

# Structure and Property Characterization of Nanograde Core-shell Polyurethane/Polyacrylate Composite Emulsion

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**ABSTRACT:** Anionic aqueous polyurethane dispersion was synthesized through self-emulsifying method from cycloaliphatic isophorone diisocyanate (IPDI) and dimethylolpropionic acid (DMPA). The carboxyl acid group in DMPA was used to make the polyurethane dispersible. The polyurethane/polyacrylate (PU/PA) composite particles were also prepared by seeded surfactant-free emulsion polymerization; the cycloaliphatic polyurethane aqueous dispersion was used as seed particles. The structures and properties of the composite emulsion as well as the physical mixture of polyurethane dispersion and polyacrylate emulsion were characterized by FTIR, DSC, dynamic light scattering, TEM, X-ray photoelectron spectroscopy (ESCA), and electronic tensile machine. The results showed that the syn-

thesized PU/PA composite emulsion was found to form inverted core-shell structure with polyacrylate as the core and with polyurethane as the shell, and its diameter of particles is in the range of nanograde, the crosslinking reaction was existed in composite emulsion. The intimate molecular mixing of crosslinking polymers are also claims to result in a superior balance of properties compared to physical blends of polyurethane dispersion and acrylate emulsion. The crosslinking mechanism of PU/PA composite emulsion was also discussed. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 3499–3504, 2008

**Key words:** core/shell polymers; polyurethane; nanocomposite; emulsion polymerization; polyacrylate

## INTRODUCTION

Acrylic polymer emulsions (PA) have been widely used for leather coatings, paper and textile finishes, cement additives, and other applications.<sup>1,2</sup> Interest in polyurethane dispersions (PU) has increased in the last decade because they are environmentally friendly materials.<sup>3–6</sup>

Acrylic polymer emulsions and polyurethane dispersions each have their own characteristic advantages and disadvantages. Acrylic polymer emulsions give excellent weather resistance and water and alkali resistant films due to the main polymer chain's carbon-carbon bonds. However, the elasticity and abrasion resistance of acrylic polymer emulsions are inferior to those polyurethane dispersions. The latter features excellent elasticity and abrasion resistance and superior low temperature impact resistance due to their morphology in which phase separation resulting in the hard diisocyanate segment aggregating into domains in the soft polyol segment, but suffer from poor water and alkali resistance because of the hydrophilic group such as carboxyl group in their molecule chains.<sup>7,8</sup>

There have been some reports to demonstrate how to increase the water resistance of aqueous polyurethane dispersions. First is adding crosslinking agents in the process of prepolymerization, or in the process of reaction, or in the finishing stage. Second is decreasing the surface tension by adding fluorine-containing agents or silicon-bearing agents. Third is hybrid method such as blend latex or core-shell latex of polyurethane and polyacrylate. The water resistance of the core-shell composite latex increased obviously has been reported.<sup>8,9</sup>

Physical blends of the two polymer systems are a popular approach to combine the beneficial attributes of each polymer. However, in many cases these blends compromise the superior performance properties because of the incompatibility of the two systems.<sup>7</sup> A more elegant way to combine the best properties of both systems is to synthesize the polyurethane/polyacrylate (PU/PA) composite latex particles. In these systems, the PU dispersion is used as seed for subsequent radical emulsion polymerization, resulting in intimately mixed composite particles; that is, both polymers are present in a single latex particle and form core-shell structure.<sup>9,10</sup> Although there have been some reports demonstrating the benefit of these type composite emulsions, but the average diameter of the composite emulsions mostly in range of micron grade and there have

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been few reports concerning the morphology of nano-grade composite polyurethane/polyacrylate (PU/PA) emulsion particles and the mechanical properties as well as the surface properties of films from these composite emulsions.<sup>11</sup>

In this article, aqueous polyurethane dispersion was prepared using carboxyl acid group to make the polyurethane dispersible, and then nano PU/PA composite latex was synthesized by soap-free emulsion polymerization method using polyurethane dispersion as seed. Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetric (DSC), dynamic light scattering, transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (ESCA), and electronic tensile machine were employed to investigate the structures and properties of the composite latex and their polymers. Meanwhile the composite emulsion and the physical blend emulsion of polyurethane dispersion and polyacrylate emulsion (PU+PA) were compared, and the crosslinking mechanism of PU and PA was also discussed.

## EXPERIMENTAL

### Materials

Isophorone diisocyanate (IPDI) was supplied by Degussa-Huels AG Company (Dusseldorf, Germany). Poly(propylene glycol) (PPG-1000, PPG-2000) was supplied by the 3rd Petrochemical Plant of Tujian. Dimethylolpropionic acid (DMPA), triethyl amine (TEA), 1,4-butanediol (BDO), dibutyltin diaurate (T-12), di-*n*-octyl phthalate (DOP), acetone, potassium persulfate (KPS), methyl acrylate (MA), butyl acrylate (BA), sodium dodecyl sulfate (SDS), were purchased from Peking Chemical Reagent Company.

PPG was dried at 70°C, 0.1 mm Hg for 72 h before use. The acetone, DOP, and BDO were used after treating with 4A molecular sieves for 72 h. IPDI, MA, BA were distilled, respectively, under reduced pressure. KPS, TEA, T-12, SDS were analytically pure grade, and were used as received. The water was deionized and distilled, the conductivity of which was below 1  $\mu\text{s}/\text{cm}$ .

### Preparation of polyurethane dispersion

The synthesis of the polyurethane dispersion was carried out in a four-neck glass reactor equipped with a mechanical stirrer, a thermometer, a nitrogen inlet, and a condenser with  $\text{CaCl}_2$  during tube. First, IPDI, PPG, DMPA, and few of drops T-12 of DOP solution were poured into the reactor; the reactor mixture was kept at 80–90°C for about 3 h, until the NCO% dropped below 3.0, BDO was added and temperature remained constant for another 1 h. Then, the reactor was cooled down to below 40–45°C

**TABLE I**  
**The Polyurethane Dispersion Recipes**

Reagents	Mole ratios
PPG-1000	0.05
PPG-2000	0.05
BDO	0.1
IPDI	0.3
DMPA	0.1

and then freshly dried acetone was added into it to bring down the viscosity of these PU prepolymer. The PU dispersion was obtained from a high shear rate mixing of these PU prepolymer with aqueous solution of TEA. The final PU dispersion had 30% solid contents with a PH value of 8.5 after acetone was removed by vacuum. In the process of synthesis, the carboxyl acid group in DMPA molecule was used to make the PU dispersible. The recipes are summarized in Table I.

### Preparation of PU/PA composite emulsion

The composite PU/PA latex was prepared by soap-free seeded emulsion polymerization using the above-synthesized anionic aqueous-based PU dispersion as seed particles. The mixture monomers of MA and BA were used in the second-stage polymerization. The second-stage soap-free seeded emulsion polymerization was carried out with KPS as initiator at 80°C for 4 h. The PU seed/monomer weight ratio was 50/50.

### Preparation of blend latex of polyurethane dispersion and polyacrylate emulsion

The blend latex was obtained by simply mixing PU dispersion and methyl acrylate–butyl acrylate copolymer latex by using the same monomer recipes and polymerization parameters as in synthesizing PU and PU/PA.

### Characterization

#### FTIR analysis

Fourier transform infrared spectra were acquired with a Bruker Equinox 55 Fourier transform infrared spectrometer (Bremen, Germany). For each sample, 16 scans at a  $4\text{-cm}^{-1}$  resolution were collected in absorption group mode.

#### Differential scanning calorimetric analysis

DSC analysis of different samples was conducted by using Perkin–Elmer (Waltham, MA) Pyris1 DSC instrument. Indium was taken as internal standard for analysis. The samples were quickly cooled to  $-100^\circ\text{C}$ , equilibrated at that temperature for 3 min,

and then heated to +100°C at a scanning rate of 10 °C/min under N<sub>2</sub> atmosphere. The sample weights were 5–8 mg. The samples for DSC analysis were cut from the polymer films which were prepared by casting the latex on the glass and were dried at 50°C for 1 week.

#### Particle size analysis

Particle size distribution curves of the PU dispersion, PA emulsion, PU/PA composite latex as well as PU+PA blend emulsion were measured on a dynamic light scattering instrument particle size analyzer (Horiba, Japan).

#### Transmission electron microscopy observation

The PU/PA composite latex particles morphology was observed with a Hitachi H-800, transmission electron microscopy (Hitachi, Japan), after negative staining with phosphotungstic acid (PTA).

#### X-ray photoelectron spectroscopy analysis

The samples for ESCA measurement were prepared by casting the latex on the glass plates and dried at 50°C for 1 week. An ESCA-PHI5300X (Perkin-Elmer Physics Electronics Company) was used. The measuring conditions were as follows: X-ray source, MgK $\alpha$  (8 kV, 30 mA); incident angle of photoelectron, 90°.

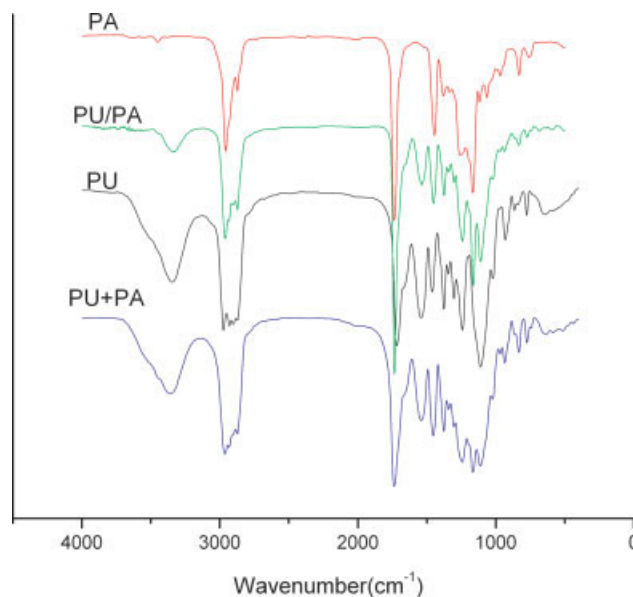
#### Static mechanical properties

A model WD-3000 electronic testing machine (Changchun, China) was employed for the tensile test. The specimens for the tensile test were dumbbell cut from sample films, which were prepared by casting the latex on the glass plates and dried at 50°C for 1 week, and carried out at a crosshead speed of 100 mm/min according to standard of ASTM-D638. A 20-mm benchmark and the original cross-sectional area were utilized to calculate their tensile properties. The ultimate tensile strength and elongation at break were automatically calculated by the computer connected to the machine. The average of at least five measurements for each sample was reported, the experimental error is  $\pm 10\%$ .

## RESULTS AND DISCUSSION

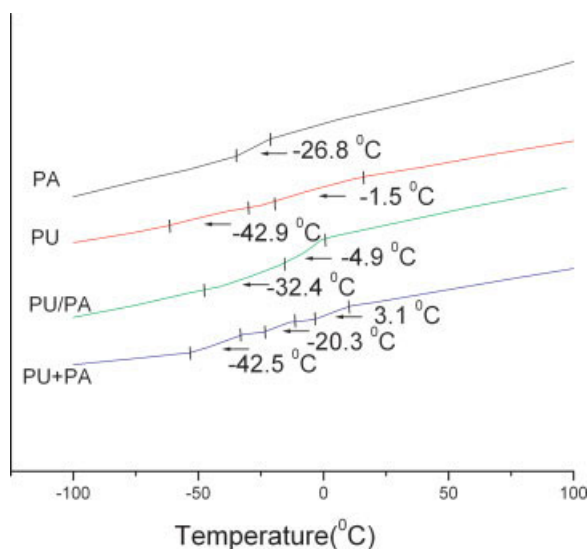
#### FTIR analysis

Figure 1 demonstrates the typical FTIR spectra of the dried films from PA, PU, PU/PA, PU+PA system, which take the peaks at 2900–3000 cm<sup>-1</sup> for stretching of C–H bond as reference. In Figure 1, the peak at 3345 cm<sup>-1</sup> for stretching of hydrogen bonding



**Figure 1** FTIR spectra of the dried polymer film. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

N–H bond and the peak at 3450 cm<sup>-1</sup> for stretching of free N–H bond have relatively important meaning on aspect of study.<sup>12</sup> Comparing FTIR spectra of films obtained from PU, PU/PA, PU+PA emulsion, the same condition is that the absorbing intensities of hydrogen bonding N–H bond stretching peak all are much stronger than that of corresponding free N–H bond stretching peak among the three type of emulsions, exhibiting N–H bond mostly existed in hydrogen bonding way in the above three type polymer systems from the area ratio of hydrogen bonding N–H bond absorbing peak to free N–H bond peak, and the different case is that the absorbing intensity of hydrogen bonding N–H bond peak of film obtained from PU dispersion is almost the same with that of film obtained from PU+PA blend emulsion, but is much higher than that of film from PU/PA composite emulsion. By the general knowledge about polyurethane, the lower the amounts of hydrogen bonding N–H bond, the higher the degree of uniformity of distribution between hard and soft segment phases, showing the ordered degree of hard segment phase of PU in film obtained from PU/PA composite emulsion reduced greatly because of the existence of polyacrylate molecules. However, the ordered degree of hard segment phase of PU in film obtained from PU+PA blend emulsion have not change much. This suggests that there is some chemical crosslinking reaction between the polyurethane molecules and polyacrylate molecules, which make the miscibility between polyurethane molecule and polyacrylate molecule in PU/PA composite emulsion is better than that in PU+PA blend emulsion.



**Figure 2** DSC curves of the dried polymer film. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

### Differential scanning calorimetric analysis

Figure 2 exhibits the DSC curves of the polymer films of PU, PA, PU/PA, PU+PA systems. Only one glass transition temperature  $-26.8^{\circ}\text{C}$  is observed in the film of PA emulsion. This shows PA film is a uniformity phase system. Two transitions are observed for the film from the polyurethane dispersion, in which  $-42.9^{\circ}\text{C}$  and  $-1.5^{\circ}\text{C}$  from the micro-Brownian segmental motion of soft segment and hard segment of polyurethane; this shows PU film has two phases. Three transition temperatures are observed for the polymer film from physical blend latex, in which  $-20.3^{\circ}\text{C}$  probably arise from micro-Brownian segmental motion of MA-BA copolymer with different compositions associated with the glass transition temperature  $-26.8$ ,  $-42.5$ , and  $3.1^{\circ}\text{C}$  from the micro-Brownian segmental motion of soft segment and hard segment of polyurethane. This shows film obtained from PU+PA blend emulsion is a multiphase system.

One very obvious step is observed from the DSC curve of film of PU/PA composite latex in the temperature range of  $-100$  to  $100^{\circ}\text{C}$ . This step can be divided into two part at about  $-14^{\circ}\text{C}$ ; the former is more gradual slope and the latter is more abrupt slope. This shows PU/PA film have two glass transition temperatures, in which  $-32.4^{\circ}\text{C}$  between the glass temperature of polyurethane's soft segment and the glass temperature of acrylate copolymer,  $-4.9^{\circ}\text{C}$  probably corresponds to the glass temperature of hard segment of polyurethane. The third transition temperature is not observed. Furthermore, the interval between glass temperatures from film of PU/PA emulsion is shorter than that from film of

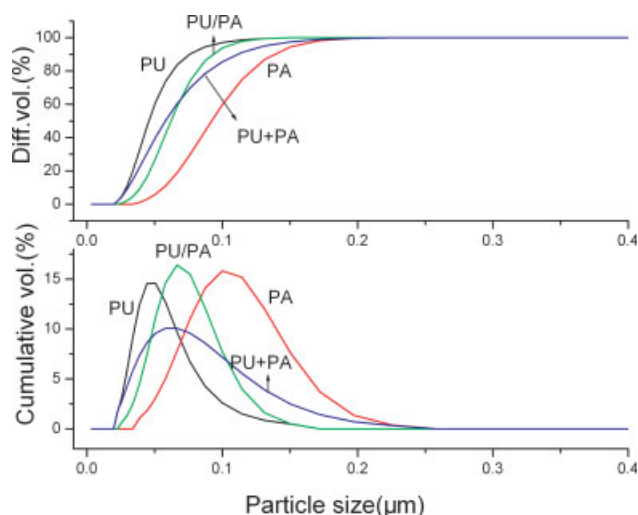
blend latex. By the general knowledge in polymer science aspects, the shorter the interval is between the glass temperatures of two phases, the higher the degree of uniformity of distribution between two phases, suggesting that there is some chemical cross-linking reaction between the polyurethane molecules and polyacrylate molecules. This result is good agreement with the result of FTIR. In addition, this further shows the particle morphology of PU/PA composite emulsion is core-shell structure.

### Particle size analysis

Figure 3 shows the results of particle size distribution of PU, PA, PU/PA, PU+PA system. Evidently, the particle size distribution of PU/PA composite emulsion is narrower than that of the PU+PA blend emulsion, although the average diameter of both is closer. This shows the blend emulsion is different from the composite emulsion. In addition, the volume median size of PU/PA composite emulsion particles is bigger than that of polyurethane dispersion, the former is about  $50.5\text{ nm}$ , the latter is  $\sim 65.8\text{ nm}$ . This also shows the condition in which the morphology of PU/PA composite emulsion form core-shell structure is existed in some extent.

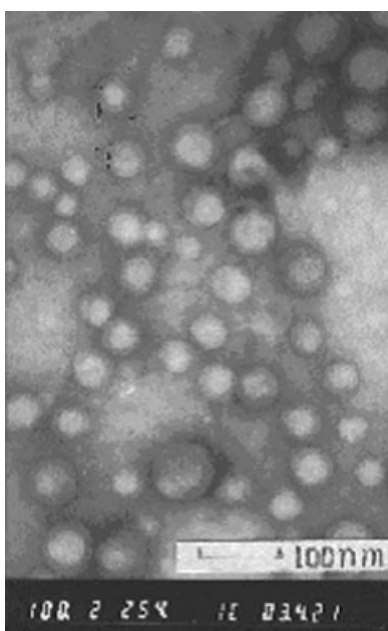
### Transmission electron microscopy (TEM) observation

The TEM photos of PU/PA composite latex particles are presented in Figure 4. The darker region of the out layer is polyurethane domains as result of a higher electronic cloud density around polyurethane chains which have bigger polarity compared to that of polyacrylate chains, and the lighter region in the core is the polyacrylate.<sup>7</sup> This shows the formation



**Figure 3** The particle size distribution of different emulsions. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]





**Figure 4** Micrograph of PU/PA composite latex particles.

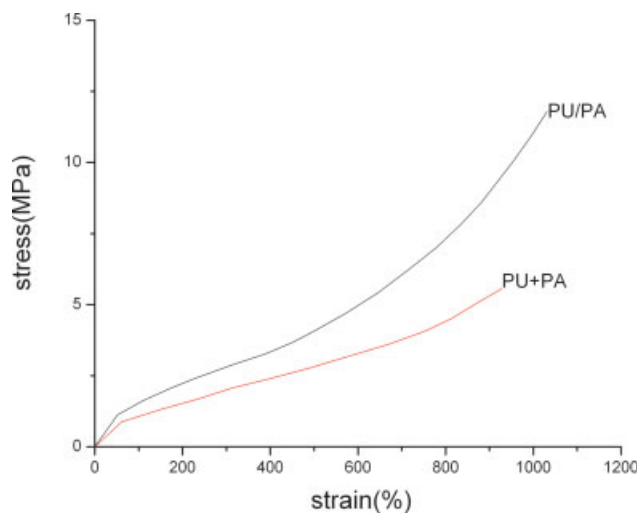
of the core-shell structure in PU/PA composite emulsion particles is also supported by transmission electron microscopy (TEM) measurements. From the information from FTIR, DSC, and observation by TEM, it is evident that the mechanism for the emulsion particles formation is by phase inversion process. This is good agreement with the result of reference.<sup>7</sup> The more hydrophilic chains in amphiphilic PU/PA composite system are selectively located in the shell region and the hydrophobic chains are concentrated in the core region of the emulsion particles in the course of phase inversion process. In addition, need to say no core-shell structure particles have been observed in the TEM photos of PA, PU, PU+PA systems.

#### X-ray photoelectron spectroscopy (ESCA) analysis

Table II shows the result of ESCA spectra of the surface layers of the films obtained from PA, PU, PU/PA, PU+PA emulsions. It was found that PA shows no signal of nitrogen atoms. Whereas PU, PU/PA, PU+PA shows the signal of nitrogen atoms. At the same time, PU/PA have almost equal content of

**TABLE II**  
Surface Element Compositions for Different Films

Sample	Atomic mole fraction (%)		
	C	N	O
PA	80.93	0.00	19.07
PU	73.29	3.05	23.65
PU/PA	74.14	2.78	23.08
PU+PA	75.57	1.45	22.98



**Figure 5** Stress-strain curve of the PU/PA and PU+PA films. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

nitrogen element with PU, but PU+PA have lesser content of nitrogen element with PU. This result can be reasonably explained by the tendency of the shell component to be predominantly present at the surface of the films after coalescence in PU/PA system, and by the condition of PU and PA component all present at the surface of the films after coalescence in PU+PA system.

#### Static mechanically properties

Figure 5 shows the stress-strain behavior of the films obtained from the core-shell structure PU/PA and its corresponding blend latex PU+PA. The tensile strength and elongation at break are 11.8 MPa and 1035.0%, respectively, for film from PU/PA composite latex and 5.6 Mpa and 928.1 %, respectively, for the film from PU+PA blend latex, showing that the PU/PA composite latex with core-shell structure have better film performance properties than their corresponding PU+PA physical blend latex.

Further the PA, PU, PU/PA, PU+PA films were extracted in acetone at 80°C for 24 h, the weight of the residue for PU, PA, PU/PA, PU+PA was determined, the results were that only PU/PA had 60.1% of residual sample weight based on the initial weight. PU, PA, PU+PA were completely extracted, indicating there was some crosslinking structure in PU/PA. This is likely due to that PU molecular chains contain many  $\alpha$ -H atoms. When acrylic monomers are emulsion polymerized in the presence of aqueous PU dispersion, these  $\alpha$ -H atoms can be abstracted by the free radicals either from the decomposition of initiators or from acrylic molecular chains containing free radicals, resulting in some grafting reactions between PU molecular chains and

acrylic monomers, then crosslinking reactions happened between grafting polymers by coupling reaction of radicals.<sup>13</sup>

### CONCLUSIONS

The following conclusion could be drawn from this investigation. The PU/PA composite emulsion prepared by soap-free seeded emulsion polymerization was found to form core-shell structure in aqueous media with polyurethane as the shell and with polyacrylate as the core. The particles size of the PU/PA composite emulsion is in range of nanograde.

DSC exhibited only one glass transition for film from polyacrylate emulsion, two transitions for both films from polyurethane dispersion and from composite latex, and three transitions for the film from blend latex.

ESCA showed that the component occupying the shell region of the emulsion particles was found to orientate preferentially on the surface layer of the dried film.

It was also demonstrated that the composite emulsion had better performance properties than the corresponding blend latex determined by electronic test

machine. And there were some crosslinking reactions that occurred in preparing PU/PA composite lattices, indicated by FTIR analyses and solvent extraction.

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