Effect of Acrylic Monomer Content on the Properties of Waterborne Poly(urethane-urea)/Acrylic Hybrid Materials

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ABSTRACT: Stable waterborne poly(urethane-urea) (WBPU; soft segment content: 57%; dimethylol propionic acid: 19 mol %/5.8 wt %)–polyacrylate(methyl methacrylate/n-butyl acrylate) (weight ratio: 4/1) hybrid latex (emulsions) with different acrylic contents [0, 10, 20, 30, and 40 wt % based on poly(urethane-urea)] and without external surfactant were successfully prepared by *in situ* polymerization during a prepolymer mixing process. However, the as-polymerized hybrid latex containing 50 wt % of acrylic monomer content was found to be unstable, indicating that about 50 wt % of acrylic monomer content was beyond the limit value of self-emulsifying ability of WBPU anionomer prepared in this study. The breadth of particle size distribution of hybrid latex increased markedly from 20–75 to 55–275 nm with increasing acrylic monomer content from 0 to 40 wt %. The pristine WBPU and hybrid latex samples containing 10, 20, and 30 wt % of acrylic monomer showed unimodal distributions, whereas the hybrid sample having 40 wt % acrylic monomer content displayed a bimodal distribution with the broadest breadth. As acrylic monomer content increased, the yield point of stress–strain curve, hardness, glass transition, and water resistance of hybrid film samples increased, whereas their abrasion resistance, elongation at break, and elasticity decreased. The tensile strength of hybrid film samples (10–30 wt % of acrylic monomer content) was almost the same as that of pristine WBPU film sample, indicating the intimate molecular mixing between poly(urethane-urea) and polyacrylate molecules in hybrids. However, the hybrid sample having 40 wt % acrylic monomer showed significantly diminished performance, which might be due to the deviation from intimate molecular mixing. From these results, the optimum acrylic monomer content was found to be about 30 wt %, which realized reasonably advantages of both poly(urethane-urea) and acrylic polymer. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 5113–5121, 2012

Key words: waterborne polyurethane; acrylic monomer; hybrid; latex

INTRODUCTION

One of the most important characteristics of many polyurethane ionomers is their ability to disperse in water. To be dispersible in water, polyurethane should contain ionic and/or nonionic hydrophilic segments in its structure. Waterborne poly(urethane-urea)s (WBPUs) are usually prepared in the form of ionomers with a molecular weight high enough to form films with excellent performance solely on physical drying. The ionic centers are located in hard segments because ionic diols are incorporated as chain extenders. Polyurethane anionomers are usually prepared by the addition of a pendant acid group such as dimethylol propionic acid (DMPA) into the backbone of the polyurethane prepolymer. The pendant carboxylic acid groups are neutralized with base (tertiary amine) to form internal salt-group-containing prepolymers that can easily be dispersed in water. However, dried films of WBPUs are generally water sensitive because of the presence of ionic groups. Therefore, the ionic content should be kept to a minimum for the formation of water-resistant WBPUs. We found that it was very difficult to obtain stable WBPU dispersions with low concentration of ionic moieties (<10 mol % or 2 wt %).[1] We also found that it was very important to adjust the water resistance and dispersion stability via the subtle control of the hydrophilic–hydrophobic balance through the use of the hydrophobic component and enough ionic moieties for WBPUs.[2] In addition, in many cases, no external surfactants are present to contribute adversely to water sensitivity of WBPU-based coatings. One of the most preferred methods to prepare WBPU dispersions is the prepolymer mixing process. There are three steps in this process: (1) formation of isocyanate-terminated prepolymer by reacting an excess of diisocyanate with a polyol/carboxylic acid-functional diol; (2) neutralization and dispersing the resulting prepolymer in water for particle formation; and (3) chain extension by adding a water-soluble diamine to react the residual isocyanate for higher molecular weight and urea linkage formation.

Recently, WBPU is considered as one of the most important commercial polymers because of its environmental benefits and tremendous usefulness when compared with conventional solvent-based polyurethanes. WBPU films show excellent mechanical properties, elasticity, abrasion, and solvent resistance depending on their structure. In addition, WBPU is well known as an alternative material to solvent-based polyurethane for many applications such as adhesives, coating for wood finishing, glass fiber sizing, automotive topcoats and primers, films for packages, and other applications.[3–8] Polyurethanes are available in both aromatic and aliphatic varieties. Aromatic polyurethanes are not suitable for applications requiring low yellowing, and therefore, aliphatic polyurethanes are required for such cases in which exposure to direct or indirect sunlight occurs. Unfortunately, aliphatic WBPU has high production cost and low gloss, and WBPU materials are of inferior water resistance.

Acrylic polymers are generally considered to be of low cost and have good water and weathering resistance, proper mechanical properties, and gloss. Despite these advantages, acrylic polymers show low elasticity and abrasion resistance. As a result, formulators have sought ways to combine the advantageous properties of these two polymers. To take advantage of the potential cost reduction and good water resistance afforded by the acrylics and maintain a greater share of the advantageous WBPU properties, so-called hybrid systems were developed. The hybrids incorporate both the urethane-urea and acrylic polymers into the same dispersion.

The most popular strategy is to blend the WBPU with an acrylic emulsion that costs less than one-half of a standard aliphatic WBPU. Although the acrylics reduce the system cost, they also reduce the overall performance of the binder. The reduction in performance can be lower than what would be predicted from an arithmetic rule of mixtures. One possible reason for this behavior is that, on a molecular level, the acrylic polymers are not soluble in the WBPU polymers. Therefore, the acrylic/WBPU polymers remain phase separated during film formation. The resultant discontinuous phase morphology is mainly responsible for the diminished performance. Thus, direct blending of acrylic emulsions and WBPU dispersions results in properties of lower quality to those predicted by the "rule of mixtures" because of limited miscibility between polyurethane and acrylic polymers and a high amount of phase separation between two polymers.[9–11] Therefore, to overcome this problem, there are many studies[9,10,12–28] dealing with combinations of polyurethane with polyacrylate using grafting/crosslinking in emulsion/miniemulsion/microemulsion polymerization and seeded emulsion polymerization. It was found that an external emulsifier (surfactant) was mostly used in most of these emulsion polymerizations for polyurethane–polyacrylate hybrid latex. This study takes an approach different from other studies done in this area so far in that its objective is to find the optimum composition of high-performance coating material with stable WBPU/acrylic hybrid latex formation and without external surfactant via *in situ* polymerization using a prepolymer mixing process, which facilitates the attainment of intimate molecular mixing through the formation of urethane prepolymer particles absorbing acrylic monomer.

In this study, WBPU/acrylic hybrid latex with different acrylic contents (0, 10, 20, 30, 40, and 50 wt %) were prepared from poly(tetramethylene adipate)-glycol (PTAd; number-average molecular weight [M_n] = 2000), 4,4'-dicyclohexylmethane diisocyanate (H$_{12}$MDI), triethylamine (TEA), ethylene diamine (EDA), DMPA, dibutyltin dilaurate (DBTDL) as a catalyst, acrylic monomers (weight ratio of methyl methacrylate [MMA]/n-butyl acrylate [BA]: 4/1), and ammonium persulfate (APS; 2 wt % based on acrylic monomer content) as an initiator. The effect of acrylic monomer content on the stability, particle size distribution, and mean particle size of the hybrid latex (emulsion) was investigated. The effect of acrylic monomer content on the glass transition, dynamic mechanical and mechanical properties, hardness, abrasion resistance, and water resistance of hybrid film materials was also investigated.

EXPERIMENTAL

Materials

PTAd (M_n = 2000 g/mol; Aldrich Chemical, Milwaukee, WI) was dried at 90°C under 1–2 mmHg for 3 h before use. H$_{12}$MDI (Aldrich Chemical, Milwaukee, WI), TEA (Junsei Chemical Co., Japan), EDA (Aldrich Chemical, Milwaukee, WI), acetone (Aldrich Chemical, Milwaukee, WI), and N-methyl-2-pyrrolidone (NMP; Aldrich Chemical, Milwaukee, WI) were used after dehydration with 4-Å molecular sieves for 1 day. DMPA (Aldrich Chemical, Milwaukee, WI) was dried in a vacuum oven for 5 h at 100°C. DBTDL, distillated deionized water, MMA, BA, and APS (all obtained from Aldrich Chemical, Milwaukee, WI) were used without further purification.

Preparation of the pristine WBPU and WBPU/acrylic hybrids

The pristine WBPU and poly(urethane-urea) hybrid samples were synthesized by the prepolymer mixing process (Scheme 1). PTAd was placed in a four-necked separating round-bottomed flask equipped with a thermometer, a mechanical stirrer, a

$$n\,HO\text{\textasciitilde}OH \;+\; n\,HOCH_2\overset{CH_3}{\underset{COOH}{\overset{|}{\underset{|}{C}}}}CH_2OH \;+\; 3n\,OCN\text{—}R\text{—}NCO$$

Polyol(PTAd)　　　　　　DMPA　　　　　Ecxess diisocyanate(H$_{12}$MDI)

3h, 85°C

$$OCN\cdot R\cdot N\text{-}C\text{-}O\cdot CH_2\text{—}\overset{CH_3}{\underset{COOH}{C}}\text{-}CH_2\text{-}O\text{-}C\text{-}N\text{-}R\text{-}N\text{-}C\text{-}O\text{\textasciitilde}O\text{-}C\text{-}N\text{-}R\text{-}NCO$$

Neutralization(TEA)　　30min, 65°C

$$OCN\text{-}R\text{-}N\text{-}C\text{-}O\text{\textasciitilde}O\text{-}C\text{-}N\text{-}R\text{-}N\text{-}C\text{-}OCH_2\text{-}C\text{-}CH_2\text{-}O\text{-}C\text{-}N\text{-}R\text{-}N\text{-}C\text{-}O\text{\textasciitilde}O\text{-}C\text{-}N\text{-}R\text{-}NCO$$
$$COO^- \overset{+}{N}H(Et)_3$$

- Acetone
- Dispersion into distilled water for 30min
- Chain extension by EDA for 2h,40°C

- Acrylic monomer
- Distillled water dispersion 30min
- Preliminary chain extension by EDA for 1h, 40°C

$$OCH_2\overset{CH_3}{C}CH_2OC\text{-}N\text{-}R\text{-}N\text{-}CO\text{\textasciitilde}OC\text{-}N\text{-}R\text{-}NCN\text{-}CH_2CH_2\text{-}NCN\text{-}R\text{-}N\text{-}CO\text{\textasciitilde}O\text{-}C\text{-}N\text{-}R\text{-}NCO\text{-}CH_2\overset{CH_3}{C}CH_2\text{—}$$
$$COO^- NH(Et)_3 \qquad\qquad COO^- NH(Et)_3$$

Acetone removal

Pristine WBPU

In situ polymerization by heating up to 70°C

- Chain extension by EDA
- Polymerization of acrylic monomer using initiator APS

Where,

$$\text{\textasciitilde} = \text{—}O\text{-}C\text{-}(CH_2)_4\text{-}C\text{-}(CH_2)_4\text{—}$$

$$R = \text{—}\hexagon\text{-}CH_2\text{-}\hexagon\text{—}$$

WBPU/acrylic hybrids with IPN structure

Scheme 1 The preparation of pristine WBPU and WBPU/acrylic hybrids.

condenser with a drying tube, an inlet of dry nitrogen, and a heat jacket and was degassed in vacuum at 90°C for 1 h. DMPA/NMP (1/1 w/w) was added to the flask, and the mixture was allowed to cool to 45°C under moderate stirring (175–200 rpm). H$_{12}$MDI was then slowly dropped into the flask, and the reaction mixture was allowed to react at 85°C under stirring (175–200 rpm) until the theoretical NCO content was reached. The change in the NCO value during the reaction was determined with the standard dibutylamine back-titration method (ASTM D 1638). Then, acetone (20 wt % based on urethane prepolymer weight) for the pristine WBPU was added to the NCO-terminated prepolymer mixture to adjust the viscosity of the solution. However, acetone (10 wt %)/acrylic monomer (10 wt %) and 20, 30, 40, and 50 wt % of acrylic monomer were used instead of pure acetone for hybrid materials. TEA was added to the

TABLE I
Sample Designation, Composition, Average Particle Size, Viscosity, and Shelf Stability
of Pristine WBPU and WBPU/Acrylic Hybrids

Sample designation	Composition (molar ratio)					Acrylic monomer (wt %)	APS (wt %)	Average particle size (nm)	Viscosity (cP/25°C)	Shelf stability[a]
	PTAd	DMPA	H$_{12}$MDI	TEA	EDA					
WBPU	0.3	0.45	1.19	0.45	0.44	0	0	43.5	57.2	Stable
WBPU/AC10	0.3	0.45	1.19	0.45	0.44	10	2	60.1	28.8	Stable
WBPU/AC20	0.3	0.45	1.19	0.45	0.44	20	2	71.8	27.2	Stable
WBPU/AC30	0.3	0.45	1.19	0.45	0.44	30	2	126.3	21.6	Stable
WBPU/AC40	0.3	0.45	1.19	0.45	0.44	40	2	142.6	18.4	Stable
WBPU/AC50	0.3	0.45	1.19	0.45	0.44	50	2	–	–	Unstable

[a] The shelf stability after 4 months for WBPU and WBPU/AC10–40 samples. The stability of as-polymerized WBPU/AC50 sample.

reaction mixture to neutralize the carboxyl group of the NCO-terminated prepolymer. After 30-min neutralization, the reaction mixture was cooled to 40°C, and distilled water (about 70 wt %) was added to the mixture with vigorous stirring (1300–1500 rpm). To obtain the pristine WBPU, the neutralized NCO-terminated prepolymer mixture was chain extended by dropping EDA/water (1/13 w/w) at 40°C for 2 h, and the reaction continued until the NCO peak (2270 cm^{-1}) in the IR spectra had completely disappeared. The WBPU (30 wt % solid content) was obtained by the evaporation of acetone and the subsequent addition of an adequate amount of distilled water. For urethane-urea/acrylic hybrid polymer emulsions, distilled water was added to the neutralized NCO-terminated prepolymer/acrylic monomer mixture with vigorous stirring (1300–1500 rpm), and the prepolymer/acrylic monomer emulsion was preliminarily chain extended by dropping EDA/water (1/13 w/w) at 40°C for 1 h, and then water/radical initiator (APS: 2 wt % based on the acrylic monomer weight) was added to the emulsion, and then the chain extension of prepolymer and radical polymerization of acrylic monomer subsequently took place at the same time by slowly heating to 70°C until the NCO peak (2270 cm^{-1}) and the vinyl group peak (959 cm^{-1}) in the IR spectra had completely disappeared. The sample designation and composition of the pristine WBPU and urethane-urea/acrylic hybrid materials prepared in this study are given in Table I.

Preparation of WBPU and WBPU/acrylic hybrid films

Films were prepared for test by pouring the dispersion into a Teflon disk at ambient conditions. The films (typically about 0.5–0.6 mm thick) were dried at room temperature for about 24 h, and then the remaining moisture was removed at 40°C under 20 mmHg for 24 h and stored in a desiccator at room temperature.

Characterization

A Fourier transform infrared spectrometer (Impact 400D; Nicolet, Madison, WI) with attenuated total reflectance was used to confirm chemical components. For each samples, 32 scans at 4 cm^{-1} resolution were collected in the transmittance mode and recorded in the range of 4000–400 cm^{-1}.

The mean particle size was measured by using laser-scattering equipment (Autosizer; Melvern IIC, Malvern, Worcester, UK). A small amount of the dispersion was added into a deionized water tank, and this was followed by the pinhole being set at 200 μm. The average particle diameters were measured at 25°C. The viscosity of the WBPU dispersion and hybrid emulsions was measured at 25°C with a Brookfield digital viscometer (model LVDV-II+; MA). The spindle number is 2, and the speed rate of the spindle is 100 rpm. The dynamic mechanical properties of film samples were measured at 3 Hz using dynamic mechanical thermal analyzer (DMA; TA-Q800; TA Instrument, USA) with a heating rate of 5°C/min in the temperature range from −80 to 140°C. The tensile properties were measured at room temperature with a Universal Testing Machine (5567 System using Standard Video Extensometer; Instron, USA) according to the ASTM D 638 specifications. A cross-head speed of 50 mm/min was used throughout these investigations to determine the ultimate tensile strength and modulus and the elongation at break for all samples. The values quoted are the average of five measurements. Tensile recovery test was carried out using a Universal Testing Machine on dumbbell specimens of 50 × 4 mm^2 area at room temperature. The samples were clamped and subjected to successive given elongation in 35%. The number of cycling was four times, and the cross-head speed was 50 mm/min. The hardness was measured with a durometer of shore A type (Asker, Kobunshi Keiki, Japan) following the ASTM D 2240. The films were overlapped and used

at a test. The values quoted are the average of five measurements. The abrasion resistance of sample films was measured using a Taber Rotary Abraser (model 5155; Taber, France) according to ASTM D 4060. The speed of turntable was about 60 min^{-1}, and an abrasion wheel H-22 was used. The Taber Wear Index of the samples was calculated by using the following equation:

$$I = 100(A - B)/C \quad (1)$$

where I is the wear index, A is the weight of test specimen before abrasion, B is the weight of test specimen after abrasion, and C is the number of cycles of abrasion recorded. The values obtained are the average of three measurements. To measure swelling in water, films were immersed in water for 48 h at 25°C. The water swelling of the films was calculated by using the following equation:

$$\text{Swelling}(\%) = 100(W - W_0)/W_0 \quad (2)$$

where W_0 is the weight of the dried film and W is the weight of the film at equilibrium swelling.

RESULTS AND DISCUSSION

Preparation of WBPU/acrylic hybrid latex

In this study, a prepolymer mixing process was used to prepare pristine WBPU and WBPU/acrylic hybrid latex. The process consisted of three steps: (1) isocyanate-terminated urethane prepolymer containing carboxylic acid groups was formed, and acrylic monomers were added to the prepolymer; (2) the prepolymer was neutralized and dispersed in water without external surfactant; and (3) the urethane prepolymer was preliminarily chain extended and then *in situ* polymerization (chain extension of urethane-urea prepolymer and polymerization of acrylic monomers) was performed. To attain the intimate molecular mixing between WBPU and acrylic polymer components, acrylic monomers instead of solvent acetone was used as a diluent to adjust the viscosity of viscose urethane prepolymer and also to incorporate acrylic monomer into the urethane prepolymer mixture simultaneously. The urethane prepolymer and acrylic monomer were homogeneously mixed prior to dispersion, and chain extension/addition polymerization subsequently took place at the same time. Prepolymers containing acrylic monomer were dispersed in water environment as nanoparticles stabilized by self-emulsifying ability of urethane prepolymer anionomer, that is, no external surfactant was used that could contribute adversely to water sensitivity and physical properties of WBPU-based coatings.

Shelf stability, particle size, and particle size distribution of WBPU/acrylic hybrid latex

In our earlier work, we found that increased hydrophilic component of DMPA content enhanced the shelf stability of WBPU and resulted in smaller particle and higher viscosity.[1,29] From the shelf stability results for WBPU/acrylic hybrid latex (see Table I), we found that the pristine WBPU emulsion and hybrid latex samples having acrylic monomer contents (10, 20, 30, and 40 wt %) were stable after 4 months; however, the hybrid latex sample containing higher content of acrylic monomer (50 wt %) was not stable. This behavior indicated that the stability of hybrid emulsions was primarily dependent on the content of the relatively hydrophobic component of acrylic monomer at a fixed composition of WBPU components (soft segment contents: 57 wt %, DMPA: 19 mol %/5.8 wt %). The self-emulsifying ability of WBPU anionomer must be dependent on the content of ionic component of DMPA. Therefore, the effect of DMPA content on the shelf stability of WBPU/acrylic hybrid latex containing various acrylic monomer contents should be made in further research.

As the content of relatively higher hydrophobic component soft segment (triblock glycol) increased, the particle size of WBPU dispersion increased while their viscosity decreased.[30] The particle size distribution curves of pristine WBPU and hybrid emulsions are shown in Figure 1, and the mean particle size and viscosity *versus* acrylic monomer content are shown in Table I. As acrylic monomer content increased, the particle size of the hybrid latex increased; however, the viscosity of the hybrid latex decreased markedly. The breadth of particle size distribution of hybrid latex also increased from 20–75 to 55–275 nm with increasing acrylic monomer content from 0 to 40 wt %. The pristine WBPU emulsion
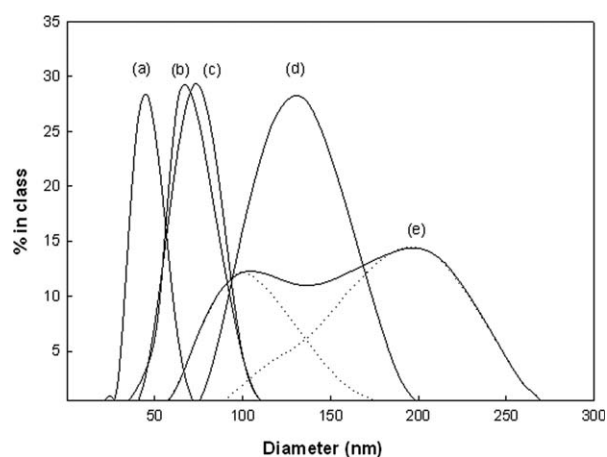
Figure 1 Particle size distribution of (a) pristine WBPU, (b) WBPU/AC10, (c) WBPU/AC20, (d) WBPU/AC30, and (e) WBPU/AC40.
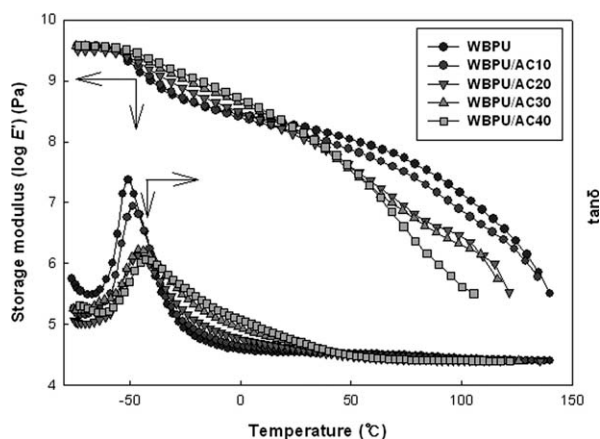
Figure 2 DMA curves of pristine WBPU and WBPU/acrylic hybrids.

and hybrid latex samples containing 10, 20, and 30 wt % of acrylic monomer showed unimodal distributions; however, the hybrid sample with 40 wt % acrylic monomer content displayed a bimodal distribution. Arguably, this broad bimodal distribution was at least partly attributable to two different kinds of particles (particles containing relatively lower and higher contents of hydrophobic acrylic component). The mean particle size also increased as acrylic monomer content increased up to 40 wt %. However, in the case of 50 wt % of acrylic monomer content, the particles of latex coagulated and thus stable hybrid emulsion was not obtained. Not surprisingly, the hybrid particles (WBPU molecules particles having acrylic component) containing relatively higher hydrophobic acrylic monomer content grew bigger until the lipophilic value of hydrophilic–lipophilic balance in WBPU particles reached the limit value of around 40 wt %, beyond which particles agglomerated. From these results, the 50 wt % of acrylic monomer content was found to be beyond the limit value of self-emulsifying ability of WBPU anionomer (ionic content: 19 mol %/5.8 wt %) prepared in this study.

Dynamic mechanical analysis

The dynamic storage modulus (E') and loss tan δ of the pristine WBPU and WBPU/acrylic hybrid films samples are shown in Figure 2. The E' of samples was maintained constant in the glassy plateau region, and then it was rapidly decreased due to the glass transition of soft segment of WBPU. The temperature range in the glassy plateau region increased with increasing acrylic monomer content. The hybrid film samples with higher acrylic monomer contents had higher storage modulus up to the room temperature; however, the trend was adverse beyond the room temperature. The loss tan δ peak of WBPU at

about −54°C is assigned to the glass transition of soft segment (PTAd) of WBPU. As acrylic monomer content increased, the tan δ peak point (T_g) increased a little; however, the temperature range of single tan δ peak broadened out and was greatly extended to higher temperature region. The single peak of tan δ strongly evidences a significant amount of polymer–polymer mixing, in which, presumably, the different polymer molecules [soft segment molecule of poly (urethane-urea) and acrylic molecule] are intertwined similar to that of an interpenetrating network.

Tensile properties/elastic recovery, hardness, abrasion resistance, and water resistance

The stress–strain curves of film samples are shown in Figure 3. The tensile strength of hybrid film samples (10–30 wt % acrylic monomer content) was almost the same as that of pristine WBPU film sample; however, the hybrid film sample having 40 wt % acrylic content had a little lower tensile strength. However, the tensile elongation at break of hybrid film sample was markedly decreased with increasing acrylic monomer content. The yield point in stress–strain curve and initial modulus (slope of stress–strain curve) increased significantly with increasing acrylic monomer content. The stress–strain hysteresis curves of film samples for a given strain (35%) are shown in Figure 4. The instant elastic recovery strain during unloading and the stress at the given strain (35%) increased a little as the acrylic monomer content was increased from 0 to 30 wt % and the number of cycle from 1 to 4. However, the hybrid film sample containing 40 wt % of acrylic monomer had relatively higher instant elastic recovery strain than those of hybrid film samples containing 10–30 wt % of acrylic component. The decrease of elasticity of hybrid film sample with increased acrylic component should be attributed to the lower elasticity of
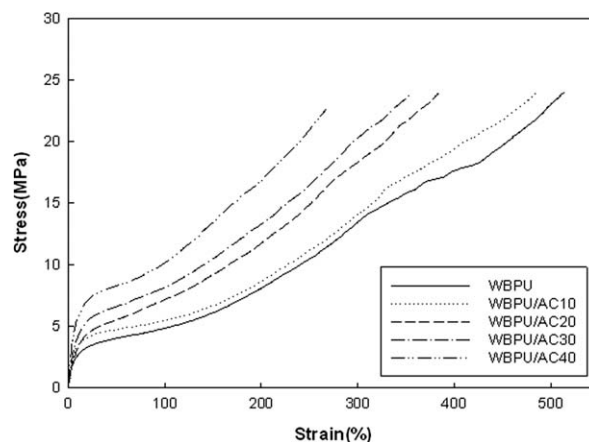
Figure 3 Strain–stress curves of pristine WBPU and WBPU/acrylic hybrids.
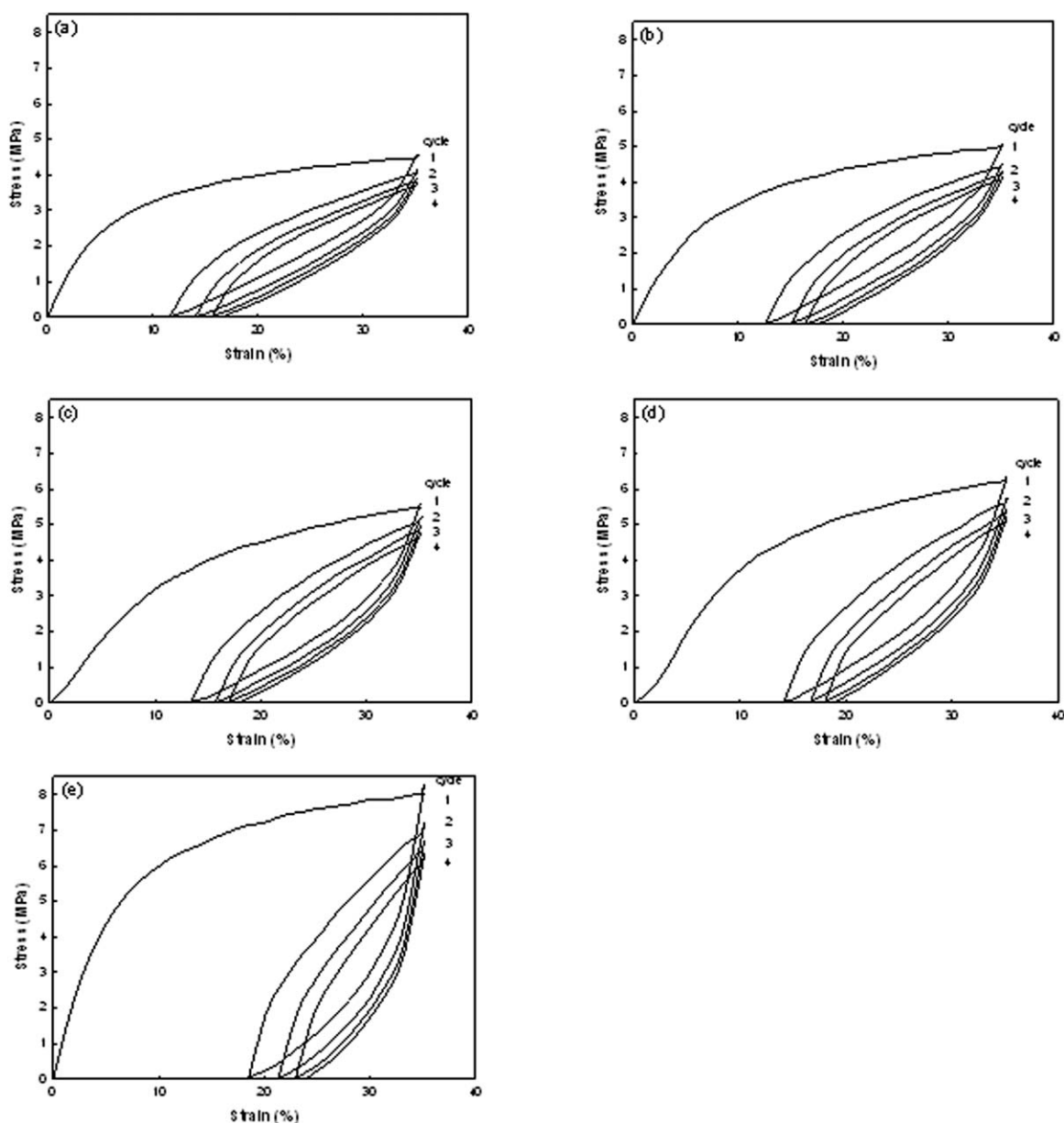
Figure 4 Stress hysteresis curves of (a) pristine WBPU, (b) WBPU/AC10, (c) WBPU/AC20, (d) WBPU/AC30, and (e) WBPU/AC40.

acrylic polymer when compared with poly(urethane-urea).

The hardness of film samples with increased acrylic monomer content is shown in Table II. Generally, hardness reflects the resistance to local deformation, which is a complex property related to plasticity, rigidity/modulus, porosity, and density/crosslink density. The hardness of film sample increased with increasing acrylic monomer content. This behavior might be due to the higher rigidness of acrylic polymer component than poly(urethane-urea) component as well as the higher compactness of hybrid texture.

Films with a diameter of 10 cm were prepared and then fixed on wearing machine with load 9.8 N. The weight loss was measured after 200 and 500 cycles, and wear indexes of samples are shown in Figure 5. The wear index slightly increased with increasing acrylic monomer content up to 30 wt % and increased sharply at 40 wt % acrylic content. The wear index is the reciprocal proportion to the abrasion resistance. Therefore, the abrasion resistance decreased a little as the acrylic monomer content was increased up to 30 wt %. However, the hybrid sample having 40 wt % acrylic monomer content exhibited a significantly low abrasion resistance. This behavior might be due to the lower abrasion resistance of polyacrylate polymer when compared with poly(urethane-urea) as well as the lower compatibility between poly(urethane-urea) and acrylic components at higher acrylic content.

TABLE II
**Glass Transition Temperature (T_g) and Mechanical Properties of Pristine WBPU and WBPU/Acrylic Hybrids**

Sample designation	T_g (°C)	Yield strength (MPa)	Tensile strength (MPa)	Elongation at break (%)	Hardness	Onset strain (%)				Recovery (%)			
						First	Second	Third	Fourth				
						Elongation (%): 35				First	Second	Third	Fourth
WBPU	−51.3	3.1	24.0	513.5	67	11	14	15	16	70	60	55	53
WBPU/AC10	−48.7	3.8	23.9	485.0	72	12	15	16	17	64	57	53	50
WBPU/AC20	−46.1	4.7	23.9	383.3	78	13	16	17	18	62	55	52	49
WBPU/AC30	−45.5	5.7	23.8	336.0	90	14	17	18	19	59	53	48	46
WBPU/AC40	−41.8	7.5	22.7	267.4	95	18	21	23	24	47	39	35	32

The water resistance of WBPU material is in reverse proportion to the stability of WBPU dispersion. Thus, it is very difficult to obtain high water-resistance WBPU materials from fully stable WBPU dispersions with high ionic moiety content. Therefore, it is very important to adjust the water resistance through the combination of hydrophobic polyacrylate component and WBPU with enough high ionic moiety (19 mol %/5.8 wt %) in hybrid materials. The water swelling percentage of hybrid film samples prepared in this study was significantly decreased with increasing acrylic monomer content (see Fig. 6), indicating that the increase of acrylic monomer content increased the water resistance of the hybrid material. The water swelling percentage of the hybrid sample containing 30 wt % acrylic content was about half that of pristine WBPU. The decrease of water swelling percentage should be due to the excellent water resistance of acrylic component.

CONCLUSIONS

To take advantage of the potential cost reduction and water resistance afforded by the acrylics and greater share of the advantageous WBPU properties (high tensile strength, abrasion resistance, and elasticity), a series of WBPU (soft segment content: 57 wt %, DMPA: 19 mol %/5.8 wt %)–polyacrylate(MMA/BA) (weight ratio: 4/1) hybrid latex with different acrylic contents [0, 10, 20, 30, 40, and 50 wt % based on poly(urethane-urea)] and without external surfactant were prepared by *in situ* polymerization using a prepolymer mixing process. The effect of acrylic monomer content on the shelf stability, mean particle size, particle size distribution, and viscosity of hybrid latex, and the glass transition behavior, tensile properties/elasticity, abrasion resistance, hardness, and water resistance of hybrid film samples were investigated. The hybrid emulsions containing up to 40 wt % of acrylic monomer content were found to be stable after 4 months; however, the as-polymerized hybrid sample containing higher content of acrylic monomer (50 wt %) was not stable, indicating that around 50 wt % of acrylic monomer content was beyond the limit value of self-emulsifying ability of WBPU anionomer prepared in this study. As a result of increased acrylic monomer content from 0 to 40 wt %, a noticeable growth from 20–75 to 55–275 nm was achieved in the breadth of particle size distribution of latex. Although the pristine WBPU and hybrid latex samples with 10, 20,
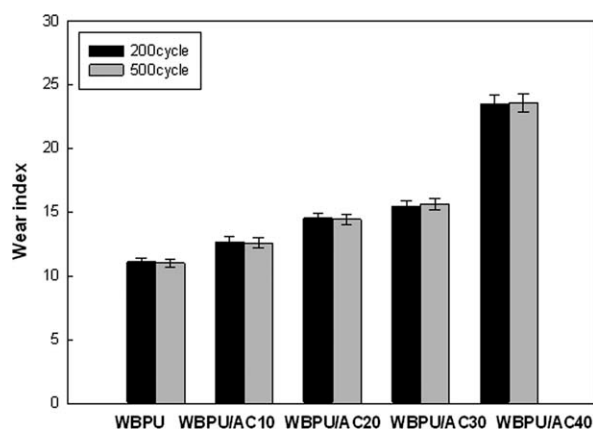
Figure 5 Wear index of pristine WBPU and WBPU/acrylic hybrids.
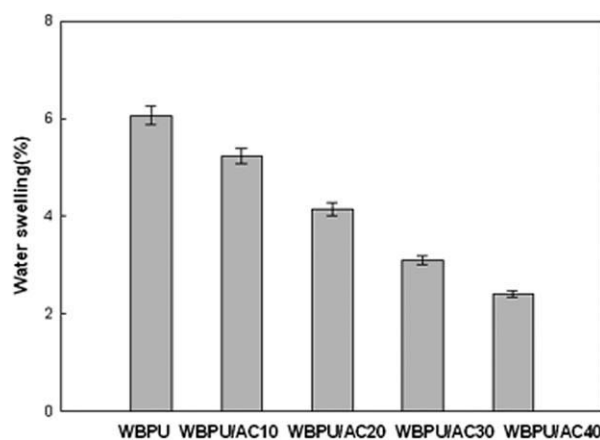
Figure 6 Water swelling ratio of pristine WBPU and WBPU/acrylic hybrids.

and 30 wt % of acrylic monomer exhibited unimodal distributions, the hybrid sample containing 40 wt % of acrylic monomer content showed a bimodal distribution with the broadest breadth. The viscosity of hybrid emulsions decreased markedly with increasing acrylic monomer content. As the acrylic monomer content of hybrid film samples increased, the single tan δ peak temperature (T_g) of soft segment (PTAd) in pristine WBPU increased a little; however, the temperature range of single tan δ peak broadened out and was greatly extended to higher temperature region. The single peak is a strong evidence for a significant amount of polymer–polymer mixing, in which, presumably, the different polymer molecules [relatively hydrophobic soft segment molecules of poly(urethane-urea) and acrylic molecules] are intertwined similar to that of an interpenetrating network. As the acrylic monomer content increased, the yield point of stress–strain curve, hardness, and water resistance increased, whereas the abrasion resistance, elongation at break, and elasticity of hybrid film samples decreased. The tensile strength of hybrid film samples (10–30 wt % of acrylic monomer content) was almost the same as that of pristine WBPU film sample; however, the hybrid film sample having 40 wt % acrylic content had a little lower tensile strength. Especially, the hybrid sample having 40 wt % acrylic monomer showed sudden changes in all these properties. The relatively better mechanical properties of the hybrid materials containing acrylic monomer content up to 30 wt % might be due to higher compatibility between poly(urethane-urea) and acrylic components. From these results, it was found that the optimum acrylic monomer content of hybrid materials prepared in this study was about 30 wt %, which realized reasonably advantages of both poly(urethane-urea) and acrylic polymer.

References

1. Rahman, M. M.; Kim, H. D. J Appl Polym Sci 2006, 102, 5684.
2. Lee, Y. H.; Kim, E. J.; Kim, H. D. J Appl Polym Sci 2011, 120, 212.
3. Yen, M. S.; Tsai, P. Y.; Hong, P. D. Colloids Surf A 2006, 279, 1.
4. Kim, H. D.; Kim, T. W. J Appl Polym Sci 1998, 67, 2153.
5. Kwon, J. Y.; Kim, E. Y.; Kim, H. D. Macromol Res 2004, 12, 303.
6. Rahman, M. M.; Kim, H. D.; Lee, W. K. J Adhes Sci Technol 2009, 23, 177.
7. Kim, B. S.; Kim, B. K. J Appl Polym Sci 2005, 97, 1961.
8. Scrinzi, E.; Rossi, S.; Defleorian, F.; Zanella, C. J Prog Org Coat 2011, 72, 81.
9. Kukanja, D.; Golob, J.; Zupancic-Valant, A.; Krajnc, M. J Appl Polym Sci 2000, 78, 67.
10. Hirose, M.; Zhou, J.; Katsutoshi, N. Prog Org Coat 2000, 38, 27.
11. Otts, D. B.; Dutta, S.; Zhang, P.; Smith, O. W.; Thames, S. F.; Urban, M. W. Polymer 2004, 45, 6235.
12. Okamoto, Y.; Hasegawa, Y.; Yoshino, F. Prog Org Coat 1996, 29, 175.
13. Hirose, M.; Kadowaki, F.; Zhou, J. Prog Org Coat 1997, 31, 157.
14. Lam, P. K. H.; George, M. H.; Barrie, J. A. Polymer 1989, 30, 1332.
15. Zhang, T.; Wu, W. J.; Xiaojie, Y. M. J Prog Org Coat 2010, 68, 201.
16. Chen, G. N.; Chen, K. N. J Appl Polym Sci 1999, 71, 903.
17. Wang, H.; Wang, M.; Ge, X. Radiat Phys Chem 2009, 78, 112.
18. Zhang, Y.; Heath, R. J.; Hourston, D. J. J Appl Polym Sci 2000, 75, 406.
19. Dadbin, S.; Chaplin, R. P. J Appl Polym Sci 2001, 81, 3361.
20. Li, M.; Daniels, E. S.; Dimonie, V.; Sudol, E. D.; El-Aasser, M. S. Macromolecules 2005, 38, 4183.
21. El-Aasser, M. S.; Sudol, E. D. JCT Res 2004, 1, 21.
22. Wang, C.; Chu, F.; Guyot, A.; Gauthier, C.; Boisson, F. J Appl Polym Sci 2006, 101, 3927.
23. Lu, Y.; Larock, R. C. Biomacromolecules 2007, 8, 3108.
24. Wang, C.; Chu, F.; Graillat, C.; Guyot, A.; Gauthier, C.; Chanper, J. P. Polymer 2005, 46, 1113.
25. Amalvy, J. I. Pigment Resin Technol 2002, 31, 275.
26. Honig, H. L.; Balle, G.; Keberle, W. U.S. Pat.3,705,164 (1972).
27. Loewrigkeit, P.; van Dyk, K. A. U.S. Pat.4,644,030 (1987).
28. Vijayendran, B. R.; Dervy, R.; Gruber, B. A. U.S. Pat.5,173,526 (1992).
29. Kwak, Y. S.; Kim, E. Y.; Yoo, B. H.; Kim, H. D. J Appl Polym Sci 2004, 94, 1743.
30. Kwak, Y. S.; Kim, H. D. Fibers Polym 2002, 3, 153.