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Effect of Total Acrylic/Fluorinated Acrylic Monomer Contents on the Properties of Waterborne Polyurethane/Acrylic Hybrid Emulsions

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Abstract: Stable emulsions of waterborne poly(urethane-urea) (WBPU, soft segment content: 57 wt%, dimethylol propionic acid: 19 mol%/5.8 wt%)/*n*-butyl acrylate (BA)/glycidyl methacrylate (GMA)/perfluorodecyl acrylate (PFA) (weight ratio of BA/GMA/PFA: 5/3/2) hybrid materials containing 0-30 wt% of acrylate content (fluorinated acrylate content: 0-6 wt%) were successfully prepared by an emulsifier-free/solvent-free prepolymer mixing process. However, the as-polymerized hybrid emulsion containing 40 wt% of acrylic monomer content was found to be unstable, indicating that near 40 wt% in acrylic monomer content was beyond the limit of the self-emulsifying ability. By the curve fitting analysis of IR-peaks and X-ray photoelectron spectroscopy (XPS) analysis, the C-F content was found to increase with the increase in acrylate content. The average particle size of emulsion, young modulus/yield point in stress-strain curve, hardness, thermostability, and water/methylene iodide-contact angles of the film sample increased with increasing acrylate content. However, the viscosity of emulsion, the elongation at break, water swelling and surface energy of film samples were significantly decreased with increasing acrylate content. The tensile strength of film sample decreased a little with increasing acrylate content. These results point to the strong potential of WBPU (70 wt%)/acrylate copolymer (30 wt%) hybrid as a coating material with the lowest surface energy (18.18 mN/m) and the highest contact angles (water: 111.76°, and methylene iodide: 79.95°).

Keywords: fluorinated acrylic monomer, waterborne polyurethane, acrylate copolymer, hybrid, emulsion.

Introduction

Waterborne poly(urethane-urea)s (WBPUs) dispersions are nontoxic and nonflammable materials. They also exhibit excellent adhesion to many substrate surfaces including glass, rubber, leather and fibers.[1-4] Most WBPUs contain ionic groups in their molecular structure, and show excellent mechanical properties due to the presence of inter-chain Columbic forces and hydrogen bonding.[4] The pendant carboxylic salt groups of dimethylol propionic acid (DMPA) in the WBPUs are hydrophilic and act as anionic centers and internal emulsifiers. 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%, 2 wt%).[5] 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.[6]

Acrylic polymers are generally considered to be inexpensive with good water and weathering resistance, proper mechanical properties and gloss, but they exhibit poor elasticity and abrasion resistance. As a result, various formulators have examined ways of combining the advantages of WBPU and acrylic polymer. A so-called hybrid system was developed to exploit the potential cost reduction and good water resistance afforded by the acrylic polymers and maintain a greater share of the advantageous WBPU properties. The hybrids incorporated both urethane-urea and acrylic polymers into the same dispersion. The most popular strategy is to blend WBPU with an acrylic emulsion, which costs less than half that of standard aliphatic WBPU. On the other hand, the direct blending of acrylic emulsions and WBPU dispersions results in a poorer quality product compared to those predicted by the "rule of mixtures" because of the limited miscibility between polyurethane and acrylic polymers and the large amount of phase separation between the two polymers.[7-9] Therefore, to overcome this problem, many studies have evaluated combinations of polyurethane with polyacrylate through grafting/crosslinking in emulsion/miniemulsion/microemulsion polymerization and seeded emulsion polymerization.[7,8,10-24] It was found that an external emulsi-

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fier was mostly used in these emulsion polymerizations. No external surfactants are present to contribute adversely to water sensitivity of WBPU-based coatings. A previous study[25] reported the optimum composition of a high-performance coating material with stable WBPU/acrylic hybrid latex formation without an external surfactant by *in situ* polymerization using a prepolymer mixing process. This process allows intimate molecular mixing through the formation of acrylic monomer absorbed-urethane prepolymer.

With regard to the surface modification of the coating materials, the hydrophilic segment of WBPU adversely affects the water and soil repellency due to its relatively high surface energy. One method to complement the defect is to incorporate strong hydrophobic components (fluorinated monomers) into the WBPU structure. Acrylate copolymers containing perfluoroalkyl side chains have been the focus of many studies because of the good reactivity of perfluorinated acrylate with fluorine-free acrylate and the good adhesion to matrices. Fluorinated polymers are becoming increasingly important because of their unique surface properties (very low surface energy, and water- and oil-repellency) and are predestined for utilization as soil-repellent coating systems.

The lower critical surface energy of many polymers containing fluorocarbon side chains has been attributed mainly to the higher content of CF_3 groups on their surfaces.[26-29] In fluoroalkyl acrylate homopolymers, the packing of the perfluoroalkyl side chains becomes tighter with increasing side chain length, resulting in denser $-CF_3$ terminal groups at the surface. Therefore, fluoroalkyl acrylate homopolymers with long side chains have very low critical surface tension, ranging from 10 to 11 mN/m.[26] The critical surface tension of closely packed $-CF_3$ groups (6mN/m) is lower than that of $-CF_2-$ surfaces (18 mN/m).[30] The main disadvantage of a fluorinated monomer is its relatively high cost. Therefore, the content of fluorinated monomers should be minimized whilst maintaining reasonable water/oil repellency (surface tension). The very low surface energy of copolymers containing perfluoroalkyl groups can be explained by the orientation of the perfluoroalkyl groups to the outmost layer of the polymer-air interface.

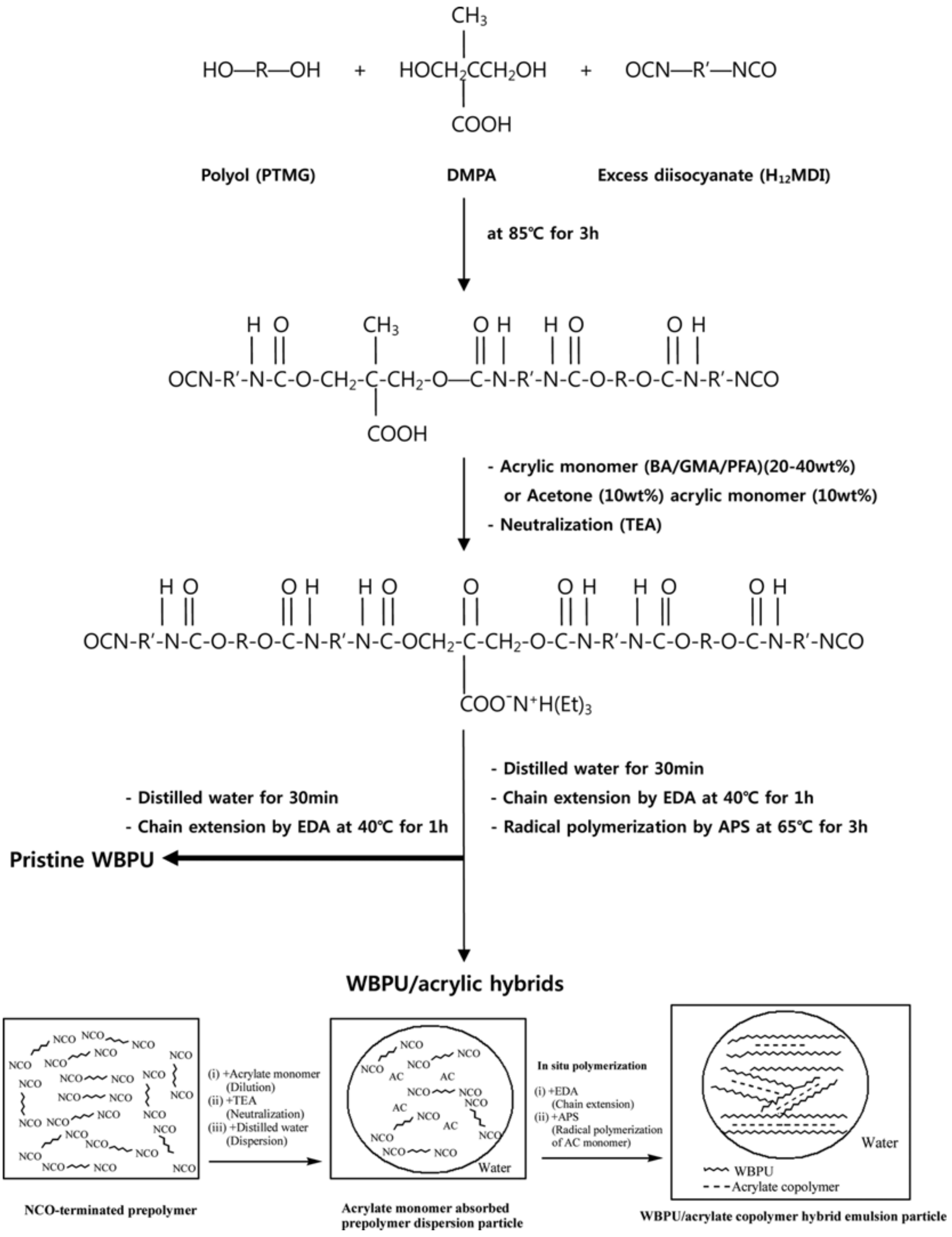
The hybridization of polyurethane with a fluorinated acrylate polymer on the molecular level is expected to improve the properties of the resulting materials.[26,30,31] However, research works related to hybrid materials of waterborne poly(urethane-urea) with acrylate copolymer containing fluorine are rare in the open literature. The main aim of this study was to improve the surface properties (high contact angle/low surface energy, and water- and oil-repellency) of coating materials using WBPU/fluorinated acrylate copolymer hybrid.

In this study, a series of waterborne poly(urethane-urea)/acrylate [*n*-butyl acrylate (BA)/glycidyl methacrylate (GMA)/perfluorodecyl acyrlate (PFA)] hybrid containing total acrylate content (0-40 wt%)/fluorinated acrylate content (0-8 wt%) were prepared by *in situ* polymerization using a prepolymer mixing process that was solvent free/emulsifier free. This study focused on the effect of total acrylate monomer (BA/GMA/PFA: 5/3/2) content (0, 10, 20, 30, and 40 wt%)/PFA content (0, 2, 4, 6, and 8 wt%) on the average particle size and viscosity of hybrid emulsions, the confirmation of the chemical structure, water swelling, water/methylene iodide-contact angles/surface free energy, thermal degradation and mechanical properties of the film samples.

Experimental

Materials. Poly(tetramethylene glycol) (PTMG M_n=2,000 g/mol; Aldrich Chemical, Milwaukee, WI) was dried at 90 °C under 1-2 mmHg for 3 h before use. 4,4′-Dicyclohexymethane diisocyanate (H_{12}MDI, Aldrich Chemical, Milwaukee, WI), triethylamine (TEA, Aldrich Chemical, Milwaukee, WI), *N*-methyl-2-pyrrolidone (NMP; Junsei Chemical, Japan), acetone (Aldrich Chemical, Milwaukee, WI) and ethylene diamine (EDA, Junsei Chemical, Japan) were used after dehydration with 4 Å molecular sieves for 1 day. Dimethlol propionic acid (DMPA, Aldrich Chemical, Milwaukee, WI) was dried in a vacuum oven for 5 h at 100 °C. Dibutyltin dilaurate (DBTDL, Aldrich Chemical, Milwaukee, WI), distillated deionized water, butyl acrylate (BA, Aldrich Chemical, Milwaukee, WI), glycidyl methacrylate (GMA, Aldrich Chemical, Milwaukee, WI), perfluorodecyl acrylate (PFA, Aldrich Chemical, Milwaukee, WI) and ammonium persulfate (APS, Aldrich Chemical, Milwaukee, WI) were used without further purification.

Preparation of the Pristine Waterborne Polyurethane-Urea (WBPU) and WBPU/Acrylate Hybrids. The pristine WBPU and poly(urethane-urea) hybrid samples were synthesized by the *in situ* polymerization with prepolymer mixing process (Scheme I). PTMG was placed in a four-necked separating round-bottomed flask equipped with a thermometer, a mechanical stirrer, a 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 (1/1.5 w/w) was added to the flask, and the mixture was allowed to cool to 45 °C under moderate stirring (125-150 rpm). H_{12}MDI was then slowly dropped into the flask, and the reaction mixture was allowed to react at 85 °C under stirring (125-150 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 (25 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, and 40 wt% of acrylic monomer were used instead of pure acetone for hybrid materials. TEA was added to the 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



Scheme I. Preparation process of pristine WBPU and WBPU/acrylic hybrids.

(about 70 wt%) was added to the mixture with vigorous stirring (850-1,000 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 ºC 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/fluorinated acrylic hybrid polymer emulsions, distilled water was added to the neutralized NCO-terminated prepolymer/acrylic monomer mixture with vigorous stirring (850-1,000 rpm), and the prepolymer/acrylic monomer emulsion was preliminarily chain extended by dropping EDA/water (1/13 w/w) at 40 ºC for 1 h, and then water/radical initiator (APS: 2 wt% based on the acrylic monomer weight)

Table I. Sample Designation, Composition, Average Particle Size, Viscosity and Shelf Stability of Pristine WBPU and WBPU/Acrylate Hybrids

Sample Designation	Composition (molar ratio)					Acrylic Monomer[a] (wt% based on WBPU)	APS (wt%)	Average Particle Size (nm)	Viscosity (cP/25)	Shelf Stability[b]
	H_{12}MDI	PTMG	DMPA	TEA	EDA					
WBPU	1.2	0.30	0.46	0.46	0.44	0	0	15.8	45	Stable
WBPU/AC10	1.2	0.30	0.46	0.46	0.44	10	2	17.4	36	Stable
WBPU/AC20	1.2	0.30	0.46	0.46	0.44	20	2	19.6	32	Stable
WBPU/AC30	1.2	0.30	0.46	0.46	0.44	30	2	26.5	27	Stable
WBPU/AC40	1.2	0.30	0.46	0.46	0.44	40	2	-	-	Unstable

[a]Acrylic monomer: wt ratio, BA/GMA/PFA : 5/3/2. [b]The shelf stability after 2 months.

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 the Pristine WBPU and WBPU/Acrylic Hybrid Films. Films were prepared by pouring the dispersion into a Teflon disk at ambient conditions. The films (typically about 0.3-0.4 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 6 h and stored in a desiccator at room temperature.

Characterizations. The average 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 (Brookfield LVDVII+, USA). The measurements were performed at 100 rpm using the spindle RV-3.

The chemical components of Pristine WBPU and WBPU/acylic hybrids film samples were confirmed by the Fourier transform infrared spectrometer (FTIR, NICOLET iS5, Thermo scientific, USA). The FTIR spectra of the samples were recorded in the range of 4000-650 cm^{-1} using ATR (ZnSe crystal) apparatus at a resolution of 4 cm^{-1} and 32 scans. A constant compression load was applied to the samples. The surface analysis was carried using the X-ray photoelectron spectrometer (XPS, Theta Probe AR-XPS System, Thermo Fisher Scientific, U.K). XPS was equipped with a monochromated AlK_α X-ray source (15 kV, 150 W) and spot size 400 μm was used with X-ray source. The samples for XPS were prepared by casting the polymer onto a clean glass disk. The disk was put into an oven at 60 °C for 12 h and 60 °C for 6 h under vacuum.

The contact angles of water and methylene iodide were measured at 25 °C using a contact angle goniometer (Erma Contact Angle Meter, Japan), and the reported results were the mean values of five times. The contact angle, a measure of the surface wettability, was used to determine the hydrophobicity and hydrophilicity. The surface energy of solid film can be determined by the following equation:

$$\gamma_s=\gamma_s^d+\gamma_s^p \quad (1)$$

$$\gamma_L(1+\cos\theta_L)=2(\gamma_L^d\gamma_s^d)^{1/2}+2(\gamma_L^p\gamma_s^p)^{1/2} \quad (2)$$

where γ_s represents the surface energy of solid film, γ_s^d represents the dispersion force, and γ_s^p represents the polarity force. The testing liquids used were water (L1) and methylene iodide (L2), and their γ_{L1}^d, γ_{L1}^p, γ_{L2}^d, and γ_{L2}^p were 21.8, 51.9, 1.3, and 49.5 mN/m, respectively.[32] 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:

$$\text{Swelling (\%)}=100(W-W_0)/W_0 \quad (3)$$

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

The Thermal properties of film samples were measured using thermogravimetric analyzer (TGA, SDT-Q600, TA Instrument, USA) under N_2 at a heating rate of 10 °C/min over a temperature range of 30-600 °C.

The tensile properties were measured at room temperature with a Universal Testing Machine (UTM, WL2100, WITHLAB). A cross-head speed of 10 mm/min was used throughout these investigations to determine the ultimate tensile strength and modulus and the elongation at break for all samples. 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.

Results and Discussion

Preparation and Shelf Stability of Hybrid Dispersions of WBPU/Acrylate Copolymer Containing Fluorine. Sample designation, composition, average particle size, viscosity, and shelf stability of pristine WBPU and WBPU/acrylate copolymer hybrid are shown in Table I. In this study, WBPU/acrylate copolymer hybrid dispersions were prepared by *in situ* polymerization (chain extension of urethane prepolymer and radical polymerization of acrylic monomers). The hybrid dispersions were obtained by *in situ* polymerization using prepolymer mixing process with self-emulsifier and without external solvent. There are three steps in this process: (1) The first step was the formation of isocyanate-terminated prepolymer by reacting an excess of diisocyanate (H_{12}MDI) with a PTMG (M_n=2,000)/DMPA (19 mol%/5.8 wt%), in this step the acrylate monomers [BA/GMA/fluorinated acrylate (PFA)] were added in order to reduce the viscosity of prepolymer instead of external organic solvent (diluent: acetone or methyl ethyl ketone (MEK)). (2) The second step was neutralization and dispersing the resulting prepolymer in water. (3) The third step involved chain extension by adding a water-soluble diamine (EDA) to react the residual isocyanate for higher molecular weight/urea linkage formation as well as emulsion radical-polymerization of acrylate monomers by adding a water-soluble radical initiator (APS). To attain the intimate molecular mixing between WBPU and acrylate copolymer components, acrylate monomers instead of external solvent such as acetone and MEK were used as diluent to adjust the viscosity of viscose urethane prepolymer and also to incoporate acrylate monomer into urethane prepolymer simultaneously. The chain extension of urethane prepolymer and radical polymerization of acrylate monomers subsequently took place. In this study, the hybrid dispersions containing up to 30 wt% of total acrylate monomers (BA/GMA/PFA) content were found to be stable after 4 months, however, the as-polymerized hybrid dispersion containing higher content of acrylic monomer (40 wt%) was not stable, indicating that about 40 wt% of acrylic monomer content was beyond the limit of the self-emulsifying ability of hybrid emulsion using a fixed content of neutralized DMPA as a self-emulsifier.

Average Particle Size and Viscosity of WBPU/Acrylate Copolymer Hybrid Dispersions. In our earlier study, we found that the dispersions of WBPU/acrylate [methyl methacrylate (MMA)/*n*-butyl acrylate(BA)] copolymer (0-40 wt%) were stable after 4 months. The average particle size of WBPU/acrylate (MMA/BA) copolymer hybrid latex increased with increasing acrylate copolymer content, and the hybrid samples containing 10, 20, 30 wt% of acrylic monomer showed unimodal distributions, however, the hybrid sample with 40 wt% acrylic monomer content displayed a broad bimodal distribution.

Table I shows the average particle size and viscosity of hybrid dispersion samples prepared in this study. The average particle size of hybrid emulsion also increased with increasing acrylate monomer content. Not surprisingly, the hybrid emulsion particles (acrylate copolymer included WBPU polymer particle) containing relatively higher hydrophobic acrylic monomer content grew bigger until the lipophilic value of the hydrophilic-lipophilic balance in WBPU particles reached the limit value of about 30 wt%, beyond which particles agglomerated. From these results, the 40 wt% of acrylate monomer content in hybrid emulsion was found to be beyond the limit value of self-emulsifying ability at the fixed ionic moiety (DMPA) content (19 mol%/5.8 wt%) of WBPU anionomer prepared in this study.

The viscosity of hybrid emulsion decreased with increasing acrylate monomer content. Generally, it is well known that the polymer dispersion (emulsion) of higher particle size has lower viscosity than that of lower particle size. Therefore, the lower viscosity of hybrid dispersion containing higher acrylate monomer content is caused by relatively higher particle size.

Identification of Chemical Structure of WBPU/Acrylate Copolymer Hybrid Films. Figure 1 shows the FT-IR spectra of pristine WBPU film and hybrid films containing various total acrylate-copolymer contents (0, 10, 20, 30)/PFA contents (0, 2, 4, 6 wt%). The characteristic bands at about 1713, 1082, 1105, and 3300-3500 cm^{-1} confirm the carbonyl group of urethane-urea, ether (C-O-C) of ester group, ether group (C-O-C) of PTMG and amide group in pristine WBPU, respectively. The ester carbonyl (C=O) goup of acrylate-copolymer in WBPU/acrylate-copolymer hybrid was identified by the characteristic peaks at around 1730 cm^{-1}. The stretching vibrations of $-CF_2$ group at 1150 cm^{-1}, $-CF_3$ group at 1240 cm^{-1}, 1206 cm^{-1}, and a combination of rocking and wagging vibration of CF_3 group at 656 and 701 cm^{-1} in the fingerprint region, are all detected in WBPU/acrylate-copolymer hybrid films. But we found that many peaks of ether/urethane-urea/acrylate/fluorine groups are overlapped each other. No bonding peak of C-H connecting C=C at 3107 cm^{-1} appeared indicating the complete reaction of all acrylic monomers in copolymerization.

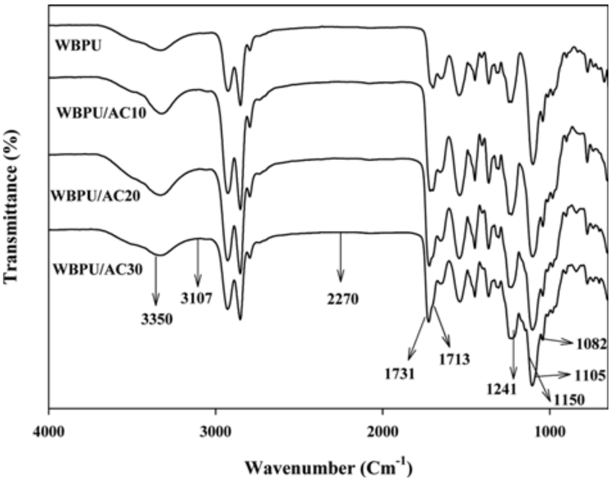


Figure 1. FTIR Spectra of pristine WBPU and WBPU/acrylic hybrid films.

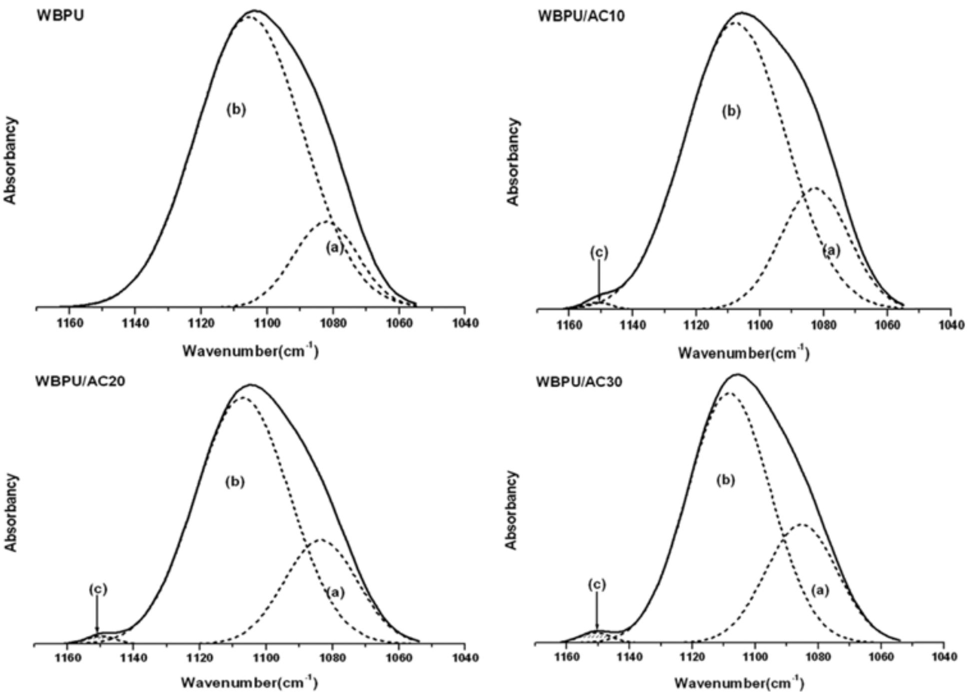


Figure 2. Decomposition of (a) C-O-C, (b) -O-, and (c) C-F bond of pristine WBPU and WBPU/acrylic hybrids.

Table II. Decomposition Results of (a) C-O-C, (b) -O-, and (c) C-F Bond of Pristine WBPU and WBPU/Acrylate Hybrids

	Peak Position (cm^{-1})			Fraction of Peak Area			
Sample Designation	(a) C-O-C (ester) Bond	(b) -O- (ether) in Urethane	(c) C-F bond (-CF_2CF_2-)	(a) C-O-C (ester) Bond	(b) -O- (ether) in Urethane	(c) C-F bond (-CF_2CF_2-)	$X_B{}^a$ (fraction)
WBPU	1082	1105	-	0.1535	0.8579	-	0
WBPU/AC10	1082	1107	1150	0.2220	0.7758	0.0050	0.0050
WBPU/AC20	1083	1107	1149	0.2444	0.7481	0.0076	0.0076
WBPU/AC30	1085	1108	1151	0.2865	0.7021	0.0110	0.0110

[a] $X_B = C_B/C_T$ [C_B: C-F bonding peak area (c), C_T: total peak area (a+b+c)]

In this study, IR spectra were analyzed with a curve-resolving technique based on linear least-squares analysis to fit the combination of Lorentzian and Gaussian curve shapes. Figure 2 shows the curve fitting of -CF_2 at 1150 cm^{-1}, -O- at 1105 cm^{-1}, and C-O-C at 1082 cm^{-1} for all samples. The small peak of -CF_2 at 1150 cm^{-1} was not appeared in the IR spectrum of the pristine WBPU. The peak point and fraction of these groups are shown in Table II. The fractions of -CF_2 in PFA and C-O-C in ester were found to increase with the increase of acrylate-copolymer/PFA content. However, the ether fraction of PTMG decreased with increasing acrylate-copolymer content. It is well known that X-ray photoelectron spectroscopy (XPS) is a surface chemical analysis technique that can be used to analyze the surface chemistry of a material as received state or after some treatment. The XPS spectra of pristine WBPU and the hybrid film samples are shown in Figure 3. The peak at 690 eV assigned to F 1s was not appeared in pristine WBPU. The peak intensity of F 1s was found to be increased with increasing PFA content in hybrid materials. In addition, it was found that the peak intensity of N 1s was very weak. This should be attributed to the very small amount of urethane-urea group in the surface layer. From these results, it was found that fluorinated component PFA was mainly introduced into the surface layer of hybrid material just as we prefer.

Surface Properties and Water Swelling of WBPU/Acrylate Copolymer Hybrid Films. Figure 4 shows the water/methylene iodide contact angles and surface energies of pristine WBPU and WBPU/acrylate-copolymer hybrid film samples. As acrylate-copolymer content increased from 0 to 30 wt%, the water and methylene iodide contact angles of hybrid film samples increased from 62.9° to 111.76°, and from 49.1° to 79.95°, respectively. Thus, the surface energy decreased with increasing acrylate/PFA content. Additionally, the fluorinated component PFA in hybrid particularly had a much lower surface energy than WBPU. When incorporating only small

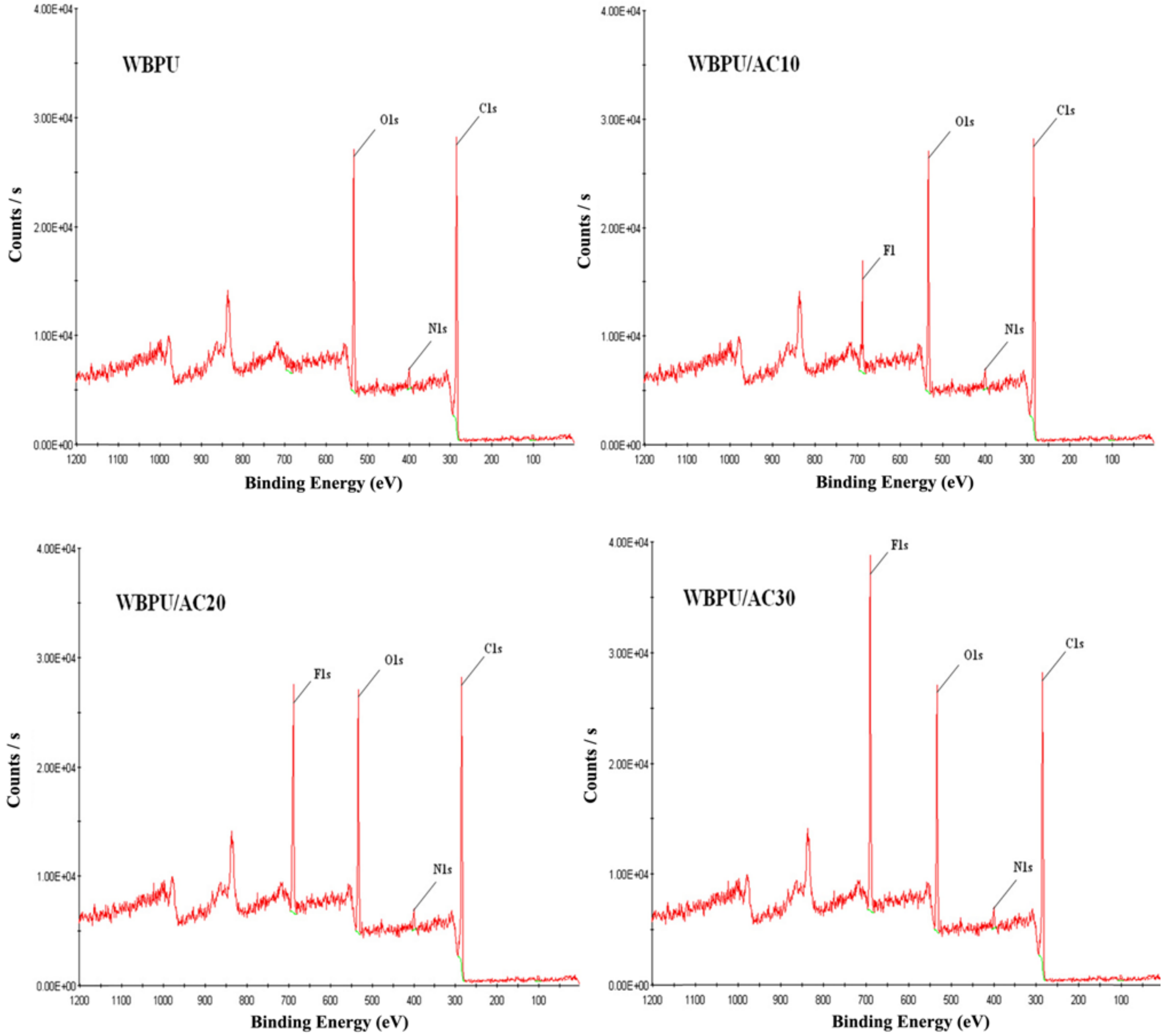


Figure 3. XPS spectra of pristine WBPU and WBPU/acrylic hybrids.

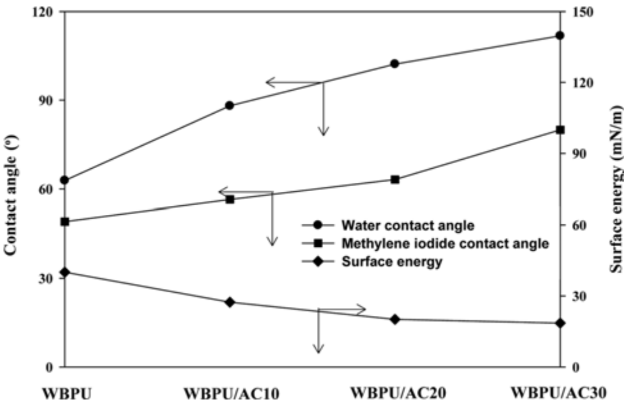


Figure 4. Water and methylene iodide contact angles and surface energy of pristine WBPU and WBPU/acrylic hybrids.

amounts of fluorinated moieties, the anisotropic configuration of these surface leads to a relatively low free energy at the surface. The very low surface energies of perfluoroalkyl polymers can be explained by the orientation of perfluoroalkyl groups to the outmost layer of the polymer-air interface. This has been confirmed by many analyses.[33-36] Therefore, the PFA component might have migrated to the surface layer during the formation of hybrid film. This is very good phenomenon to improve the water and soil repellency of coating materials. The water swelling of pristine WBPU and hybrid film sample is shown in Figure 5. The water swelling% decreased markedly with increasing acrylate-copolymer/PFA content in hybrid materials. This also should be attributable to the migration of hydrophobic PFA component to the film surface.

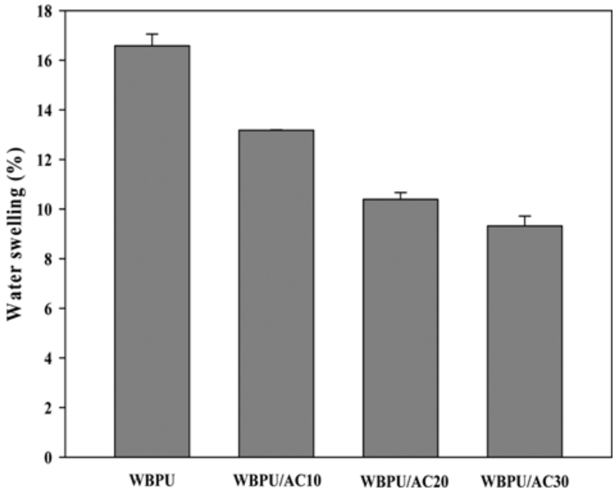


Figure 5. Water swelling ratio of pristine WBPU and WBPU/acrylic hybrids.

TGA and DTGA of WBPU/Acrylate Copolymer Hybrid Films. The thermal degradation behavior of urethane-derived polymer was investigated in detail by many researcher.[37-41] The mechanism of thermal degradation of these polymers involves at least three overlapping steps, which are sometimes difficult to distinguish from TGA curves, but become more obvious from DTGA curves (TGA derivative curve)). According to this process, the onset temperature (T_{onset}) of degradation of copolyurethane starts from 180 to 200 ºC, and the degradation is intensified at 260 ºC to produce the starting materials such as diisocyanate and polyol or some side products (amines, olefins, and carbon dioxides).[37] The chain scission of polyol such as PPG/PTMG occurs at about 370-380 ºC and produces more volatile chain fragments and rearrangement products such as acetaldehyde and propionaldehyde.[38] The final stages at about 400-600 ºC may be attributed to thermal decomposition of isocyanurate rings and carbodiimide linkages, which leads to the production of CO_2 and the formation of char in the solid state, which remained as residue.[38] Liufu[42] reported that the weight loss of polyacrylate begins at 310 ºC and ends at 380 ºC, and the major weight loss of polyacrylate is attributable to the breakage of C=O, COO^-, and C-O groups. The TGA/DTGA curves of pristine WBPU and hybrid samples are shown in Figure 6.

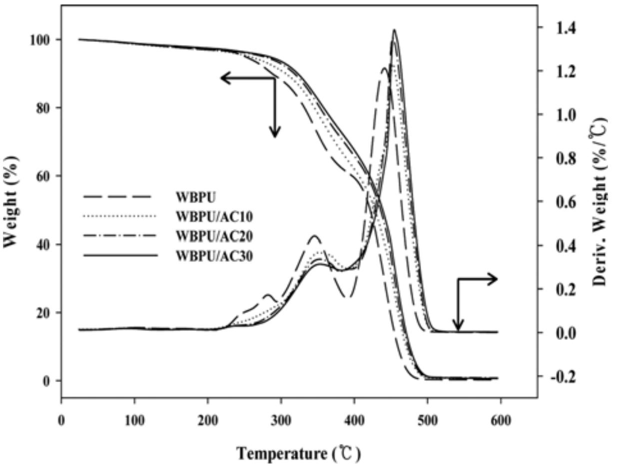


Figure 6. TGA and DTG curves of pristine WBPU and WBPU/acrylic hybrids.

The thermal degradation results are summarized in Table III. It was found that the decomposition of pristine WBPU and hybrid samples starts from near 200 ºC, and it is intensified at about 270 ºC in DTGA curve. However, this peak intensity was found to decrease significantly with increasing acrylate component. This indicates that the acrylate component in hybrid may interrupt the degradation of urethane-urea linkages. The peak temperature of second-stage degradation in DTGA curve is about 350 ºC, which is related to the scissions of polyol PTMG chains and polyacrylate chains. It was found that the final degradation occurred in the range of 400-500 ºC, where isocyanurate rings/carbodiimides/acrylates components decompose. This peak temperature was found to increase with increasing acrylate component. This might be due to the heat-resistant property of fluorinated polyacrylate component in hybrids.

Mechanical Properties and Hardness of Hybrid Films. Figure 7 shows the stress-strain curves of pristine WBPU and hybrid film samples. The yield point, tensile strength, elongation at break and hardness of film samples are shown in Table III. The tensile strength of hybrid samples decreased a little with increasing acrylate-copolymer content. As the acrylate-copolymer content increased, the elongation at break of hybrid samples (WBPU/AC10 and WBPU/AC20) also decreased a little, however, the elongation at break of the hybrid sam-

Table III. DTG Results, Mechanical Properties and Shore A Hardness of Pristine WBPU and WBPU/Acrylate Hybrids

Sample Designation	DTG Results			Mechanical Properties			Hardness (Shore A)
	1st Degradation Temperature (ºC)	2nd Degradation Temperature (ºC)	3rd Degradation Temperature (ºC)	Yield Point (MPa)	Tensile Strength (MPa)	Elongation at Break (%)	
WBPU	270.91	346.60	440.12	6.54	31.9	378.5	67
WBPU/AC10	291.25	350.70	450.07	6.73	31.2	356.5	81
WBPU/AC20	292.60	352.73	453.85	7.11	29.7	327.8	92
WBPU/AC30	295.01	354.78	455.17	11.90	28.5	219.9	95

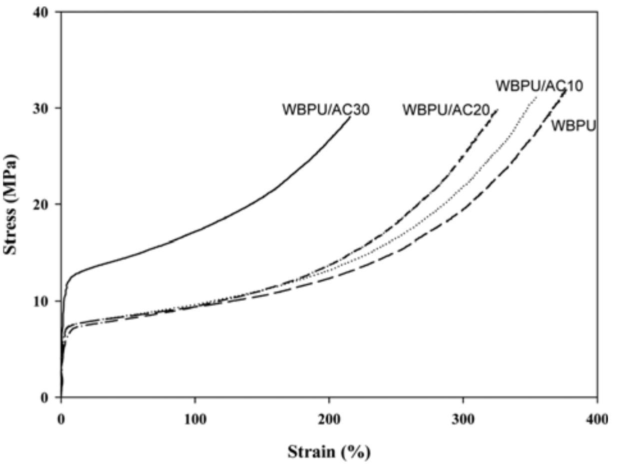


Figure 7. Strain-Stress curves of pristine WBPU and WBPU/acrylic hybrids.

ple WBPU/AC30 decreased markedly. The changing trend of yield point and initial modulus (stress/strain) was almost the same as that of elongation at break. The hardness (Shore A) of hybrid samples was significantly increased with increasing acrylate-copolymer content. This might be due to the more rigid structure of acrylate-copolymer than WBPU. In addition, the low decrease and high value of tensile strength of hybrid samples prepared in this study indicate that the molecular chains of WBPU and acrylate-copolymer were intimately associated.

Conclusions

To find the optimum composition of hybrid with waterborne polyurethane-urea (WBPU: H12MDI/PTMG/DMPA/EDA, soft segment content: 57 wt%, DMPA: 19 mol%/5.8 wt%) /acrylate copolymers (acrylic monomers BA/GMA/PFA(5/3/2 weight ratio), content: 0-40 wt%, content of fluorinated acrylate (PFA): 0-8 wt%), a series of hybrid materials were synthesized by *in situ* polymerization (chain extension of urethane/radical polymerization of acrylate monomer) during a prepolymer mixing process that was emulsifier-free/solvent-free. This study focused on the effect of acrylate monomer content on the average particle size, viscosity and shelf stability of hybrid emulsions as well as the surface properties, water swelling, hardness, and mechanical properties of film samples. The hybrid emulsions containing up to 30 wt% of acrylic monomer content were found be stable after 4 months, however, the as-polymerized hybrid emulsion containing higher content of acrylic monomer (40 wt%) was not stable, indicating that about 40 wt% of acrylic monomer content was beyond the limit of the self-emulsifying ability of hybrid emulsion using a fixed content of neutralized DMPA as a self-emulsifier. By the curve fitting analysis of IR-peaks and XPS analysis, the C-F content in hybrid was found to increase with increasing acrylate content. The average particle size of emulsion, and the thermal degradation temperature, young modulus/yield point in stress-strain curve, hardness, thermostability, and water/methylene-contact angles of film samples increased with increasing acrylate content. However, the viscosity of emulsion, and the elongation at break, water swelling and surface energy of film samples were significantly decreased with increasing acrylate content. The tensile strength of film samples decreased a little with increasing acrylate content. The optimum acrylic monomer content was found to be about 30 wt%, which provided the lowest surface energy (18.18 mN/m) and the highest contact angles (water: 111.76°, methylene iodide: 79.95°). These results suggest that the WBPU (70 wt%)/acrylate copolymer (30 wt%) hybrid has strong potential as a coating material for water-repellent material applications.

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