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Synthesis and Characterization of Sulfonated Polyol-Based Waterborne Polyurethane-Polyacrylate Hybrid Emulsions

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Abstract: Polyurethane (PU) dispersion was prepared with sulfonate groups to make the PU dispersible. Then, polyurethane-polyacrylate (PU-PA) hybrid emulsions were synthesized by seeded emulsifier-free emulsion polymerization with the previously synthesized PU dispersion as a source of seed particles. In the results of the particle-size distribution of the PU-PA hybrid emulsions, the average particle size of the hybrid emulsions increased from 1.2 to 9.1 μm when the polyacrylate content was increased from 0.2 to 1.0 by weight. In addition, the scanning electron microscopy results showed that the size of the polyacrylate latex particles was increased with increases in polyacrylate content. This result suggests that the hydrophobic polyacrylate can easily diffuse into PU particles, where the free radical chain-growth polymerization takes place. In the thermal analysis results, shifts in $T_{g,1}$ and $T_{g,2}$ were observed, which are related to the partial compatibility and inter-diffusion of the PU dispersion and PA components. The TGA curves shifted to a higher temperature with increases in polyacrylate content, which indicates a higher thermal stability of the PU-PA hybrid emulsion films. The PU-PA hybrid emulsion films showed improvement in the thermal stability and mechanical properties when compared with the pure polyurethane film, due to the increase in the formation of strong interaction between the PU and PA molecules.

Keywords: polyurethane, polyacrylate, waterborne emulsion, morphology, thermal property.

Introduction

Polyurethane (PU) provides excellent chemical, solvent and abrasion resistance, as well as outstanding hardness and toughness combined with low temperature flexibility, therefore polyurethane is suitable for many coating applications.[1] There are various ways of combining a wide variety of polyols and diisocyanates in order to produce tailored polyurethane products.[2-6]

Waterborne polyurethane (WPU) have been employed increasingly in a wide range of applications due to environmental considerations, since these materials do not contribute to the increasing amount of solvent emissions to atmosphere.[7-10] Environmental considerations have been the cause of increasing research and development of waterborne polymer systems for many different applications, particularly as coatings for several kinds of substrate.

Waterborne polyurethanes can be formulated into coatings and adhesives containing little or no co-solvent. Another advantage of aqueous polymer dispersions is that the viscosity of the dispersion is normally independent of the molecular weight of the polymer. Thus, aqueous polyurethane dispersions can be prepared at high solid contents with a molecular weight high enough to form films with excellent performance resulting solely upon "physical drying". This means that the film formation occurs by simple evaporation of water even at room temperature. Technological aspects of waterborne polyurethanes can be summarized as: low solvent or solvent free, environmentally acceptable, relatively low viscosity at relatively high molecular weights, and low temperature physical drying.[11-13]

A polyurethane ionomer used in making a polyurethane dispersion can be defined as a copolymer consisting of a polyurethane backbone with a minority of the repeat units carrying pendant acid or tertiary nitrogen groups, which are completely neutralized or quaternized, respectively, to form salts.[14,15] The presence of ionic species in ionomers has a considerable effect on many of their physical properties. Ions containing polyurethanes have received considerable attention due to their usefulness in coatings and adhesives. Ionic centers in the hard segment generally favor segregation and cohesion within the hard segment domains due to

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their strong electrostatic forces and thermodynamic incompatibility with the polymer matrix.[16]

Among polyurethane ionomers, anionic polyurethane dispersions have been most frequently used in coating and adhesive industries.[17-21] The common process for preparation of perfect, self-emulsified polyurethanes is using the dimethylol propionic acid (DMPA) as an hydrophilic monomer to react with diisocyanate. The resulting modified polyurethane can be dispersed by water after being neutralized with a tertiary amine. The main advantages of this self-emulsification[22] are as follows: the dispersing process does not require strong shear force; fine particles with improved dispersion stability are obtained; the water sensitivity of the films after evaporation of water is reduced; and resistance to nonpolar agents is high. In this process, sufficient hydrophilic monomer DMPA must be employed to endow the polyurethane dispersion with good stability; however, the dried film may exhibit poor water resistance and lack of hardness and toughness because of the presence of ionic groups in large content.

Polyacrylate (PA) emulsions possess good mechanical properties and outstanding climate and water resistance, except for the defect of hot-viscidity and cold-brittleness. The composite emulsion of polyurethane/polyacrylate combines the excellent properties of PU dispersion and PA emulsion, which greatly improves the properties of coatings.[23,24]

In recent years, many studies have been carried out on polymer blends and composites, because of the enhanced mechanical properties that these materials may possess.[25-31] Interpenetrating polymer networks (IPNs)[32,33] are more or less incompatible polymer blends in which macroscopic phase separation is prevented by suitably engineering the morphologies of the participating components. Here, one polymer is synthesized or cross-linked in the immediate presence of the other. Owing to their permanent interlocking configuration,[32] the tendency towards phase separation at the end of their synthesis is almost frozen in, so that the ultimate properties are not influenced due to ageing and the constituent polymers cannot be separated unless chemical bonds are broken. The morphology is dependent on the crosslink density and the sequence of formation of the two networks. The permanent physical interlocking of the component polymers causes a wide spectrum of properties ranging from toughened elastomers to high impact plastic.

In this study, an aqueous PU dispersion was prepared with the sulfonate groups to prepare dispersible PU, then PU-PA hybrid emulsions were synthesized by an emulsifier-free emulsion polymerization method with the PU dispersion as the seed. The morphological, thermal, and mechanical properties of these polyuretnae-polyacrylate (PU-PA) hybrid emulsions are characterized by FTIR, scanning electron microscopy (SEM), atomic force microscopy (AFM), differential scanning calorimetry (DSC), thermogravimetric analyzer (TGA), and universal testing machine.

Experimental

Materials. Polypropylene ether glycol (sulfonate type polyol, hydroxyl value=325.4, sulfonate=5.5 wt%), polypropylene glycol (PPG, M_n=1,000), polycarbonate diol (PC diol, M_n= 2,000) were used as received and they were dried at 90 ºC for 3 h before use. Ethylene diamine (EDA) and potassium persulfate were purchased by Junsei Chemical (Japan). Isophorone diisocyanate (IPDI) were purchased by Aldrich Chemical. Methyl methacrylate (MMA) and butyl acrylate (BA) were obtained from Amocoat Chemical Co. (Korea). All the materials were used as received without further purification. The structure of the sulfonate-type polyol is shown in Figure 1.

Synthesis of Waterborne Polyurethane Dispersion. Synthesis of polyurethane (PU) dispersion was carried out in a 500 mL four-neck, round-bottom flask equipped with mechanical stirrer, addition funnel, N_2 inlet, thermometer, and heating mantle. Figure 1 shows the schematic diagram of preparations of polyurethane dispersion and polyurethane-polyacrylate (PU-PA) hybrid emulsions. Sulfonate-type polyol (sulfonate content=5.5 wt%), PPG-1000 and polycarbonate (PC) diol were added into the flask and mixed at 60 ºC for 30 min. Then, isophorone diisocyanate (IPDI) was added into the mixture of sulfonate type polyol, PPG-1000 and polycarbonate diol, and prepolymerization of polyurethane was carried out at 80 ºC under N_2 atmosphere for 2 h until the NCO content reached the theoretical value. Then deionized water was added into the isocyanate terminated

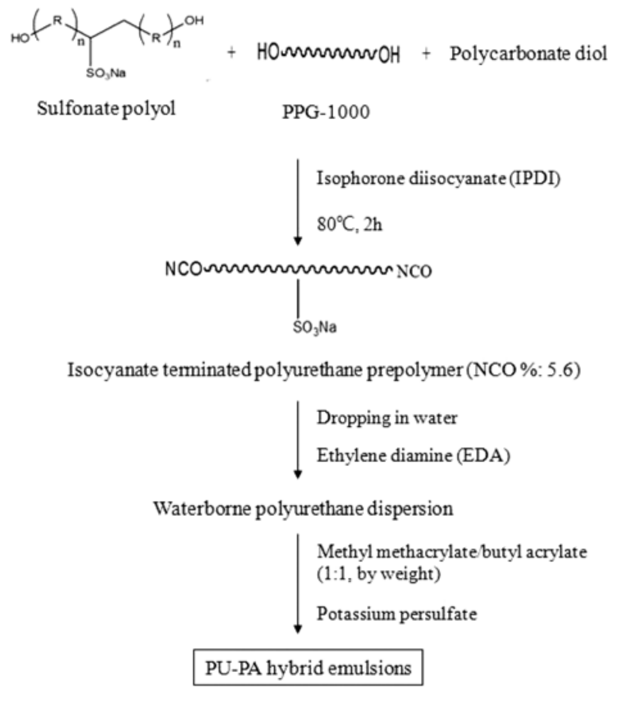


Figure 1. Schematic diagram of the synthesis of polyurethane dispersion and polyurethane-polyacrylate hybrid emulsions.

Table I. Recipe for the Preparation of Waterborne Polyurethane (PU) Dispersion

Sample	Sulfonated Polyol (g)	PPG-1000 (g)	Polycar-Bonate Diol (g)	Isophorone Diisocyanate (IPDI) (g)	Ethylene Diamine (g)	Excess NCO (%)
PU Dispersion	100.0	37.7	21.3	115.9	7.7	5.6

PU prepolymer which is the mixture of sulfonate type polyol, PPG-1000, polycarbonate (PC) diol and IPDI. The PU prepolymer was emulsified by high-speed stirring. By adding ethylene diamine (EDA) into the isocyanate terminated PU prepolymer, chain extension was carried out at 40 ºC for 2 h. The obtained aqueous PU dispersion had a solid content of about 30 wt%. The recipe for the preparation of the PU dispersion is shown in Table I.

Synthesis of Polyuethane-Polyacrylate Hybrid Emulsion. The PU-PA hybrid emulsion was prepared by emulsifier-free seed emulsion polymerization with the previously synthesized PU dispersion as the seed particle, which contained 2.0% of sulfonate content. A mixture of monomers (methyl methacrylate and butyl acrylate) was added to the PU dispersion. Then, potassium persulfate was dissolved in water as an initiator, then, fed into the PU-PA hybrid emulsion by dropwise for 30 min. The final mixture was reacted at 90 ºC for additional 4 h. The resulting product was a stable PU-PA hybrid emulsion with a solid content of about 30%. The recipes for the preparation of the PU-PA hybrid emulsions are listed in Table II.

FTIR Spectroscopy. Fourier transform infrared (FTIR) spectrometer (JASCO-4100 spectrometer Japan) was used to identify the chemical structure of polyurethane dispersion and PU-PA hybrid emulsions. The sample was coated as a thin liquid film on CF_2 pellets and dried for examination. The FTIR spectra were recorded in the range of 600-4000 cm^{-1} with nominal resolution of 4 cm^{-1} at room temperature.

Morphology. Scanning electron micrograph of the cross-sectional surface of PU-PA hybrid emulsion film was obtained using SEM (TESCAN VEGA II LSH) at 15 kV. To prepare the film of PU-PA hybrid emulsion, the emulsion was dropped onto a glass plate and then dried at room temperature. The PU-PA hybrid emulsion films were freshly broken in liquid nitrogen and the cross-sectional surfaces of the film samples were coated by gold sputtering. Average particle size distribution of the PU/PA hybrid emulsion was measured using Autosizer provide by laser light scattering (Mastersizer Micro, Malvern Instruments Corporation). The measuring range of the instrument was 0.3-300 μm. The sample was first diluted in deionized water to 0.5%, followed by ultrasonic wave treatment to homogenize the emulsion. The measurements were carried out at 23 ºC.

Thermal Analysis. Differential scanning calorimetry (DSC) of the PU-PA hybrid emulsion film was performed on a thermal analyzer (TA instrument Q20, USA). The samples were heated from -80 to 150 ºC at 10 ºC/min. The glass transition temperature (T_g) of the samples was determined from the midpoint temperature in the heat capacity change of the DSC scan. Samples of 10 mg were cut from the films and used for analysis.

TGA. Thermogravimetric analyzer (TGA) (Perkin Elmer TGA 4000 USA) was used to measure the weight loss of the PU dispersion and PU-PA hybrid emulsion films under an air atmosphere. The samples were heated from room temperature to 650 ºC at a heating rate of 20 ºC/min. Samples of 10-15 mg were used for the thermogravimetric analysis.

Mechanical Property. Mechanical properties of the PU-PA hybrid emulsion films were measured at room temperature with a tensile tester (Zwick T-1, Germany) according to the ASTM D 638 specification. A crosshead speed of 100 mm/min was used throughout the investigation of the ultimate tensile strength and the elongation at break. Five specimens were used for each measurement and the median value was used as the tensile strength.

Results and Discussion

FTIR of the PU-PA Hybrid Emulsions. Figure 2(a)-(c) shows FTIR spectrum of isocyanate terminated polyurethane prepolymer with reaction time of 30 min, 1 h and 2 h at 80 ºC after isophorone diisocyanate (IPDI) was added in the reactor, respectively. From Figure 2(a)-(c), the peak at wavenumber 2270 cm^{-1} denotes functional group of isocyanate bond (-N=C=O) and a strong C-O peak at 1110 cm^{-1} appeared. With increasing reaction of polyurethane prepolymer, the amine (-NH) group (stretch) peak at wavenumber 3335 cm^{-1} and amine (-NH) group (bend) peak at wavenum-

Table II. Recipes for the Preparation of Polyurethane (PU)-Polyacrylate (PA) Hybrid Emulsions

Samples	PU Dispersion (g)	Potassium Persulfate (g)	Methyl Methacrylate (g)	Butyl Acrylate (g)	Water (g)	PU/PA Weight Ratio
PU-PA (1.0:0.2)	50.0	0.10	5.0	5.0	23.3	1.0/0.2
PU-PA (1.0:0.5)	40.0	0.20	10.0	10.0	46.5	1.0/0.5
PU-PA (1.0:0.7)	35.3	0.25	12.3	12.3	57.6	1.0/0.7
PU-PA (1.0:1.0)	30.0	0.30	15.0	15.0	70.0	1.0/1.0

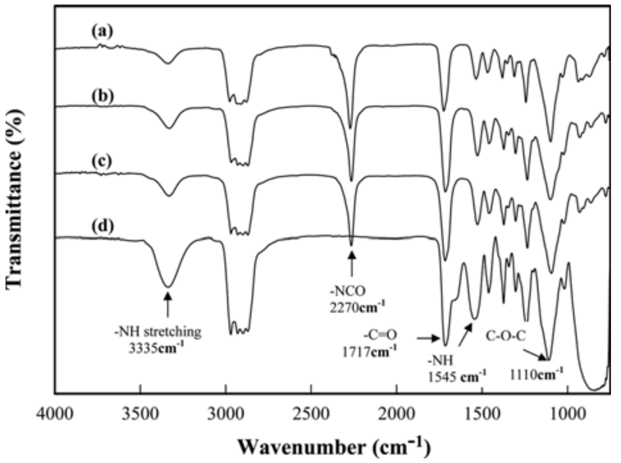


Figure 2. FTIR spectrum of urethane prepolymer with reaction time after isophorone diisocyanate (IPDI) was added to the reactor. (a) 10 min, (b) 30 min, (c) 60 min, (d) after chain-extended with ethylene diamine (EDA).

ber 1545 cm^{-1} increased gradually. Figure 2(d) shows polyurethane dispersion after chain extended with the ethylene diamine (EDA). In Figure 2(d), the isocyanate (-NCO) peak at wavenumber 2270 cm^{-1} disappears indicating that the isocyanate (-NCO) group of IPDI terminal of the synthetic compound is completely reacted.

Figure 3(a)-(e) shows FTIR spectrum of the dried films from PU dispersion and PU-PA hybrid emulsions of PU-PA=1.0:0.2, 1.0:0.5, 1.0:0.7, and 1.0:1.0 by weight, respectively. The absorption at wavenumber 3335 cm^{-1} arose from the hydrogen-bonding N-H stretching vibration. In addition, an absorption at wavenumber 1545 cm^{-1}, the intensity of amine (-NH) peak (bend) decreased with the increase of polyacrylate weight fraction of the PU-PA hybrid emulsion films. The peak at wavenumber 1717 cm^{-1} denotes carbonyl (C=O) stretching vibration of the acrylic ester groups and a peak at 1110 cm^{-1} corresponding to the C-O stretching vibration. A progressive change in the spectrum was observed with increasing acrylic content, and the intensity of the ratio of acrylic group (-C=O) to amine group (-NH) increased accordingly.

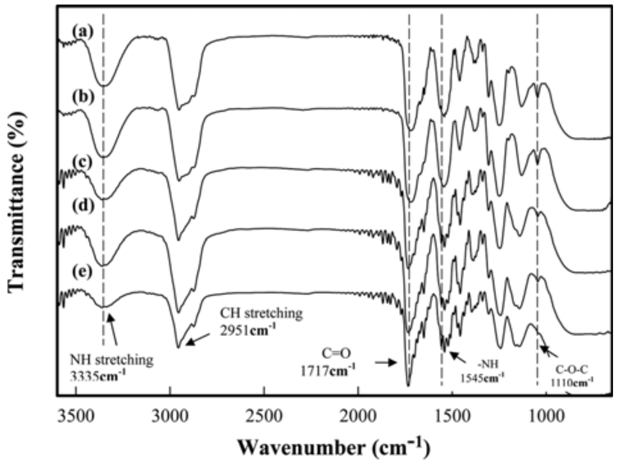


Figure 3. FTIR spectrum of PU dispersion and PU-PA hybrid emulsions: (a) PU dispersion, (b) PU-PA=1.0:0.2, (c) PU-PA=1.0:0.5, (d) PU-PA=1.0:0.7, (e) PU-PA=1.0:1.0.

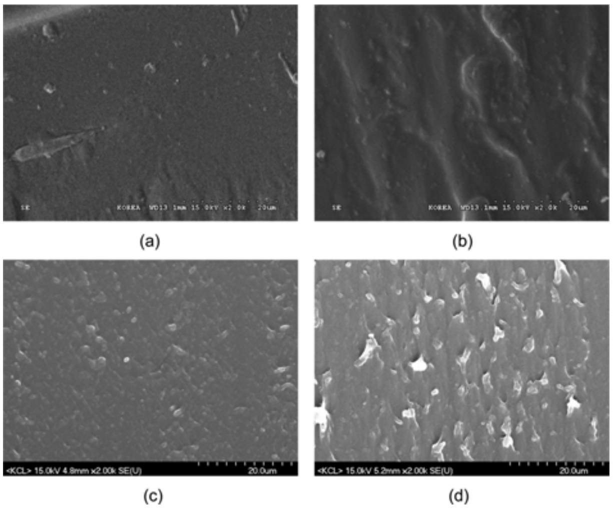


Figure 4. SEM micrographs of PU-PA hybrid emulsions cast film: (a) PU-PA=1.0:0.2, (b) PU-PA=1.0:0.5, (c) PU-PA=1.0:0.7, (d) PU-PA=1.0:1.0.

SEM of the PU-PA Hybrid Emulsions. Figure 4(a)-(d) shows scanning electron micrographs of the PU-PA hybrid emulsion films of PU:PA=1.0:0.2, 1.0:0.5, 1.0:0.7, and 1.0:1.0 by weight, respectively. From Figure 4, it shows that the PU-PA hybrid emulsions are all particles structured spheres and the particle coagulation is also observed which is that PU-PA hybrid system is partially miscible. From Figure 4, the size of the polyacrylate (core) latex particles increases with the increase of the amount of polyacrylate, which is suggested that the hydrophobic polyacrylate can easily diffuse into PU particles, where the free radical chain-growth polymerization takes place. PU (shell)-acrylate (core) forms core-shell structure due to the hydrophobic nature of acrylaye polymers.

Particle Size Distribution of the PU-PA Hybrid Emulsions. Figure 5 shows the particle size distribution of the PU dispersion and PU-PA hybrid emulsion of PU:PA=1.0:0.2, 1.0:0.5, 1.0:0.7, and 1.0:1.0 by weight. From Figure 5, it showed that the particle size of PU dispersion was smaller than that of the PU-PA hybrid emulsions. As the polyacrylate content increases from 0.2 to 1.0 by weight, the average particle size of hybrid emulsions increases from 1.2 to 9.1 μm, which may be the result of swelling tendency of acrylic monomer into the PU particles. The rapid increase in average particle size of materials with high polyacrylate contents may suggest the instability of a swelled particle with insufficient sulfonate group content on the surface, leading to particle coalescence. From Figure 5, the particle size distribution of polyurethane

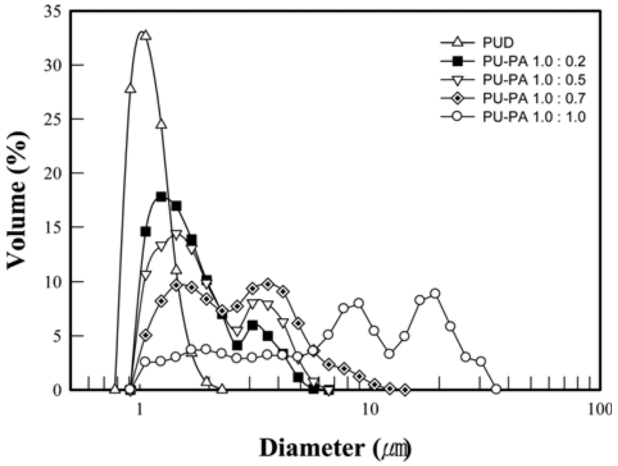
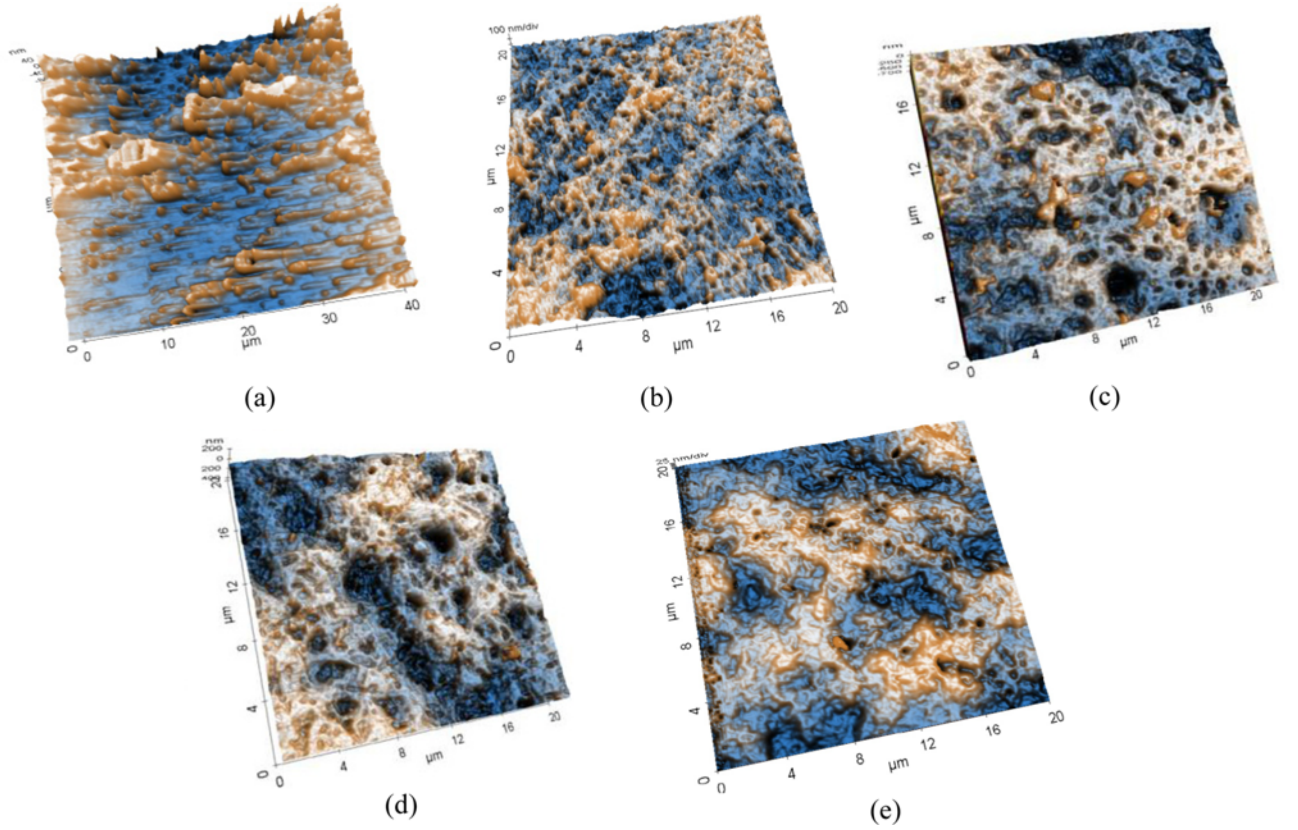


Figure 5. Average particle size distribution of PU dispersion and PU-PA hybrid emulsions: (△) PU dispersion, (■) PU-PA=1.0: 0.2, (▽) PU-PA=1.0:0.5, (◆) PU-PA=1.0:0.7, (○) PU-PA=1.0:1.0.

dispersion shows narrow compared that of the PU-PA hybrid emulsions and this is because of the polymerization of acrylic content in the polyurethane particles. Also, particle size is bimodal at high acrylate concentration implying that part of the acrylate is included in polyurethane dispersion (PUD), and others are remaining in aqueous phase with poor stability.

Atomic Force Microscopy of the PU-PA Hybrid Emulsions. Figure 6(a)-(e) shows the atomic force micrographs of PU dispersion and PU-PA hybrid emulsion films of PU:PA =1.0:0.2, 1.0:0.5, 1.0:0.7, and 1.0:1.0 by weight, respectively. Figure 6 shows different particle morphologies and particle coagulation is also observed. The surface morphology of PU dispersion film (Figure 6(a)) showed roughness surface. Also, it seems that surface morphology of PU-PA hybrid emulsion (Figure 6(b)-(e)) films is reticular. This was attributed to the fact that the PU dispersion was seeded by acryl monomer, therefore the surface morphology of PU-PA hybrid emulsion films showed reticular.

DSC of the PU-PA Hybrid Emulsions. Figure 7(a)-(e) shows the DSC curves of PU dispersion and PU-PA hybrid emulsion films of PU:PA=1.0:0.2, 1.0:0.5, 1.0:0.7, and 1.0:1.0 by weight, respectively. From Figure 7(a), two glass transitions of PU dispersion are observed at -23.5 and 41.6 °C, which are attributed to the soft segment glass transition temperature (T_g) of PU ($T_{g,1}$) and a hard segment T_g of PU ($T_{g,2}$), respectively. In Figure 7(a)-(e), the $T_{g,1}$ of PU-PA films are shifted to higher temperatures, which are -23.5, -17.4, -13.1, -12.9, and -9.3 °C, respectively, and the $T_{g,2}$ of PU-PA hybrid emulsion films are shifted to lower temperatures which are 41.6, 27.3, 28.6, 34.7, and 36.5 °C, respectively, with the increase of PA. T_g of PU dispersion seems that of mixed phase, nei-



(a) (b) (c) (d) (e)

Figure 6. AFM images of PU dispersion and PU-PA hybrid emulsions cast film: (a) PU dispersion, (b) PU-PA=1.0:0.2, (c) PU-PA=1.0:0.5, (d) PU-PA=1.0:0.7, (e) PU-PA=1.0:1.0.

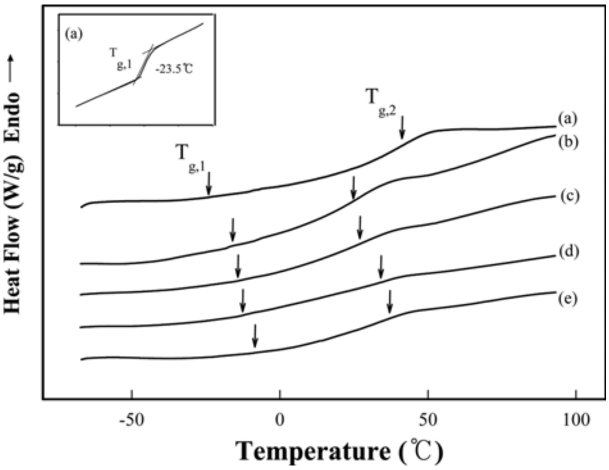


Figure 7. Glass transition temperature (T_g) of PU dispersion and PU-PA hybrid emulsions: (a) PU dispersion, (b) PU-PA=1.0:0.2, (c) PU-PA=1.0:0.5, (d) PU-PA=1.0:0.7, (e) PU-PA=1.0:1.0.

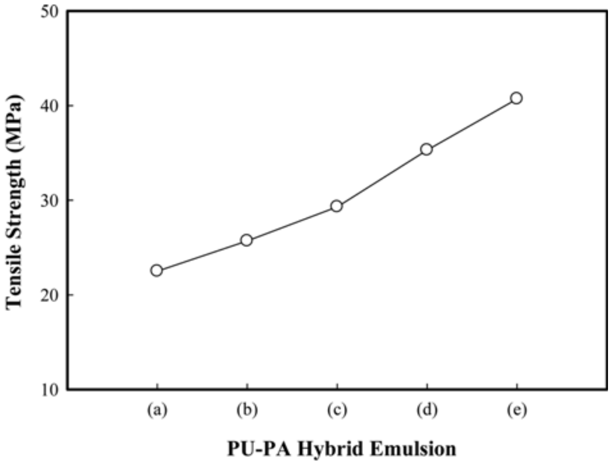


Figure 9. Tensile strength of PU dispersion and PU-PA hybrid emulsions: (a) PU dispersion, (b) PU-PA=1.0:0.2, (c) PU-PA=1.0:0.5, (d) PU-PA=1.0:0.7, (e) PU-PA=1.0:1.0.

ther soft segment nor hard segment. With the acrylate inclusion, the mixed T_g decreases as expected. From Figure 7, the shifts of $T_{g,1}$ and $T_{g,2}$ are related to the partial compatibility and inter-diffusion of the PU dispersion and PA components, which indicate some degree of miscibility. The result suggests that the intermolecular hydrogen bonds between the PU and PA molecules enhance miscibility.

Thermogravimetry Analysis of the PU-PA Hybrid Emulsions. Figure 8 shows thermal stability of the PU dispersion and PU-PA hybrid emulsion films of PU:PA=1.0:0.2, 1.0:0.5, 1.0:0.7, and 1.0:1.0 by weight. It is known that PU exhibits relatively poor thermal stability due to dissociation of the urethane bond occurring around 200 °C. In Figure 8, a slight weight loss was observed at about 200 °C, which was attributed to decomposition of urethane bonds and the onset of urethane bond dissociation was observed between 150 and 220 °C depending upon the PU/PA ratio. A rapid weight loss was observed between 300 and 400 °C, which was caused by the decomposition of the PU-PA hybrid emulsion films. From Figure 8, the TGA curves shift to a higher temperature with the increase of polyacrylic content which indicating a higher thermal stability of the PU-PA hybrid emulsions.

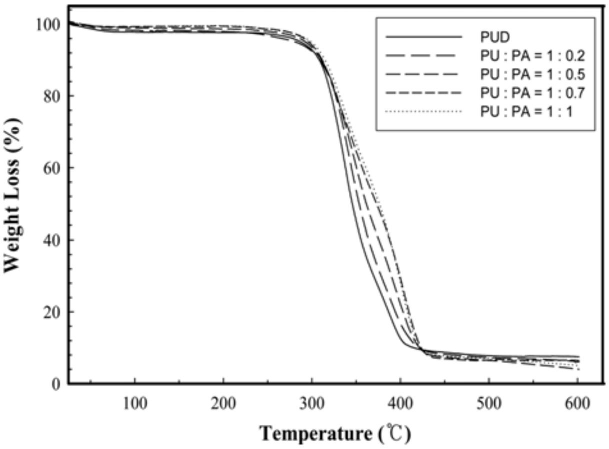


Figure 8. TGA curves of PU dispersion and PU-PA hybrid emulsions.

Mechanical Properties of the PU-PA Hybrid Emulsions. Figure 9(a)-(e) shows tensile strength of the PU dispersion and PU-PA hybrid emulsion films of PU:PA=1.0:0.2, 1.0:0.5, 1.0:0.7, and 1.0:1.0 by weight, respectively. From Figure 9, tensile strength of the PU dispersion film is found to be 22.5 MPa. The tensile strength of the PU-PA hybrid emulsion films increases with the increase in polyacrylate content from 25.7 to 40.7 MPa. From Figure 9, the PU film showed lower tensile strength than that of the PU-PA hybrid films, with the increase of PA content from 1.0:0.2 to 1.0:1.0 by weight. From the results of Figure 9, it is suggested that the increase in tensile strength of the PU-PA hybrid films is due to the increase of strong interaction between the PU and PA molecules.

Conclusions

The hydrophilic unit of sulfonate-type polyol (-SO_3Na) was used to stabilize waterborne polyurethane dispersions. The PU-PA hybrid emulsions were synthesized emulsifier-free seed emulsion polymerization with the previously synthesized PU dispersion as the seed particles. From the results of FTIR spectroscopy study, the percentage of the ratio of acrylic group (-C=O) to amine group (-NH) increased with the increase of acrylate content of the PU-PA hybrid emulsion films.

From the result of particle size distribution of the PU-PA hybrid emulsions, the average particle size of hybrid emulsions increased from 1.2 to 9.1 μm when the polyacrylate content increased from 0.2 to 1.0 by weight, which could be the swelling tendency of acrylic monomer into the PU particles. The rapid increase of average particle size with high polyacrylate contents suggests the instability of a swelled particle with insufficient sulfonate group content on the surface, leading to particle coalescence. In addition, the SEM results supported the above results that the size of the polyacrylate particles increased with the increase polyacrylate content. This result suggests that the hydrophobic polyacrylate can easily diffuse into PU particles where the free radical chain-growth polymerization takes place.

From the thermal analysis results, the shifts in $T_{g,1}$ and $T_{g,2}$ were observed that related to the partial compatibility and inter-diffusion of the PU dispersion and PA components. The TGA curves shift to a higher temperature with the increase of polyacrylic content, which indicated a higher thermal stability of the PU-PA hybrid emulsions because of the incorporation of the more thermally-stable polyacrylate. Tensile strength of the PU-PA hybrid emulsion films was increased with the increase of the polyacrylate content, which was due possibly to the strong interaction between the PU and PA molecules.

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