



Synthesis of Acrylic Acid/Polyurethane Hybrid Emulsions and Characterization on the Properties for Acrylic Acid/Polyurethane Films†

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AJC-11282

The acrylic acid/polyurethane (PUA) hybrid emulsion was prepared by water-borne polyurethane (WPU) modified with acrylic acid. The morphology of acrylic acid/polyurethane latex was characterized by FTIR, TEM and a light scattering method. The results displayed that the size of core-shell particles was between 60-120 nm. The result of FTIR indicated that the hydrogen bonding interaction in water-borne polyurethane changed with the addition of acrylic acid. The results of DSC indicated that the phase separation existed obviously in acrylic acid/polyurethane when acrylic acid reached 75 wt %. With the increasing of acrylic acid in the hybrid emulsions, the thermal stability, mechanical properties and water resistance of acrylic acid/polyurethane were improved.

Key Words: Hybrid emulsion, Water resistance, Mechanical properties.

INTRODUCTION

As a type of environmental friendly material, water-borne polyurethane (WPU) has been developed largely because of its excellent mechanical properties¹. However, some properties of water-borne polyurethane such as water resistance and weather resistance need to be improved further^{2,3}. On the other hand, water-borne acrylic resins (PA) have also been widely applied because of their good mechanical properties and high water resistance. But acrylic resins will become brittleness at low temperature. To improve the properties of an individual polymer system it is common to mix water-borne acrylic acid and polyurethane dispersions⁴. However, direct blending of water-borne acrylic resins emulsion and polyurethane dispersion results in the film with properties of lower quality because of limited compatibility between polyurethane and water-borne acrylic resins. In order to improve the properties of the mixture, IPN technology has been used to prepare hybrid water-borne polyurethane resin⁵.

In this paper, the acrylic acid/polyurethane hybrid emulsions (PUA) were prepared. The structure of acrylic acid/polyurethane was studied by FTIR. The thermal properties, the mechanical properties and water resistance were also characterized.

EXPERIMENTAL

The water-borne polyurethane dispersions can be obtained by used IPDI, PC-100, DMPA and HPMA. As the acrylic component a mixture of butyl acrylate (BA) and methyl methacrylate (MMA) in the mass ratio 1:1 was used. A series of acrylic acid/polyurethane hybrid emulsions with different acrylic mass ratio were prepared by emulsion polymerization of acrylic monomers in presence of water-borne polyurethane dispersion. The recipe for acrylic acid/polyurethane was shown in Table-1.

TABLE-1
RECIPE AND THE MORPHOLOGY FOR THE ACRYLIC ACID/POLYURETHANE HYBRID EMULSIONS

Samples	Mass ratio of acrylic monomers to WPU	Average diameter for particles (nm)	Stability (six months)
PU	0:100	35.2	Stability
PUA-20	20:80	56.9	Stability
PUA-35	35:65	66.4	Stability
PUA-50	50:50	93.8	Stability
PUA-75	75:25	125.6	Instability
PA	100:0	45.7	Stability

PU = Polyurethane; PUA = Acrylic acid/polyurethane; WPU = Water-borne polyurethane.

†Presented to The 5th Korea-China International Conference on Multi-Functional Materials and Application.

The average diameters of the emulsions were measured by a light scattering method, using a He-Ne laser with a wavelength of 633 nm. The TEM photograph for acrylic acid/polyurethane was performed on samples stained by exposure of the ultrathin sections to vapors of 0.5 wt % aqueous solution of RuO₄ for 0.5 h. The FTIR spectra for acrylic acid/polyurethane films removed the remaining monomers were recorded. In the DSC apparatus, the film samples eliminated the thermal history were heated at a rate of 20 °C min⁻¹ from -120 to 150 °C. The second scanning curves were recorded. Thermogravimetric experiments were performed with a heating rate of 20 °C/min from 50-600 °C, under N₂ atmosphere.

The mechanical properties of acrylic acid/polyurethane films were measured at 20 °C with across-head speed of 20 mm/min. The specimens of casted films were 30 mm × 30 mm. The water resistance of acrylic acid/polyurethane films was characterized by the degree of swelling. Dried films (30 mm × 30 mm; W₀) were immersed in water for 24 h at room temperature. After the residual water was wiped from the films using filter paper, the weight (W₁) was measured immediately. The degree of swelling was calculated as follows:

$$\text{Degree of swelling (\%)} = \frac{(W_1 - W_0)}{W_0} \times 100 \quad (1)$$

RESULTS AND DISCUSSION

Morphology of acrylic acid/polyurethane emulsions:

Fig. 1 gives the TEM photograph for acrylic acid/polyurethane. The polyurethane portion was stained by RuO₄ and appears dark as a shell layer outside the emulsion particle⁶. The core-shell structure of acrylic acid/polyurethane is observed and the boundary is indistinct.

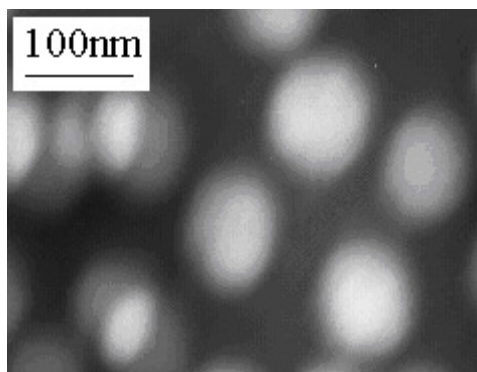


Fig. 1. TEM micrographs of acrylic acid/polyurethane-35

The average diameters of the emulsions were shown in Table-1. It can be seen that the average diameters for all sample particles are less than 150 nm. With the increasing of acrylic particles, the average diameter increases. The acrylic monomers have to diffuse into the inside of the polyurethane microspheres before copolymerization. With the acrylic acid increasing, the diffusion resistance and the volume of the core increase and the storage stability of the emulsions is weakened.

FTIR for acrylic acid/polyurethane films: Fig. 2 displays FTIR spectra for polyurethane and acrylic acid/polyurethane. Comparison to polyurethane, the characteristic bands of acrylic can be observed at 1460, 1380 and 1160 cm⁻¹ obviously in

acrylic acid/polyurethane spectrum. The absorption band of NH groups shifts from 3375-3340 cm⁻¹, this indicates that the hydrogen banding interaction strengthens in acrylic acid/polyurethane. Because the mass ratio of acrylic arrives 50 % in acrylic acid/polyurethane sample, the band for C=O groups appears at 1733 cm⁻¹ and the absorption peaks of urethane C=O and ester C=O form shoulder.

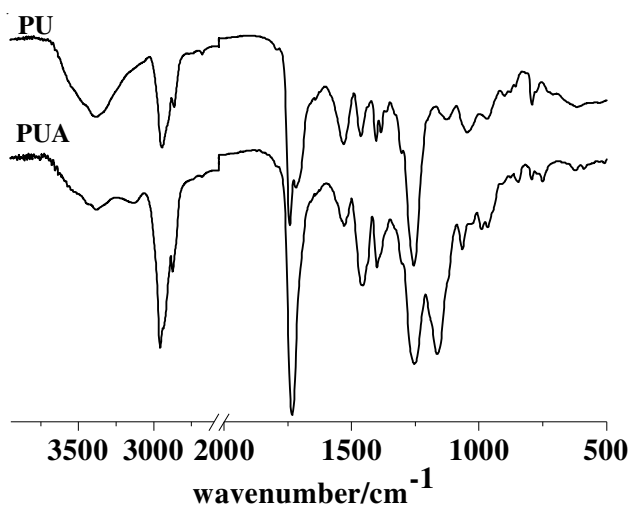


Fig. 2. FTIR spectra of polyurethane and acrylic acid/polyurethane

Thermal properties of acrylic acid/polyurethane films:

DSC curves for acrylic acid/polyurethane films are shown in Fig. 3. No endothermic peak is observed. Only one T_g has been observed for acrylic acid/polyurethane-20, acrylic acid/polyurethane-35 and acrylic acid/polyurethane-50 between -34 and -10 °C (T_g for water-borne acrylic resins), which indicates polyurethane chains and acrylic chains in acrylic acid/polyurethane are compatible. When water-borne acrylic resin chain is above 75 %, the degree of phase separation increases and two glass transition temperatures attributed to water-borne acrylic resins and polyurethane, respectively are observed.

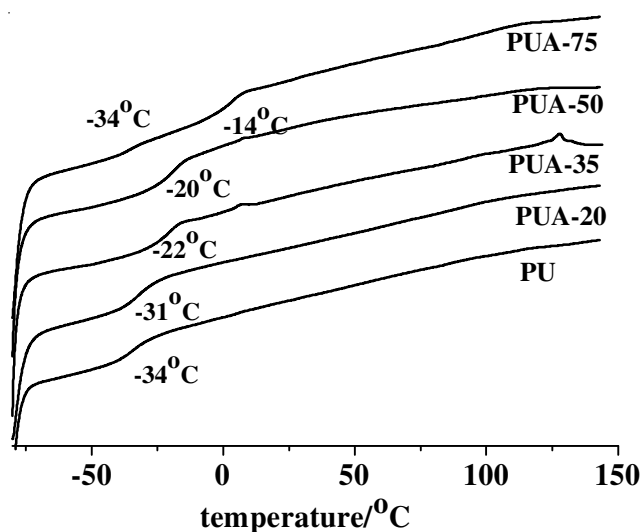


Fig. 3. DSC curves of polyurethane and acrylic acid/polyurethane

Fig. 4 displays DTG curves for samples. The curves indicate the decomposition of polyurethane and water-borne acrylic resins begins at about 200 and 280 °C and the largest

thermogravimetric rate (T_{max}) at 363 and 422 °C, respectively. All acrylic acid/polyurethane samples decompose by two steps: polyurethane chains are at lower temperatures and water-borne acrylic resins chains at higher temperatures. But with increasing of the content of water-borne acrylic resins chains, the T_{max} of polyurethane chains shifts to higher temperature and of water-borne acrylic resins chain shifts to lower temperature. It is obvious that the thermal stability of acrylic acid/polyurethane is improved.

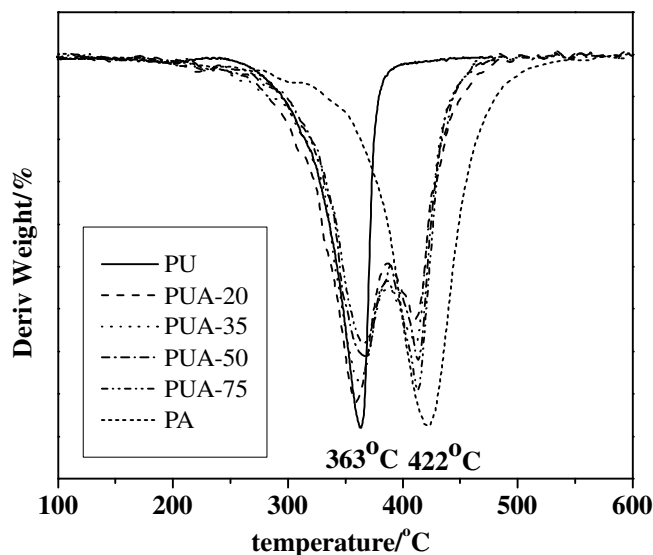


Fig. 4. DTG curves of polyurethane and acrylic acid/polyurethane

Mechanical properties and water resistance of acrylic acid/polyurethane films: The mechanical properties of at least three measurements of each sample are shown in Fig. 5. With the content of acrylic acid increasing, the tensile strength and the elastic modulus of acrylic acid/polyurethane increase until the content of acrylic acid reaches 75 %. These results may be induced by the phase separation occupied in acrylic acid/polyurethane.

The water resistance results are also shown in Fig. 5. Comparison to polyurethane, the value of degree of swelling decreases obviously for acrylic acid/polyurethane. polyurethane modified by acrylic acid has better water resistance.

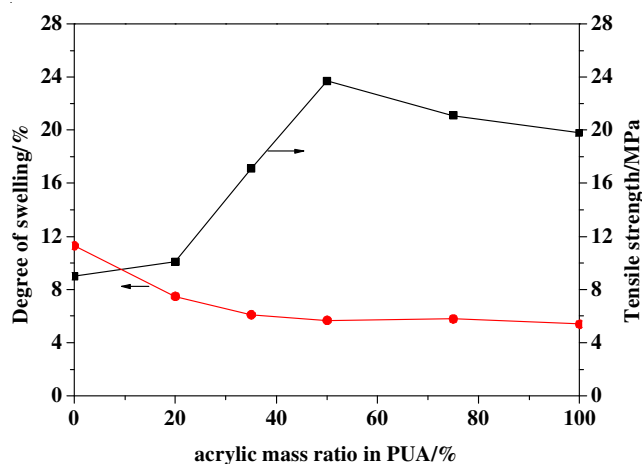


Fig. 5. Tensile strength and degree of swelling for acrylic acid/polyurethane

Conclusion

Acrylic acid/polyurethane hybrid emulsions were prepared by water-borne polyurethane modified with acrylic monomers. The particles of acrylic acid/polyurethane emulsions with core-shell structure can be observed and the average diameters between 60-120 nm. The reinforcement of the hydrogen bonding interaction induced the boundary of core-shell indistinctly. When the mass ratio of acrylic acid portion in acrylic acid/polyurethane reached 75 %, the phase separation existed obviously in acrylic acid/polyurethane. Before the mass ratio of acrylic acid arrived 75 %, with the increasing of acrylic acid portion in the hybrid emulsions, the thermal stability, mechanical properties and water resistance of acrylic acid/polyurethane were improved but elongation at break of acrylic acid/polyurethane decreased.

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