO peak at 2270 $\mathrm{cm^{-1}}$ and the appearance of some typical absorption peaks that are indicative of the strong bonds of C=O at 1730 cm^{-1},[3] the stretching vibration of hydrogen-bonded N–H at 3360 cm^{-1}, and deformation vibration of N–H at 1540 cm^{-1}.[4]

On the one hand, the systematic vibration peaks of carboxylate at 1420 cm^{-1} intensified, indicating the number of carboxylates in the structure increased due to the increase of the DMPA content. More and more $COO^-NH_4^+(C_2H_5)_3$ carboxylates formed ionic pairs by negatively charged carboxyl groups COO^- and positively charged ammonium groups $NH_4^+(C_2H_5)_3$. On the other hand, as shown in Figure 5b, the absorptions of hydrogen-bonded urea groups at 1650 cm^{-1} gradually weakened showing the hydrogen bonds decreased due to more N–H participating in the ionic groups.[5] Because of the attractive interaction, more and more ions aggregated to form the new domains interacting by Coulombic forces.

However, the new domain was influenced by the mutual interaction of the hydrogen bonds and the Coulombic forces resulting in the delicate changes of the microphase separations in the WPU structure.

As in Figure 4, the vitrification points of the hard segments shifted to lower temperature at about 105 °C when DMPA increased from 6% to 7%, contrary to the transition when DMPA increased from 5% to 6%. It indicated that the microphase separation between the soft and the hard segments had decreased due to the presence of the new domain.

While it was discovered that the microphase separation also could be evaluated by thermal gravimetric analysis (TGA) which was performed on a SDTQ600 instrument (TA, USA). 3–6 mg samples were deposited in an aluminum pan and heated from 30 to 500 °C under N_2, at a heating rate of 10 °C min^{-1}.

It has been recognized that the degradation of polyurethane can be mainly divided into three processes: the first degradation step corresponds to the urethane group decomposition; the second belongs to the urea group decomposition, while the last is the degradation of the soft domains,[6–8] corresponding to the mainly three peaks from DTG curves.

In Figure 6, a sample with 7% DMPA content displayed several small decomposition peaks due to the release of more volatile compounds derived from more quaternary ammonium salts compared to samples with lower DMPA content. The first process at around 200 °C is attributed to the degradation of urethane groups. The second peak is attributed to that of the urea groups. And the last is associated with that of the soft domains. The three integrate peaks described the phase distribution in the WPU structure. In addition, when DMPA content increased from 5% to 6%, the maximum decomposition peaks of the urea and the soft domains shifted to higher temperature, which behaved inversely when DMPA content increased to 7%. The shift of the decomposition peaks revealed that by increasing DMPA content, the microphase was improved as DMPA content dropped below 6%, but when DMPA was 7%, the microphase decreased instead. Properly the new domain formed by the aggregated ions retarding the microphase separation between the soft and the hard segments of which the mechanism should be further studied in the future.

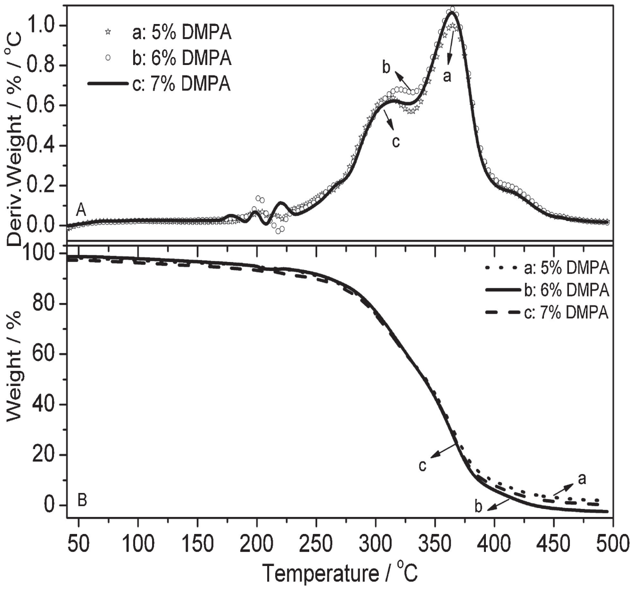

Figure 6. TGA curves of WPU films with different WPU content.

In summary, we changed the ionic groups introduced to the IPDI-based waterborne polyurethanes by changing the DMPA content. The results showed that the increase of the ions and counter ions contributed to the conformation of the new domain within the WPU structure which made important effects on the microphase separation between the soft and the hard segments.

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