

Preparation and properties of emulsifier/*N*-methylpyrrolidone-free crosslinkable waterborne polyurethane-acrylate emulsions for footwear adhesives. I. Effect of the acrylic monomer content

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ABSTRACT: Stable emulsions of emulsifier/*N*-methylpyrrolidone-free crosslinkable waterborne polyurethane-acrylates (C-WBPUAs) with various acrylic monomer contents (0, 10, 20, and 30 wt %) for footwear adhesive materials were successfully prepared in this study. The effects of the acrylic monomer content on the shelf stability, mean particle size, and viscosity of the C-WBPUA emulsions; the tensile properties and dynamic mechanical thermal properties of the C-WBPUA film samples; and the adhesive strengths between the upper (synthetic leather) and the sole (ethylene vinyl acetate rubber) in both the dry and wet states of the formulated adhesives (C-WBPUA emulsion-thickener-hardener) were examined. The adhesive strengths of the formulated adhesives for footwear (leather-sole) in both the dry and wet states increased with increasing acrylic monomer content up to 20 wt %; after this, they almost levelled off. Thus, C-WBPUA20 and C-WBPUA30, where the number indicates the acrylic monomer content, can be recommended as high-performance adhesive materials for footwear. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43758.

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INTRODUCTION

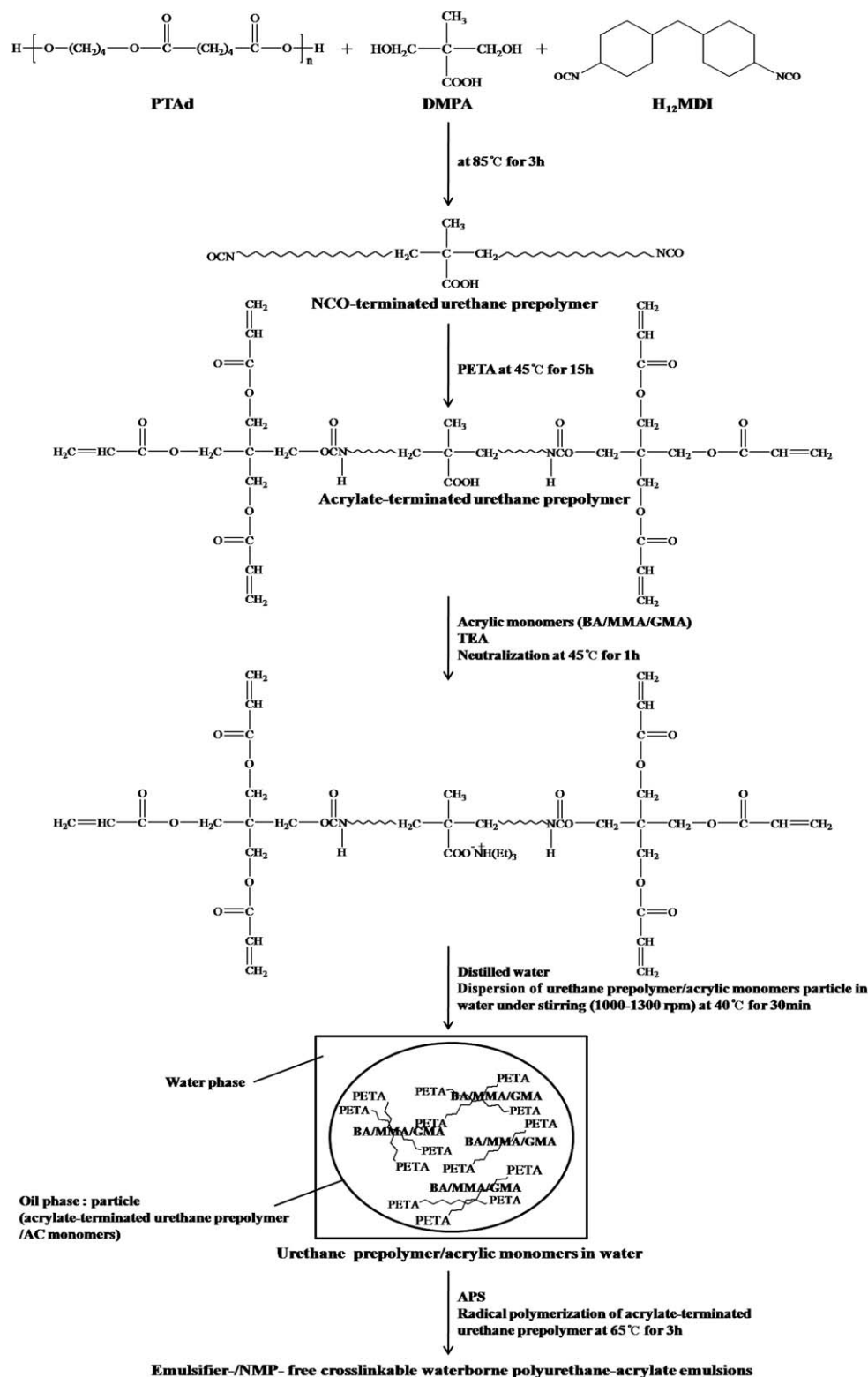
There are various types of adhesives (hot-melt reactive polyurethanes and solvent- and water-based contact adhesives) available in several forms (rod, powder, web, granules, pellets, and liquids). Adhesives are widely used in the manufacturing of most types of industrial products. Generally, adhesives used for sole attachment are either solvent based or water based.

A lot of work has already been done on solvent-based polyurethane adhesives.^{1–8} Solvent-based adhesives are composed of a polymer dissolved in a solvent such as toluene, typically at a ratio of one part polymer to three to four parts solvent. There are two main types of polymer used: polychloroprene rubber (a.k.a. neoprene) and polyurethane. Neoprene adhesives are not compatible with some materials, such as poly(vinyl chloride). However, polyurethane adhesives are more popular because they are compatible with a greater number of different materials.

However, solvent-based adhesives are gradually being replaced with water-based adhesives. There is a natural resistance within the footwear industry to move away from solvent-based

adhesives for a number of reasons; these include the price, ease of use, and perceived problems with achieving good bond strengths with water-based systems.

Waterborne polyurethane (WBPU) dispersions are used widely in coatings, adhesives, glass fiber sizing, automotive topcoats and primers, films for packages, and other applications mainly because of environmental considerations.^{9–20} Most WBPU contain ionic groups in their molecular structure and show excellent mechanical properties because of the presence of interchain Columbic forces and hydrogen bonds.¹⁷ The pendant carboxylic salt groups of dimethylol propionic acid (DMPA) in the WBPU are hydrophilic and act as anionic centers and internal emulsifiers. Accordingly, the dried films of WBPU 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 WBPU. We found that it was very difficult to obtain stable WBPU dispersions with a low content of ionic moieties (<10 mol %, 2 wt %).²⁰ Thus, it is 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



Scheme 1. Synthesis process of the emulsifier/NMP-free C-WBPUA emulsions. AC = acrylic.

WBPU_s.^{10,15–17,19–23} In addition, the crosslinking of water-based materials is also very important to the improvement of the water resistance and the mechanical properties.

Kwak *et al.*¹⁵ studied the effect of DMPA on the adhesive strength of the polyester-based WBPU. They reported that the adhesive strength increased with increasing DMPA content.

Nakamae *et al.*^{6,8} found that the adhesive strength on aluminum plates in both the dry and wet states increased with increasing hard-segment content and amount of carboxyl groups. Sanchez-Adsuar *et al.*¹ reported that the adhesive strength increased with the hard-segment/soft-segment ratio. Yang *et al.*²¹ studied the effect of different types of neutralizing agents on the adhesive strength of polycaprolactone-based WBPU. Kim and Kim¹⁹ studied the adhesive strengths of different types of polyester polyol-based WBPUs. Kwon and Kim²² used a crosslinker to increase the adhesive force of WBPU. However, few studies are available on WBPU adhesives in the open scientific literature.

Generally, WBPUs are environmentally friendly materials with good adhesion and excellent elasticity, flexibility, and abrasion resistance. However, WBPUs have the shortcomings of a high cost, low pH stability, and limited outdoor durability.

In general, acrylic polymers are considered to be inexpensive with good water and weathering resistance and proper mechanical properties and gloss, but they exhibit poor elasticity and abrasion resistance. As a result, formulators have sought ways to combine the advantages of WBPU and acrylic polymer.^{24–28} The polyurethane–acrylic hybrid emulsion was developed to exploit the potential cost reduction and good water resistance afforded by acrylic polymers and to maintain a greater share of the advantageous WBPU properties.

No external surfactants were present to contribute adversely to the water sensitivity of the WBPU-based materials. A previous study reported the optimum composition of a high-performance coating material with a stable WBPU–acrylic hybrid latex formation without an external surfactant by *in situ* polymerization with a prepolymer mixing process.^{23,25}

One disadvantage of both urethane–acrylic hybrid emulsions and WBPU emulsions is the inclusion of an *N*-methylpyrrolidone (NMP) solvent, which is commonly a necessary processing solvent and is included at levels ranging from about 3 to 15%. Most studies on NMP-free water-based adhesives have been done in industrial laboratories, and these have rarely been published in the open literature. Therefore, the aim of this study was to investigate the effect of the acrylic monomer content on the properties of emulsifier/NMP-free crosslinkable waterborne polyurethane–acrylate (C-WBP UA) adhesive materials.

In this study, a series of emulsifier/NMP-free C-WBP UA with various acrylic monomer contents (0, 10, 20, and 30 wt %) were prepared from acrylate-terminated urethane prepolymers {4,4'-dicyclohexymethane diisocyanate (H_{12} MDI)–poly(tetramethylene adipate glycol) (PTAd)–DMPA–pentaerythritol triacrylate (PETA)–dibutyltin dilaurate (DBTDL)–triethylamine (TEA)–acrylic monomers [butyl acrylate (BA)–methyl methacrylate (MMA)–glycidyl methacrylate (GMA)]}. The footwear adhesives were formulated from emulsifier/NMP-free WBPU/acrylate emulsions, a thickener, and a hardener. The effects of the acrylic monomer content on the shelf stability, mean particle size, and viscosity of the emulsions, the water swelling percentage, the tensile properties and dynamic mechanical thermal properties of the film samples, and the adhesive strengths of the formulated adhesives between the upper (synthetic leather) and

the sole [ethylene vinyl acetate (EVA)] in both the dry and wet states were investigated.

EXPERIMENTAL

Materials

PTAd [number-average molecular weight (M_n) = 2000 g/mol; DAEWON, Korea] was dried at 90 °C under 1–2 mmHg for 3 h before use. H_{12} MDI (Aldrich Chemical, Milwaukee, WI), TEA (Aldrich Chemical), and acetone (Aldrich Chemical) were used after dehydration with 4-Å molecular sieves for 1 day. DMPA (Aldrich Chemical) was dried in a vacuum oven for 5 h at 100 °C. DBTDL (Aldrich Chemical), distilled deionized water, PETA (Aldrich Chemical), BA (Aldrich Chemical), MMA (Aldrich Chemical), GMA (Aldrich Chemical), and ammonium persulfate (APS; Aldrich Chemical) were used without further purification. The EVA polymer (Haksan, Korea), synthetic leather (Haksan, Korea), thickener (UH420, Adeka Korea Corp., Korea), hardener (ARF40, Henkel Technologies, Korea), ultraviolet (UV) primer (P-7-2, Henkel Technologies, Korea), and primer (W-104, Henkel Technologies, Korea) were used as received.

Preparation of the Emulsifier/NMP-Free Crosslinkable Waterborne Polyurethane–Acrylate (C-WBP UA) Emulsions

The emulsifier/NMP-free C-WBP UAs were synthesized with a prepolymer mixing process (Scheme 1). This process was divided into three steps:

1. The first step was the formation of the vinyl-terminated urethane prepolymer by the reaction of PETA (17 mol %) with an NCO-terminated urethane prepolymer prepared from H_{12} MDI (46 mol %)–PTAd (M_n = 2000, 15 mol %, soft-segment content = 60 wt %)–DMPA (22 mol %). PTAd and DMPA were placed in a four-necked, round-bottomed flask equipped with a thermometer, mechanical stirrer, condenser with a drying tube, an inlet for dry nitrogen, and a heat jacket and were degassed *in vacuo* at 90 °C for 1 h. The mixture was allowed to cool to 50 °C with moderating stirring (175–200 rpm). H_{12} MDI was then dropped slowly into the flask, and the reaction mixture was allowed to react at 85 °C 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). The reaction mixture of the NCO-terminated urethane prepolymer was cooled to 45 °C, and acetone (10 wt % on the basis of the urethane prepolymer weight) was added to the NCO-terminated prepolymer mixture to adjust the viscosity of the solution. Then, PETA was added dropwise. To obtain a vinyl-terminated urethane prepolymer, the capping reaction of the NCO-terminated urethane prepolymer with PETA was continued until the NCO content reached zero, as evidenced by the disappearance of the IR NCO peak.
2. The second step was the neutralization of the vinyl-terminated urethane prepolymer with the tertiary amine TEA and the formation of mixtures of neutralized vinyl-terminated urethane prepolymer and acrylic monomers (BA, MMA, and GMA) to allow copolymerization between the

Table I. Sample Designations, Compositions, Mean Particle Sizes, Viscosities, and Shelf Stability of the Emulsifier/NMP-Free C-WBPUA Emulsions

Sample designation	C-WBPU composition (molar ratio)				DMPA (mol %)/soft-segment content (wt %)	Acrylic monomer (wt %)				C-WBPU/AC (wt %)	Mean particle size (nm)	Viscosity (cP at 25 °C)	Shelf stability ^a
	H _{1,2} MDI	PTAd	DMPA	PETA		TEA	BA	MMA	GMA				
C-WBPUA0	1.000	0.333	0.481	0.372	0.481	0	0	0	100/0	85	49	Stable	
C-WBPUA10					22/60	4	3	3	90/10	86	49	Stable	
C-WBPUA20						8	6	6	80/20	123	29	Stable	
C-WBPUA30						12	9	9	70/30	142	22	Stable	

^a After 6 months.

vinyl-terminated urethane prepolymer and the acrylic monomers: The acrylic monomer mixture (BA, MMA, and GMA: 0–30 wt %) was then added to the vinyl-terminated prepolymer mixture to adjust the viscosity of the solution. TEA was added to the reaction mixture to neutralize the carboxyl group of the vinyl-terminated prepolymer. After 30 min of neutralization, the reaction mixture was cooled to 40 °C, and distilled water was added to the mixture with vigorous stirring (1000–1300 rpm).

- The third step involved the radical copolymerization of the acrylate monomers and urethane prepolymer. A water-radical initiator (APS, 2 wt % on the basis of the acrylate content) was added to the emulsion, and the radical polymerization of acrylate groups (vinyl group) was performed by the slow heating of the mixture to 65 °C until the vinyl group peak in the IR spectra disappeared. The emulsifier/NMP-free C-WBPUA (38 wt % solid content) was obtained by the evaporation of acetone.

Table I lists the sample designations and compositions of the emulsifier–NMP-free C-WBPUA emulsions.

Preparation of the C-WBPUA Films

We prepared the C-WBPUA films by pouring the dispersion into a Teflon disc and drying it under ambient conditions for 24 h. The films were then peeled off from the Teflon disc. The films were vacuum-dried at 45 °C for 24 h under 20 mmHg to remove the moisture and unreacted monomer. The vacuum-dried films were stored in a vacuum desiccator at room temperature.

Formulation of Adhesives for Footwear

Footwear adhesive materials were formulated from the C-WBPUA emulsions, a thickener, and a hardener. An appropriate amount of C-WBPUA emulsion was mixed with the thickener (UH420, 1.5 wt % on the basis of C-WBPUA) and the hardener (ARF40, 5.0 wt % on the basis of C-WBPUA) to obtain a homogeneous mixture at room temperature.

Process of Adhesion between the Upper (Synthetic Leather) and the Sole (EVA) of the Footwear

The steps typically required to bond the upper (synthetic leather) to the EVA sole were as follows: a UV primer (P-7-2) was coated onto the EVA sole and then dried at 60 °C for 2 min. This was followed by UV curing. A mixture of the primer (W-104) and hardener (ARF40, 5.0 wt % on the basis of W-104) was coated onto both the UV-primer-treated EVA sole and the upper leather and then dried at 60 °C for 5 min. Formulated adhesive was brushed onto the sole surface by hand and then allowed to dry at 60 °C for 5 min. The two surfaces (leather and sole surfaces) were brought into contact and pressed two times with the roller and then dried at room temperature for 30 min and 24 h.

Characterization

The mean particle size of the C-WBPUA emulsions was measured at 25 °C with an LS 13 320 laser diffraction particle size analyzer (Beckman Coulter). The viscosity of the C-WBPUA emulsions was measured at 25 °C with a Brookfield LVDV II + digital viscometer (Brookfield). The measurements were

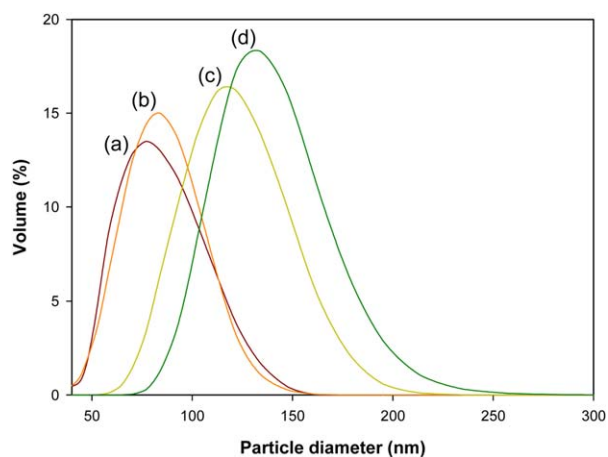


Figure 1. Particle size distributions of (a) C-WBPUA0, (b) C-WBPUA10, (c) C-WBPUA20, and (d) C-WBPUA30. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

performed at 100 rpm with RV-3 and RV-4 spindles. The chemical components of the pristine C-WBPUA samples were confirmed with a Nicolet iS5 Fourier transform infrared (FTIR) spectrometer (Thermo Scientific). The FTIR spectra of the sample were recorded in the range $4000\text{--}650\text{ cm}^{-1}$ with an attenuated total reflection (ZnSe crystal) apparatus at a resolution of 4 cm^{-1} and 32 scans. A constant compression load was applied to the samples. The dynamic mechanical properties of the C-WBPUA film samples were examined by dynamic mechanical analysis (DMA; DMA Q800, TA Instruments) at 1 Hz and a heating rate of $10\text{ }^{\circ}\text{C}/\text{min}$ over a temperature range from -100 to $150\text{ }^{\circ}\text{C}$. The tensile properties were measured at room temperature with a 5582 system universal testing machine (Instron) according to ASTM D 638. A crosshead speed of $100\text{ mm}/\text{min}$ was used throughout these investigations to determine the ultimate tensile strength and modulus and the elongation at break for all of the samples. The values quoted are the average of three measurements. To measure the swelling in water, the films were immersed in water for 48 h at $25\text{ }^{\circ}\text{C}$. The water swelling of the films was calculated with the following equation:

$$\text{Swelling (\%)} = [(W - W_0) / W_0] \times 100 \quad (1)$$

where W_0 and W are the weights of the dried film and the film at equilibrium swelling, respectively.

The adhesion strengths of the dry samples ($\text{Width} \times \text{Length} = 2 \times 10\text{ cm}^2$) dried for 30 min and 24 h at room temperature and wet samples (samples dried for 24 h and then soaked in water for 24 and 48 h at room temperature) were measured with a LT2100C universal testing machine (Labtron CO., Korea) operated at a crosshead speed of $150\text{ mm}/\text{min}$ according to a T-peel test. The values quoted are the average of five measurements.

RESULTS AND DISCUSSION

Preparation and Shelf Stability of the C-WBPUA Emulsions

The preparation process of the emulsifier/NMP-free C-WBPUA emulsions consisted of three steps, as shown in Scheme 1:

1. The first step was the formation of the acrylate-terminated polyurethane prepolymer through the reaction of PETA (17 mol %) with an NCO-terminated urethane prepolymer prepared from H_{12}MDI (46 mol %)-PTAd ($M_n = 2000$, 15 mol %, soft-segment content = 60 wt %)-DMPA (22 mol %).
2. The second step was the neutralization of the acrylate-terminated urethane prepolymer with the tertiary amine TEA and the formation of mixtures of neutralized acrylate-terminated urethane prepolymer and acrylic monomers (BA, MMA, and GMA).
3. The third step involved the dispersion of the acrylate-terminated urethane prepolymer-acrylic monomers in water and the copolymerization of various acrylate groups through the addition of a water-soluble radical initiator (APS).

The sample designation, composition, mean particle size, viscosity, and shelf stability of the C-WBPUA emulsions prepared in this study are given in Table I. In this study, a series of C-WBPUA emulsions were successfully obtained by emulsifier-free emulsion copolymerization and an NMP-free method. Acrylic monomers (BA, MMA, and GMA)/external solvent (acetone) were incorporated as a diluent into acrylate-terminated urethane prepolymer instead of single external solvents, such as acetone and MEK, to achieve intimate molecular mixing between the acrylate-terminated urethane prepolymer and acrylic monomer. The solvent acetone was evaporated to obtain C-WBPUA emulsions. The radical copolymerization/homopolymerization of the acrylate-terminated urethane prepolymer-acrylic monomers (BA, MMA, and GMA) took place simultaneously.

In our earlier studies, WBPU-urea-acrylic monomer (0–40 wt %) hybrid emulsions and the WBPU-acrylic monomer (0–30 wt %) hybrid emulsions were stable after 4 months.^{23,25} In an earlier investigation of the synthesis and properties of waterborne fluorinated polyurethane-acrylate prepared with a solvent-/emulsifier-free method, the obtained emulsions containing 0–40 wt % of the total acrylic monomer contents were stable after 2 months, but the as-polymerized emulsions containing a

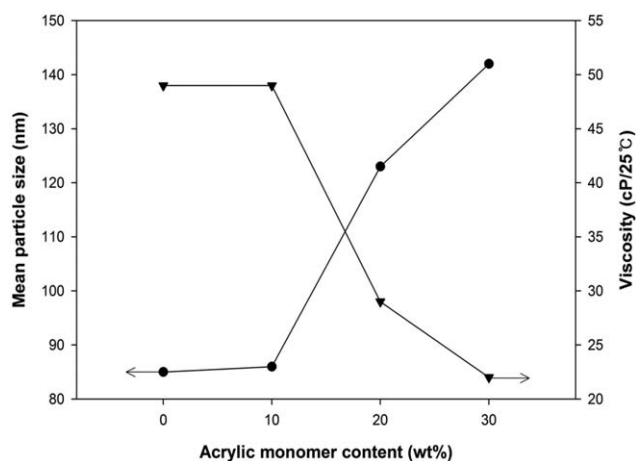


Figure 2. Effect of the acrylic monomer content on the mean particle size and viscosity of the C-WBPUA emulsions.

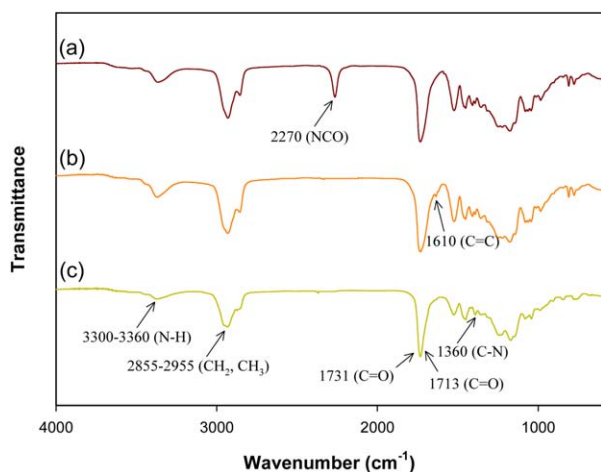


Figure 3. FTIR spectra of the (a) NCO-terminated urethane prepolymer, (b) acrylate-terminated urethane prepolymer, and (c) C-WBPUA emulsions. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

higher acrylic monomer content (50 wt %) were unstable.²⁴ In this study, the emulsions containing 0–30 wt % of the total acrylic monomer [BA (0–12 wt %)/MMA (0–9 wt %)/GMA (0–9 wt %)] contents were stable after 6 months. However, the as-polymerized emulsions containing a higher acrylic monomer

content (40 wt %) was unstable; this indicated that near 40 wt % of the acrylic monomer content was beyond the self-emulsifying ability of the emulsion when a fixed content of neutralized DMPA (22 mol %) was used as a self-emulsifier.

Mean Particle Size and Viscosity of the C-WBPUA Emulsions

The particle size distributions of the C-WBPUA emulsions are shown in Figure 1. The mean particle size and viscosity versus the acrylic monomer content are shown in Figure 2. As the acrylic monomer content increased, the particle size of C-WBPUA increased. However, the viscosity of the emulsion decreased. It was apparent that the mean particle size and viscosity began to change sharply around 10 wt % of the acrylic monomer. This indicated that an acrylic monomer content of greater than 10 wt % was a critical content for changing the particle size or viscosity of the emulsion. Generally, smaller particles lead to larger hydrodynamic volumes and, therefore, induce higher viscosities. However, depending on the specific application, an optimum mean particle size and viscosity exist, and so it is important to be able to control these values via the chemical composition. It is generally known that the mean particle size is not directly related to the physical properties of WBPU cast films. However, the control of the mean particle size is important with respect to the particular application of a WBPU dispersion. For example, relatively larger particles are preferred in surface coatings for rapid drying, and smaller ones

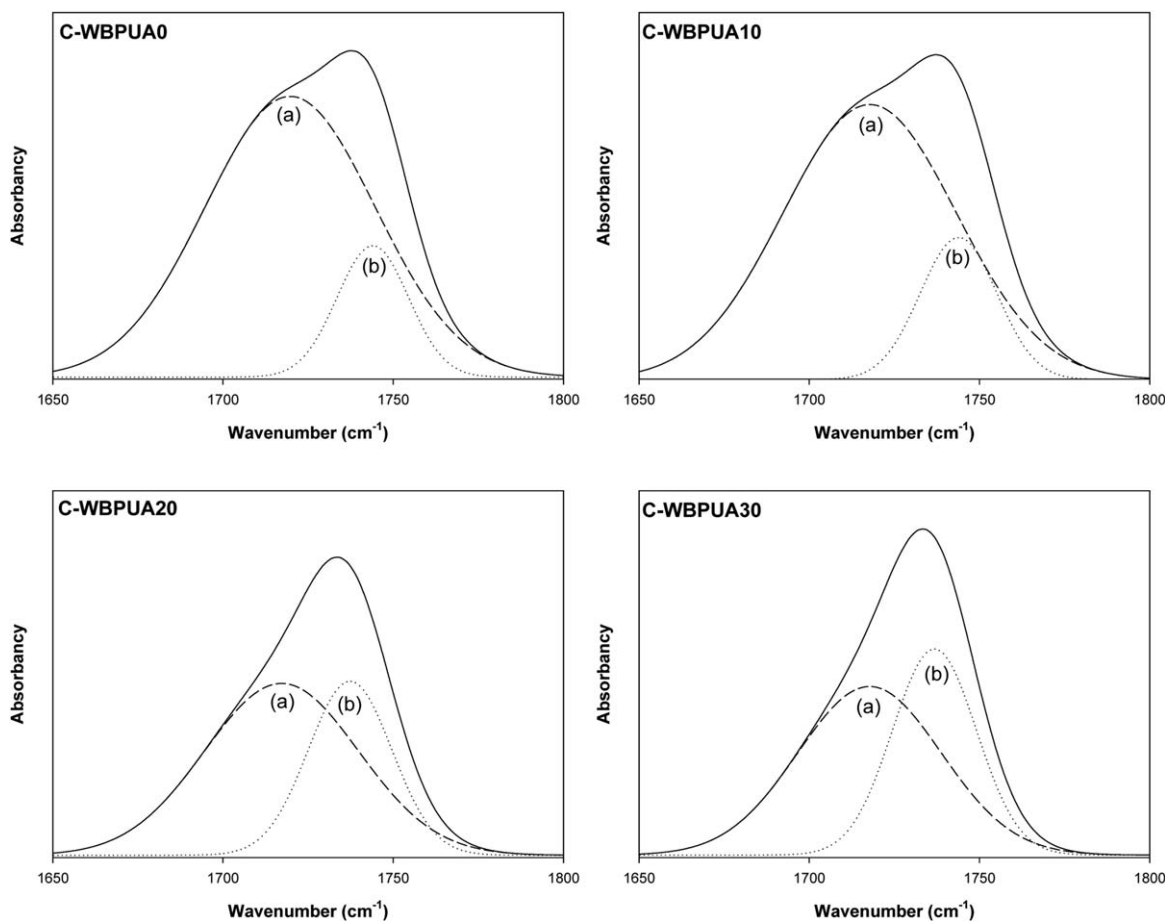


Figure 4. Decomposition of (a) C=O in urethane and (b) C=O in acrylate of the C-WBPUA emulsions.

Table II. Decomposition Results for C=O in Urethane and C=O in Acrylate, DMA Results, and Mechanical Properties of the C-WBPUA Films

Sample designation	Peak position (cm ⁻¹)		Fraction of the peak area		DMA results		Mechanical properties		
	C=O in urethane	C=O in acrylate	C=O in urethane	C=O in acrylate	T_{gs} (°C)	T_{gh} (°C)	Tensile strength (MPa)	Elongation at break (%)	Modulus at 5% strain (MPa)
C-WBPUA0	1720	1744	0.835	0.165	-45.2	33.8	23.96	800.00	21.17
C-WBPUA10	1718	1743	0.813	0.187	-46.2	42.9	23.52	412.22	59.68
C-WBPUA20	1717	1737	0.645	0.355	-47.0	50.8	22.29	218.89	66.69
C-WBPUA30	1718	1737	0.583	0.417	-54.1	71.9	22.06	190.00	85.45

are desirable when the deep penetration of the dispersion into a substrate is essential. We found that the C-WBPUA emulsions (mean particle size = 85–142 nm) prepared here were suitable for footwear (leather–EVA sole) adhesive materials.

Identification of the Chemical Structure of C-WBPUA

Figure 3 shows FTIR spectra of the NCO-terminated urethane prepolymer, the acrylate-terminated urethane prepolymer, and the C-WBPUA emulsion. The characteristic bands at 1082–1085, 1713–1720, and 3300–3500 cm⁻¹ confirmed the ether (C–O–C) of the ester group, carbonyl group of urethane, and amide group in C-WBPUA, respectively. The carbonyl (C=O) group of the urethane was identified by the characteristic peaks at 1717–1720 cm⁻¹. The ester carbonyl (C=O) group of the acrylate copolymer in C-WBPUA was identified by the characteristic peaks at 1744–1730 cm⁻¹. The acrylate vinyl group (C=C) peak at 1610 cm⁻¹ appeared in the acrylate-terminated urethane prepolymer sample. However, no bonding peak of the acrylate at 1610 cm⁻¹ in the isocyanate-terminated urethane prepolymer or the C-WBPUA samples was observed; this indicated the complete reaction of all acrylate vinyl groups in the acrylate-terminated urethane prepolymer.

Figure 4 shows the decomposition of C=O in urethane and C=O in the acrylate of the C-WBPUAs. The decomposition results of C=O in urethane and C=O in the acrylate of C-WBPUA are shown in Table II. As the acrylic monomer content

increased, the fraction of the acrylate C=O group increased, whereas the fraction of the urethane C=O group decreased. This indicated that the acrylic monomer was proportionally incorporated into the C-WBPUAs with increasing acrylic monomer content.

DMA Properties and Mechanical Properties of the C-WBPUA Films

Generally, polyurethane has two phases (soft-segment and hard-segment phases). Because the two-phase structure is important to the function of the polyurethane material, the glass-transition temperature (T_g) values of these two phases [soft-segment glass-transition temperature (T_{gs}) and hard-segment glass-transition temperature (T_{gh})] are very important characteristics of polyurethanes. Generally, the T_g values of these two phases depend on the chemical composition, phase mixing and separation, and the molecular weight of these two phases. Figure 5 shows $\tan \delta$ as function of the temperature for the C-WBPUA film samples. These T_g values are shown in Table II. As the acrylic monomer content increased, T_{gs} shifted from -45.2 to -54.1 °C, whereas T_{gh} shifted from 33.8 to 71.9 °C. The shifts in T_{gs} and T_{gh} suggest that the soft and hard segments of the polyurethane in C-WBPUA were partially miscible with the polyacrylate components. The partial miscibility might have been due to the intimate molecular mixing through the formation of

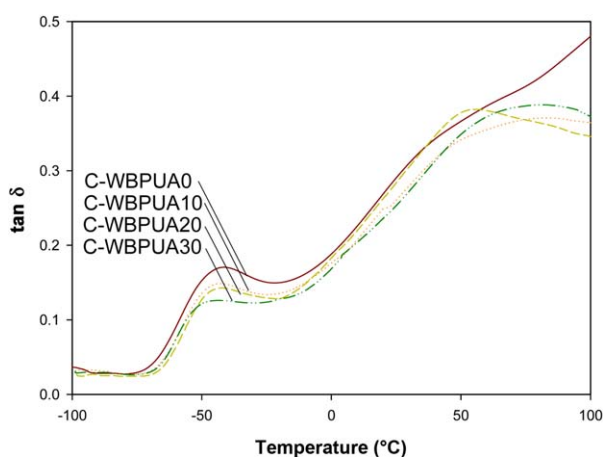


Figure 5. $\tan \delta$ of the C-WBPUA films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

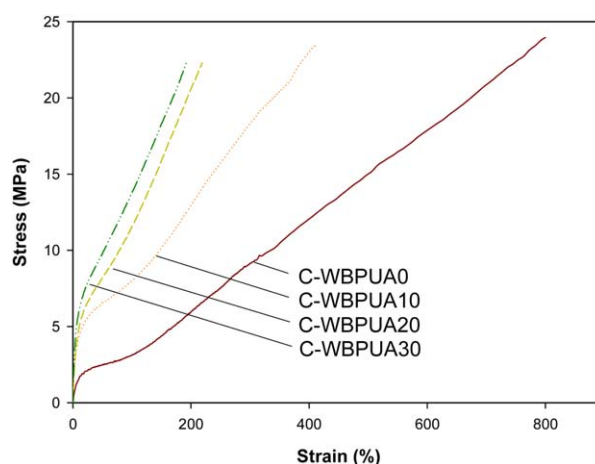


Figure 6. Stress–strain curves of the C-WBPUA films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

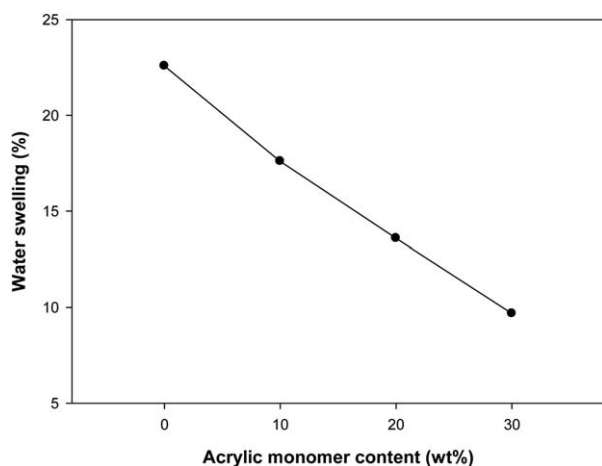


Figure 7. Effect of the acrylic monomer content on the water swelling of the C-WBPUA films.

the acrylic monomer absorbed acrylate–urethane prepolymer and the copolymerization and crosslinking reaction between acrylate–urethane containing trifunctional groups and acrylic monomer.

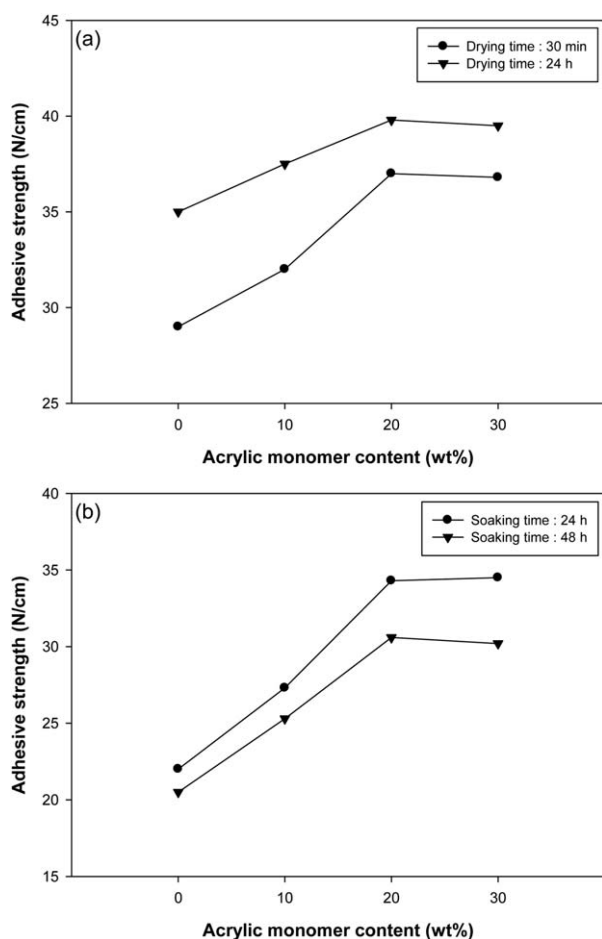


Figure 8. Effect of the acrylic monomer content on the adhesive strength of the formulated adhesives for footwear (leather–sole) in the (a) dry and (b) wet states.

Table III. Adhesive Strengths of the Formulated Adhesives

Sample designation	Adhesive strength (N/cm)			
	Drying time		Soaking time	
	30 min	24 h	24 h	48 h
C-WBPUA0	29.0	35.0	22.0	20.5
C-WBPUA10	32.0	37.5	27.3	25.3
C-WBPUA20	37.0	39.8	34.3	30.6
C-WBPUA30	36.8	39.5	34.5	30.2

Figure 6 shows the stress–strain curves of the C-WBPUA film samples. The tensile strength, modulus, and elongation at break of the C-WBPUA film samples are shown in Table II. The tensile strength of the samples decreased a little with increasing acrylic monomer content. Generally, the tensile strength and modulus of polyurethane–acrylate decreased significantly with increasing acrylic monomer content.²⁴ The small decrease in the tensile strength in this study should have been due to the crosslinking of polyurethane–acrylate and the intimate molecular mixing between the hard-segment component of polyurethane and the acrylic monomer component. The elongation at break of the samples decreased significantly with increasing acrylic monomer content. The large decrease in the elongation at break might have been due to the decrease in the urethane content in the polyurethane–acrylate copolymer with increasing acrylic monomer content. The tensile modulus of the film samples increased markedly with increasing acrylic monomer content. This increase in the modulus was attributable to not only the crosslinking between PETA and the acrylic monomer but also the bulkiness of the MMA and GMA components.

Water Swelling of the C-WBPUA Films

Figure 7 shows the water swelling of the C-WBPUA film samples. The water swelling percentage of the C-WBPUA film samples containing a high DMPA content (22 mol %) prepared in this study decreased markedly from 22.58 to 9.68% with increasing acrylic monomer content from 0 to 30 wt %. This was attributed to the higher hydrophobicity of the acrylic component compared to that of the urethane component. From this result, we found that the water resistance of WBPU–acrylate could be easily controlled through the adjustment of the content of the acrylic monomer. The water swelling percentage of the C-WBPUA materials was directly related to the adhesive strength in the wet state, as described later.

Adhesive Strengths of the Formulated Adhesives for Footwear

Figure 8 and Table III show the adhesive strengths of the formulated adhesives (C-WBPUA emulsion–thickener–hardener) for footwear (leather–sole) in the dry and wet states. The adhesive strengths in the dry state [peel strength of the footwear dried for 30 min and 24 h at room temperature after adhesion] and in the wet state [peel strength after soaking the samples dried for 24 hours for 24 and 48 h in water] increased with increasing acrylic monomer content up to 20 wt % and then almost levelled off. This indicated that the high-performance

adhesive materials for footwear were demonstrated to be C-WBPUA20 and C-WBPUA30, where the number indicates the acrylic monomer content. However, the adhesive strengths (35.0–39.8 N/cm) of all of the samples containing acrylic monomer contents (10, 20, and 30 wt %) in both the dry state (24 h) and wet state (48 h) passed the footwear adhesion criteria (peel strength in the dry state > 27 N/cm and peel strength in the wet state > 25 N/cm). However, the adhesive strength (20.5 N/cm) of C-WBPUA0 (without acrylic monomer) did not pass the footwear adhesion requirement.

CONCLUSIONS

To obtain footwear adhesives, a series of emulsifier/NMP-free C-WBPUA emulsions with different acrylic monomer contents (0–30 wt %) were prepared from crosslinkable PETA-terminated urethane prepolymers [H_{12} MDI–PTAd ($M_n = 2000$ g/mol)–DMPA–PETA–DBTDL–TEA]/acrylic monomers (BA, MMA, and GMA). This study focused on the effect of the acrylic monomer content (weight percentage) on the shelf stability, mean particle size, and viscosity of the emulsions; the tensile properties and dynamic mechanical thermal properties of the film samples; and the adhesive strengths of the formulated adhesives (C-WBPUA emulsions–thickener–hardener) between the upper (synthetic leather) and the sole (EVA) in both the dry and wet states. The mean particle size of the C-WBPUA emulsions increased with increasing acrylic monomer content; however, the viscosity decreased. The tensile strength of the C-WBPUA film samples decreased a little with increasing acrylic monomer content. When the acrylic monomer content increased, T_{gh} increased from 33.8 to 71.9 °C, whereas T_{gs} decreased from –45.2 to –54.1 °C. The adhesive strength in the dry state (peel strength of the footwear dried for 30 min and 24 h at room temperature after adhesion) and in the wet state [peel strength after soaking the samples dried for 24 h for 24 and 48 h in water] increased with increasing acrylic monomer content up to 20 wt % and then almost levelled off. This indicated that the high-performance adhesive materials for footwear were demonstrated to be C-WBPUA20 and C-WBPUA30. However, the adhesive strengths (35.0–39.8 N/cm) of all of the samples containing acrylic monomer in both the dry state (24 h) and wet state (48 h) passed the footwear adhesion requirement (peel strength in the dry state > 27 N/cm and peel strength in the wet state > 25 N/cm).

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