Thermal and Crystalline Properties of Water-borne Polyurethanes Based on IPDI, DMPA, and PEBA/HNA

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ABSTRACT: A series of water-borne polyurethanes (WPUs) with different soft segments, various COOH contents, and various hard segment contents were prepared through a prepolymerization process. Thermal and crystalline properties of their films were studied by the measurement of differential scanning calorimetry (DSC), X-ray diffraction (XRD), and thermogravimetry (TG), respectively. Two T_g areas in DSC of WPUs with polyethylene-butylene adipate glycol (PEBA) as the soft segment were found; an endothermic peak at $\sim 33°$C was also found with polyhexane neopentyl adipate glycol (HNA) as the soft segment. The DSC of WPUs with the mixture of PEBA/HNA as soft segment was investigated to show similarity to those from HNA, but with a relatively smaller endothermic peak at $\sim 34°$C. Three sharp diffraction peaks at $2\theta = 20.50°$, $21.72°$, and $24.54°$ in XRD of water-borne PUs from HNA were found to indicate the crystallization of soft segments, which was disrupted by the addition of polyacrylate (PA), as evidenced by the amorphous shoulder at $\sim 2\theta = 20°$. TG analysis and differential thermogravimetric (DTG) analysis were measured to indicate that the films lost weight in two stages, and the decomposition temperatures of the films depended on the COOH content. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 1936–1941, 2007

Key words: polyurethanes; thermal properties; crystallization; TGA

INTRODUCTION

Since Schlack[1] first reported the formation of water-based PUs in 1942, the study in ionic polyurethanes became popular. Until 1970, potentially more industrially significant segmented polyurethane ionomers were synthesized by Dieterich et al.[2] WPUs can be defined as binary colloidal systems in which PU particles are dispersed in continuous aqueous media.[3] WPUs have been given great importance, due to environmental and legislative pressures.[3–5] The polymer can be tailored for a specific application by varying the chemical structure of the soft segments, the distribution and length of the hard segments or the molecular weight and degree of branching of the chains. In contrast to the solvent-borne polyurethanes, where the PUs form solutions in solvents, the WPUs exist as aqueous dispersions, and these have found applications in the automobile, construction, furniture, adhesive, and textile industries. The preparation and properties of anionic polyurethane dispersions have been fully researched.[6–13] The increasing acceptance of WPU is motivated by more stringent environmental requirements.[14,15] In addition, the superior quality of WPUs over solvent-bornes is also a cause.[6,8]

Phase segregation of linear block polyurethanes due to thermodynamic incompatibility between the hard and soft segments is a common phenomenon, which contributes in part to the excellent physical properties of PUs. It has been shown that the hard segments govern the hardness, strength and toughness of the polymers, the soft segments determine the flexibility and glass transition temperature.[16–18] Although many papers have dealt with the study of phase separation of PUs, many have been related to solvent-borne PUs[19–21]; for water-based PUs, an undiscovered area remains to be explored. In our previous article,[22] partial crystallization of water-borne was proved by IR. This article is a continuing study that focuses on the thermal and crystalline properties of WPUs through differential scanning calorimetry (DSC), X-ray diffraction (XRD), and thermogravimetry (TG) methods. We hope to provide some findings and explanation thereof for advancing the research of WPU science.
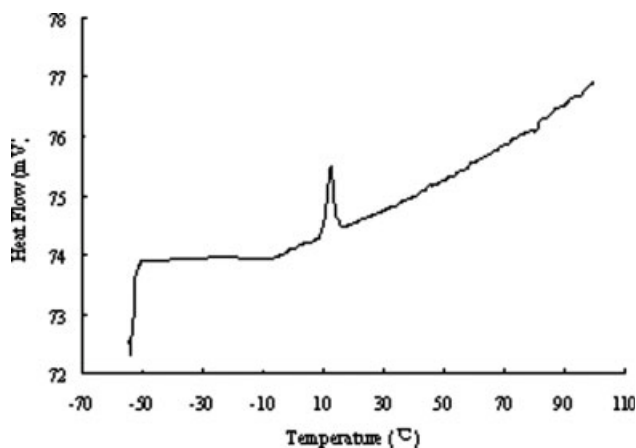
Figure 1 Differential scanning calorimetry of PEBA.

EXPERIMENTAL

Materials

Isophorone diisocyanate (IPDI) (Degussa, Germany) was used as received. Dimethylolpropionic acid (DMPA) (Bayer AG, Germany) was dried at 105°C, and HNA (MW = 2,000) and PEBA (MW = 2,000) (Yantai Huada Chemicals, People's Republic of China) was dehydrated at 120°C under vacuum before use. N-Methylpyrrolidone (NMP) was dried over 4 Å sieves before use. All percentages are by weight throughout the present work, unless otherwise indicated.

Preparation of prepolymers

Polyester diol was dehydrated in a reaction kettle equipped with a thermometer, stirrer, inlet, and outlet of dry nitrogen, and heating jacket at 120°C under vacuum for 2 hours. After cooled to 80°C, IPDI, 0.1% dibutyl tin dilaurate (DBTDL), and DMPA dissolved in NMP were placed simultaneously in the kettle with stirring. The reaction was carried out under the protection of a dry nitrogen atmosphere in a constant temperature of 80°C for ∼ 5 h to obtain NCO-terminated prepolymer. The NCO group content by weight was measured by titration with dibutylamine.

Chain extension of prepolymers

On achieving the theoretical NCO value, the prepolymer was neutralized with triethylamine at the same temperature for 10 min, followed by cooling to 50°C; an emulsion was obtained on the addition of deionized water to the reaction mixture under rapid stirring for 5 min. Ethane diamine dissolved in water was added dropwise for 5 min. This reaction kettle was kept at 50°C for another 2 h to finish the chain extension. The milky-white product was a PU anionomer dispersion with a solid content of ∼ 35%. Films from

the samples were prepared by pouring the dispersion into an aluminum mold coated with a release agent. The films were allowed to dry at room temperature for 2 days. The residual solvent was removed by placing the films overnight into a vacuum oven at 40°C. These films were then used for DSC, XRD, and TG analysis.

Differential scanning calorimetry

DSC thermograms, under nitrogen and over the temperature range −70–200°C were obtained using a Diamond DSC (Perkin-Elmer) apparatus at a heating rate of 10°C min^{-1} and ambient loading temperature, with sample weights of 10–15 mg.

X-ray diffraction

The crystalline properties of samples were examined with a D/Max 2400 automatic X-ray diffractometer (Rigaku) using Cu K$_\alpha$ radiation (40 kV, 100 mA).

Thermogravimetric analysis

TG was carried out using a TGA/SDTA851^e thermogravimetric analyzer (Mettler-Toledo), with sample weights of 5–10 mg. Runs were performed from 50 to 600°C, at a heating rate of 5°C min^{-1} in a nitrogen atmosphere. Before thermal analysis, the samples were well dried in a vacuum oven at room temperature.

RESULTS AND DISCUSSION

DSC of HNA and PEBA

The DSC of raw materials, HNA and PEBA, were measured to show there was an endothermic peak at ∼ 13°C for PEBA as shown in Figure 1, while there were two endothermic peaks for HNA 20°C and 40°C, respectively, as shown in Figure 2. It was suggested
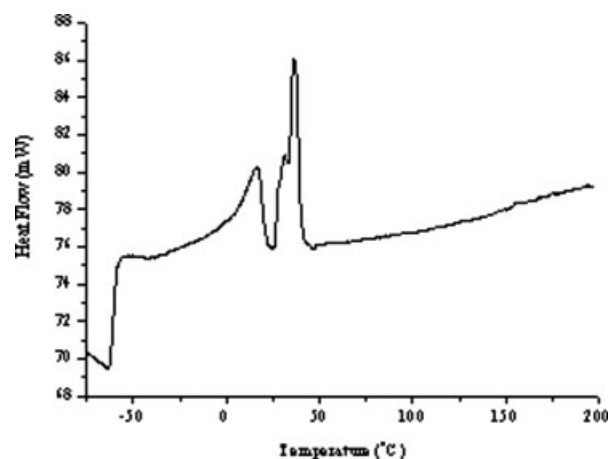

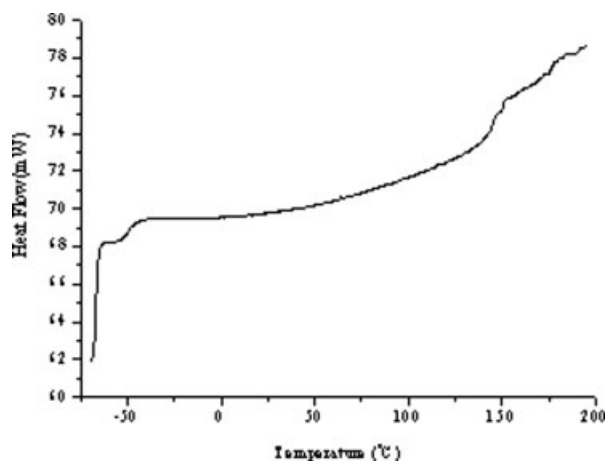**Figure 2** Differential scanning calorimetry of HNA.

Figure 3 Differential scanning calorimetry of a water-borne polyurethane based on PEBA.

that these endotherms reflected the melting behavior that was associated with the disappearance of the long-range order.[23] Therefore, the melting point of PEBA was ~ 13°C, whereas HNA had two melting points, indicating that this compound was not homogeneous, and partial crystallization in the DSC could also give different crystal size populations. The DSC difference between PEBA and HNA may be one of the reasons for the different properties of products therefrom. The T_gs of PEBA and HNA are believed lower than −50°C, so their T_gs do not show in Figures 1 and 2.

DSC of WPUs

The DSC of WPUs from PEBA showed typical characteristics of PU DSC with two T_gs: soft segments at a
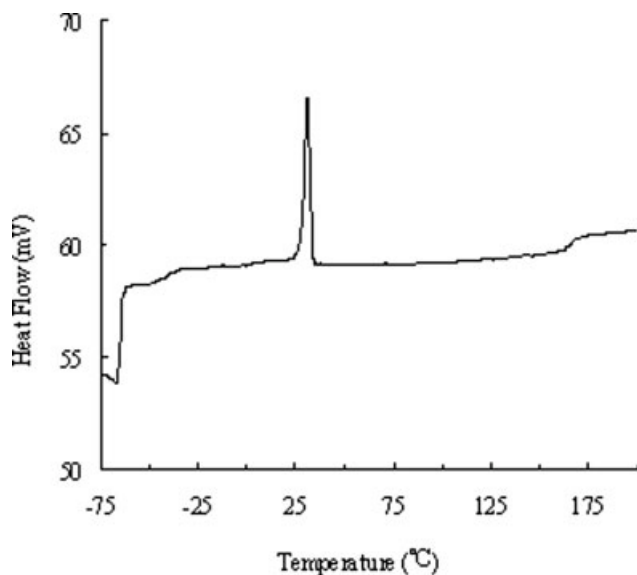

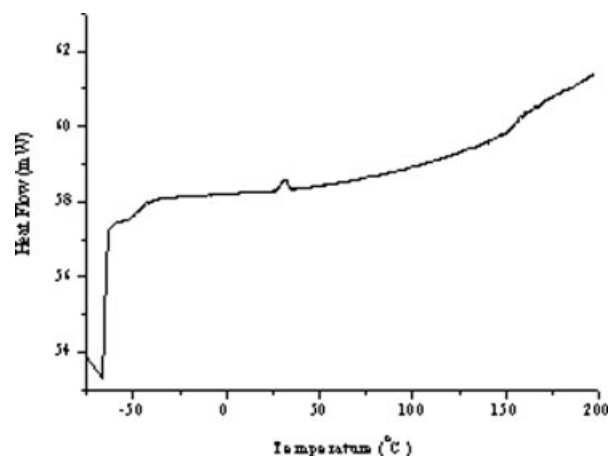**Figure 4** Differential scanning calorimetry of a waterborne polyurethane based on HNA.

Figure 5 Differential scanning calorimetry of a waterborne polyurethane based on the mixture of PEBA/HNA.

lower temperature of ~ −40°C, and hard segments at a higher temperature of ~ 150°C, as shown in Figure 3. It has been suggested that two phases exist in PUs: hard microdomains and soft microdomains with some trapped hard segments.[24,25] The hard segments are often composed of a diisocyanate reacted with a diol or a diamine chain extender or DMPA. The soft segments are a low-molecular-weight α–ω hydroxyl-terminated polymer. The T_g of soft segment was ~ −40°C higher than that of PEBA itself. The increase suggested that hard segments were dispersed in soft segments, and the chain mobility of the soft segments was restricted by the trapped hard segments, bringing about an elevated T_g of the soft segments. It has been proved that a higher extent of phase mixing could cause shifts of T_g to higher temperatures, and the extent of mixing of hard and soft segments in PUs was reflected, at least qualitatively, by the T_g of the soft segments.[26]

The curve of WPUs from HNA also showed two T_gs: one at −38.4°C and the other at 162.5°C, and a difference from PEBA with an endothermic peak at 33.4°C as shown in Figure 4. It has been suggested that the endotherms attributed to the disappearance of long range order or the microcrystal in the hard segment microdomain in PU DSC often occur within the temperature range of 160–220°C.[8] The endothermic peak appearing at 33.4°C was attributed to the crystallization of soft segments in WPUs from HNA. The same result has been published by Phillips et al.[27]

TABLE I
T_g of Soft Segments of PEBA PU Series at Different COOH and Hard Segment Contents

Hard segment content	23%	26%	29%
COOH = 0.8%	−42.3	−41.6	−40.3
COOH = 1.0%	−43.5	−40.4	−39.4
COOH = 1.2%	−40.4	−40.7	−40.8

TABLE II
T_g of Hard Segments of PEBA PU Series at Different COOH and Hard Segment Contents

Hard segment content	23%	26%	29%
COOH = 0.8%	149.7	—	166.9
COOH = 1.0%	146.8	151.9	—
COOH = 1.2%	158.6	—	−161.0

TABLE III
Assignment of Peaks in Figure 6

Peak no.	2θ	FWHM	d-value	Intensity	I/I$_0$
1	9.28	0.188	9.5220	886	18
2	20.50	0.424	4.3288	4876	100
3	21.72	0.188	4.0883	4336	89
4	24.54	0.212	3.6245	2663	55
5	28.42	0.282	3.1379	1357	28
6	29.20	0.165	3.0558	1056	22
7	32.44	0.212	2.7576	1312	27

and Yang et al.[28] Figures 3–5 showed that the hard segments exhibited very little crystallinity, which may be attributed to the various configurational and conformational isomers possible in the hard segments, which increased the degree of the morphological form.

It was amazing that WPUs from PEBA did not have the melting point of a soft segment according to Figure 3. The reason may arise from the morphology of soft segment from PEBA or more mixing between hard segment and soft segment, the study about that is being undertaken. The DSC of WPUs from the mixture of PEBA/HNA (1 : 1 by weight) (Fig. 5) showed similarity with the ones from HNA, but with a relatively smaller endothermic peak at 34.3°C. That indicated PEBA type WPUs could reduce the degree of crystallinity of soft segments of WPUs based on HNA. It was suggested that the crystallization of soft segments in PUs could be adjusted through mixing different polydiols, and consequently resulting in the modification of physical properties.

The T_gs of soft segments with different COOH and hard segment contents are listed in Table I, and the T_gs of hard segments in Table II. When COOH contents were 0.8% and 1.0%, there was a slight increase of T_g with the increase of hard segment content, this trend was not found with 1.2% COOH content. Cooper et al.[29,30] reported that the increase of the hard segment content increased the extent of phase mixing, as indicating by the higher T_gs of the soft segment.
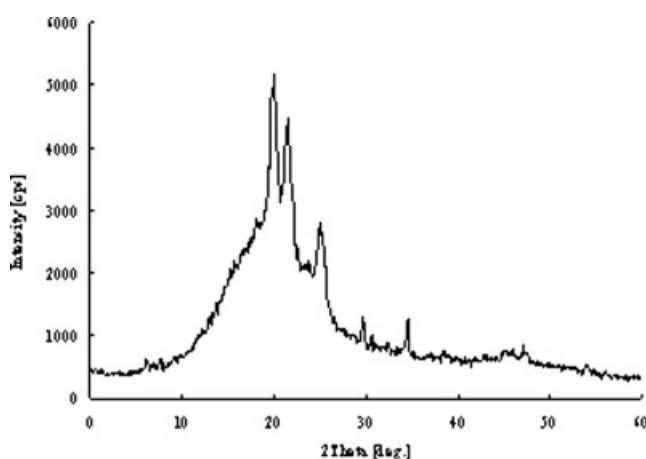
Ahn et al.[31] found that when the concentration of hard segments dissolved in soft domains decrease, T_g of soft segments will tend to shift to its original T_g. Frisch and colleagues[8] proposed that the increased hard segment content tended to promote irregularity in packing of the hard segments, resulting in domains of lower density and crystallinity because of the increase in the concentration of the pendant salt groups. The effect of hard segment content on T_gs seems no a constant rule to be conformed to, though it is generally believed that there is a slight increase of T_g with the increase of hard segment content. As only ~1% of COOH was incorporated into the anionomers, according to Tables I and II, T_gs presented irregularity with different COOH contents. It should be pointed out that the effects of COOH and hard segment contents on T_gs are very complicated, which may closely correlate with the systems studied.

X-ray diffraction of WPUs

The crystallization of WPUs from HNA was proved by XRD. Figure 6 and Table III shows the XRD pattern and the intensity of peaks. Three sharp and clear diffraction peaks at 2θ = 20.50°, 21.72°, and 24.54° were presented in Figure 6. This was due to the crystalliza-

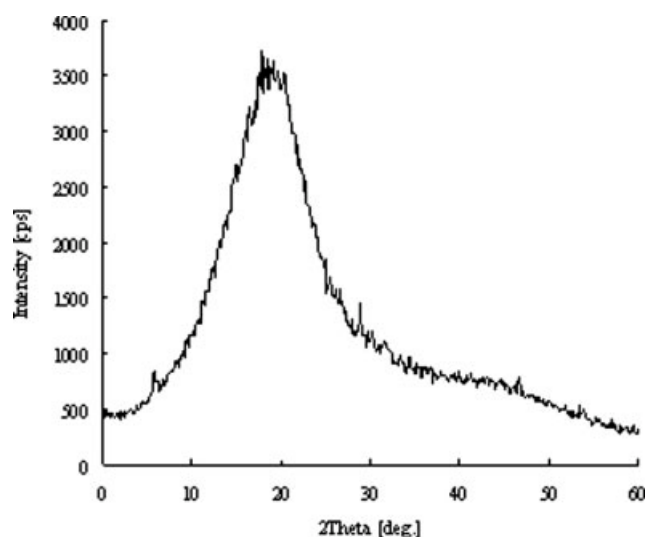**Figure 6** X-ray diffraction of a water-borne polyurethane based on HNA.

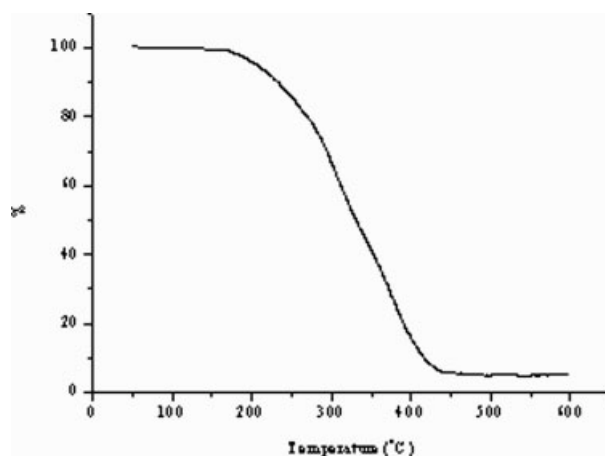**Figure 7** X-ray diffraction of the mixture of PU/PA.

Figure 8 Thermogravimetry of a water-borne polyurethane.

tion formation resulting from the HNA component in the soft segment. It has been suggested that the PCL component in the soft segment showed two peaks at $2\theta = 21.5°$ and $23.9°$.[32] This was consistent with the DSC of WPUs from HNA in which there existed an endothermic peak at $\sim 34°C$ indicating the crystallization of soft segments. These sharp peaks in Figure 6 disappeared as shown in Figure 7 when PA was added to the PU system. The addition of PA was believed to disrupt the order of soft segments, and an amorphous shoulder around $2\theta = 20°$ became evident; a similar result was also reported by Kim et al.[4]

Thermogravimetric analysis

TG and DTG curves of the films of WPU based on HNA are shown in Figures 8 and 9, respectively. The curve in DTG indicated that there were different stages of degradation, which was not perceptible in TG curves. It has also been proved that the amount of weight loss of the first region was well correlated with
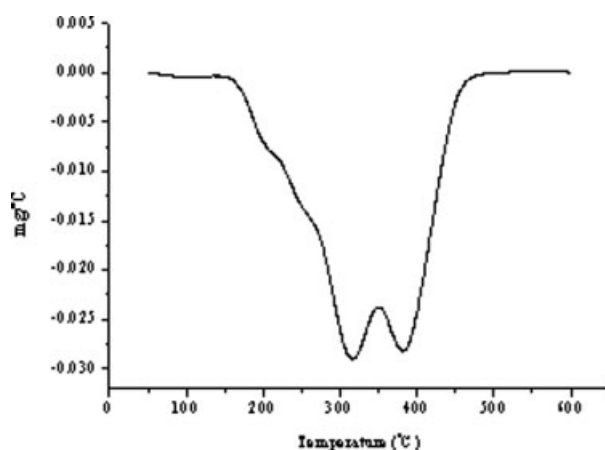

Figure 9 Differential thermogravimetry of a water-borne polyurethane.

TABLE IV
Effect of COOH Content on TG of WPUs

COOH (%)	Onset (°C)	T_{10} (°C)	T_{50} (°C)
0.8	253.17	238.57	335.98
1.0	332.07	295.88	367.89
1.2	346.68	304.06	385.97

the hard segment concentration, suggesting that the degradation started in the hard segment.[33,34] Thus, it is generally believed that soft segments are more thermal-stable than hard segments in two stages of film weight loss. The first part of the degradation corresponded to the hard segment starting at $250°C$, while the second peak corresponded to the degradation of the soft segment at $350°C$, as shown in Figure 9. The initial loss of films resulted from the degradation of hard segments with the cleavage of a N—C bond[33,35]; thus, the first observable weight loss occurred through degradation of the urea or urethane groups.[16]

Wang and Hsieh[17] reported that decomposition temperatures increased with the increase of soft segment proportions. Ethylene diamine was used as chain extender by us, as thermal stability is higher when a diamine chain extender is used, in comparison with a diol, probably because of the higher hydrogen-bonding capacity of urea groups.[18] The decomposition temperature of PU is mostly influenced by the chemical structure of the component having the lowest bond energy.[36] It has been proposed that the decomposition of polyurethanes generally follows a combination of two reactions.[7] The two reactions can be incorporated here for the explanation of TG. The decomposition temperatures were correlated with the COOH content in WPU according to Table IV, indicating that the decomposition temperatures increased with the increase of COOH content. This may result from the formation of salts presented in the PU structure whose content increases with increasing the COOH content.

CONCLUSION

The synthesis, thermal property, and crystalline property of WPUs with different soft segments, COOH content, and hard segment content have been described. Two T_g areas in DSC of WPUs with PEBA as soft segment were found, whereas WPUs from HNA not only presented two T_g areas, but also an endothermic peak at $33.4°C$, which was presumed to be due to the crystallization of soft segments. The DSC of WPUs from the mixture of PEBA/HNA showed similarity with those from HNA, but with a relatively smaller endothermic peak at $34.3°C$. The effects of COOH and hard segment content on T_g were more complicated, so that no rule was found in the study. The crystallization of soft segments was

proved with three sharp and clear diffraction peaks at $2\theta = 20.50°$, $21.72°$, and $24.54°$ by XRD indicated the crystallization of soft segments in WPUs, which was disrupted by the addition of PA, this was evidenced by the amorphous shoulder around $2\theta = 20°$. Two stages of weight loss in DTG were discovered, the first part corresponded to the degradation of hard segments, and the second peak corresponded to the degradation of the soft segment. The decomposition temperatures increased with increased COOH content. This investigation may present useful information for further study of thermal and crystalline properties of WPUs.

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