Synthesis and Characterization of Urethane/Acrylate Composite Latex

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ABSTRACT: Polyurethane dispersion and urethane/acrylate composite latex were synthesized and characterized by using a particle size analyzer, gel permeation chromatograph (GPC), Fourier transform infrared spectroscopy coupled with attenuated total reflectance (FTIR-ATR), dynamic mechanical analysis (DMA), and instron test machine. The amount of solvent and dimethylolpropionic acid (DMPA) used during synthesis of polyurethane resin straightway affected the average particle size and stability of aqueous polyurethane dispersion. The particle size of polyurethane dispersion had nothing to do with that of composite latex. FTIR-ATR analyses displayed both air-facing and substrate-facing surfaces, containing more polyurethane component than the average composition. Some crosslinking reactions occurred in preparing urethane/acrylic composite latex, as indicated by FTIR analyses and solvent extraction. DMA demonstrated three glass transitions for the film from composite latex. Instron tests exhibited better film performance properties for the composite latex than for the corresponding blend latex. A possible particle growth mechanism for preparing urethane/acrylate composite latex was proposed. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 84: 1620–1628, 2002; DOI 10.1002/app.10526

Key words: urethane/acrylic composite latice; particle size; FTIR-ATR

INTRODUCTION

Acrylic polymer latex (PA) and polyurethane dispersions (PU) each have their own characteristic advantages and disadvantages. Acrylic polymer latex films possess excellent weatherability, hardness, and water and alkali resistance due to the main polymer chain's carbon–carbon bonds and have been widely used for coatings, paper and textile finishes, cement additives, and other applications. However, the elasticity and abrasion resistance of PA are inferior to those of PU. The latter features exceptional performance properties such as excellent elasticity, mar resistance, toughness, adhesion, and superior low-temperature impact property due to their morphology in which the soft segment is usually formed by polyol and the hard segment is usually formed by the diisocyanate, phase separation, resulting in the hard segment aggregating into domains in the soft segment matrix, and have been largely applied for various coatings, but suffer from poor hardness, water, and alkali resistance.
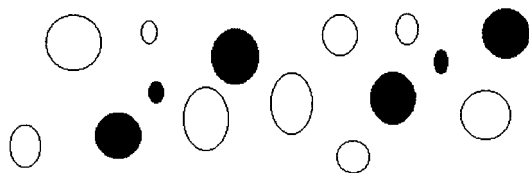
Physical blends of the two polymer systems are a popular approach to combine the beneficial attributes of each of polymer. However, in many cases these blends compromise the superior performance properties because of the incompatibility of the two systems in which the different polymers are present in separate particles, as follows:

Blend of polyacrylate ○ and polyurethane ● dispersions

For these simple physical blends, there are distinct urethane and acrylate regions within the wet coating and it would be expected that these regions would still partially exist within the coating after film formation. A more elegant way to obtain this balance is to synthesize the urethane/acrylate composite latex particles. In these systems, the PU dispersion is used as a seed for subsequent radical emulsion polymerization, resulting in intimately mixed composite particles; that is, both polymers are present in a single latex particle, shown as:
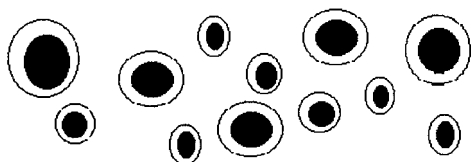
Polyacrylate ○ and polyurethane ● composite particles

The exact structure in these cases depends on the type of urethane/acrylate. These composite particles combine the best properties of both systems (the mechanical properties and resistance of the urethanes combined with the versatility and lower cost of the acrylates). Other approaches to improve the balance of performance properties of the two systems include introductions of hydrogen-bonding interaction,[1] anion–cation interactions,[2] ion dipole interactions,[3] and building covalent bonding, which generally give polymer blends, alloys, and IPNs with remarkable properties.[4]

In this article, aqueous PU dispersion was prepared first, and then urethane/acrylate composite latex was synthesized with aqueous PU dispersion as the seed and emulsion polymerization. Latex-particle size analyzer, gel permeation chromatograph (GPC), Fourier transform infrared spectroscopy (FTIR), dynamic mechanical analysis (DMA), and Instron test machine were employed to investigate the structure and properties of the composite latex and their polymers.

EXPERIMENTAL

Materials

Isophorone diisocyanate (IPDI) trimers (solid content: 70%; NCO: 12%) were acquired from Bayer Co. Neopentyl glycol (NPG, 98%), dimethylolpropionic acid (DMPA, 98.5%), 1,4-butanediol (98.5%), dibutyltin dilaureate (99%), ethylenediamine (98.5%), ethyl acetate (98.8%), tetrahydrofuran (THF, 97%), ammonium persulfate, and sodium bicarbonate were purchased from Shanghai Chemistry Reagent Co. (Shanghai, China). Styrene (St, 98%), butyl acrylate (BA, 99%), and acrylic acid (AA, 98.5%) were supplied by Shanghai Gaoqiao Petroleum and Chemical Co. (Shanghai, China). Anionic surfactant, polyoxyethyene alkyl phenyl ether ammonium sulfate (moles of ethylene oxide = 4), and nonionic surfactant, polyoxyethyene octyl phenyl ether (moles of EO = 40), were kindly supplied by Rhone-Poulenc Inc. (France). All materials were used as received.

Preparation of PU Dispersion and Urethane/Acrylate Composite Latex

Synthesis was carried out in a 500-ml four-neck round-bottom flask equipped with mechanical stirrer, addition funnel, N_2 inlet, thermometer, and heating mantle. 1,4-Butanediol, NPG, DMPA, IPDI, and ethyl acetate were added to the flask based on around 1.2/L mol ratio for —OH to —NCO groups and stirred and heated to homogenous solution, followed by addition of 0.05% dibutyltin dilaureate (based on the total weight of all reaction monomers) and heated to 70°C at N_2 atmosphere for 1 h to obtain PU solution. This PU was then neutralized with ethylenediamine, followed by dispersion at high speed with deionized water and 2.5 wt % anionic and 5.0 wt % nonionic surfactants of PU resin used to produce aqueous PU dispersion. St, BA, and AA were preemulsified with deionized water and 5.0% surfactants on the basis of total monomer weight. Two-step addition method was employed to enhance the graft and composite efficiency. First, 15% of the preemulsified solution with a small amount of the mixture of initiator and buffer solution was added to the above aqueous PU dispersion at once and stirred and maintained at 70°C under N_2 stream for 1 h to obtain partial composite latex (PUA1), followed by the addition of the rest of the preemulsified solution and mixture of initiator and buffer solution over around 3 h through addition funnel and

Table I   The Monomer Recipes for Polyurethane Dispersion and Urethane/Acrylate Composite Latex

	IPDI (g)	1,4-Butanediol (g)	NPG (g)	DMPA (g)	BA (g)	AA (g)	St (g)
PU dispersion	8.57	1.84	1.64	0.48			
30% solid PUA composite	8.57	1.84	1.64	0.48	60	4	35
35% solid PUA composite	8.57	1.84	1.64	0.48	70	4	45
40% solid PUA composite	8.57	1.84	1.64	0.48	90	4	65

constant flow pump, respectively. After addition of all the ingredients, the reaction mixture was maintained at that temperature for an additional 1.5 h to complete the reaction of residual monomers to obtain the final urethane/acrylate composite latex (PUA). The monomer recipes used for synthesis of PU dispersion and urethane/acrylate composite latex are shown in Table I.

Preparation of PU/PA Blend Latex

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

Characterization of Latex and Polymer Films

Particle Size Analysis

Average particle sizes of aqueous PU dispersion and composite latex were determined by a Coulter LS 230 particle size analyzer (Coulter, Miami, FL), with a measurement range of 0.04–2000 μm.

Molecular Weight Determination

Molecular weight and molecular weight distribution were obtained by running 0.5 wt % polymers in THF through a Waters liquid chromatograph at 30°C. This system consisted of a Waters 150 pump, a detector of refractive index, and two ultrastyragel columns. THF was used as the eluent phase. Elution volumes were converted to apparent molecular weights by using narrow distribution polystyrene standards.

FTIR-ATR Analysis

Fourier transform infrared spectroscopy coupled with attenuated total reflectance (FTIR-ATR) spectra were obtained by using a ZnSe internal reflectance element at an incidence angle of 45° with a HATR ATR accessory, which was placed in the sample compartment of MAGNA-IR®550 FTIR (Nicolet Instruments, Madison, WI). Scanning was repeated at least 200 times before the spectra were recorded at a resolution of 2 cm^{-1}. The composite latex was cast on clean glass plates and dried to prepare the films for FTIR-ATR analysis.

Dynamic Mechanical Analysis

Dynamic mechanical measurements were carried out on DMA 242 (Netzsch Inc., Germany) in tension mode. The samples were quickly cooled to −45°C, equilibrated at that temperature for 3 min, and then heated to 120°C at a frequency of 1 Hz with a constant heating rate of 2°C min^{-1} under nitrogen atmosphere. The samples for DMA analysis were cut from the polymer films which were prepared by casting the latex on the glass and were dried at 50°C for 1 week.

Static Mechanical Property

An Instron model DXLL 1000 testing machine (Shanghai, China) was employed for the tensile test. The specimens for the tensile test were dumbbell cut from sample films, which were prepared by casting the latex on the glass plates and dried at 50°C for 1 week, and carried out at a crosshead speed of 500 mm/min according to Die C of ASTM-D412. A 25-mm benchmark and the original cross-sectional area were utilized to calculate their tensile properties. The ultimate tensile strength and elongation were automatically calculated by the computer connected to the Instron. The average of at least five measurements for each sample was reported; the experimental error is ±10%.

RESULTS AND DISCUSSION

Effect of Solvent Content on Polyurethane Dispersion

Although both ketone and ester solvents can be used for synthesis of PU resin, ethyl acetate is

Table II   The Effect of Solvent Level on the Basic Properties of Polyurethane Dispersion

	Solvent Content[a]			
	10%	20%	30%	40%
Appearance	White	Light blue	Light blue	Light blue
Particle size (μm)	1.6	12.8	205.3	215.0
Stability	Stable	Stable	Stable	Stable

[a] Based on the total weight of 1,4-butanediol, NPG, DMPA, and IPDI.

preferred as the solvent in this investigation because ketone solvents provide an unpalatable odor. Table II summarizes the effect of the ethyl acetate level on some basic properties of aqueous PU dispersion. The results demonstrate that aqueous polymer dispersion has some different colloidal properties from the latex obtained by traditional emulsion polymerization: the polymer dispersion is still stable, although it has relatively large particle size even up to around 200 μm. Obviously, this stability is not only attributed to the electrostatic repulsion from anionic surfactants and stereo hinder from nonionic surfactants but also contributed by the electrostatic repulsion from carboxylic salt groups ($-COO^-NH_4^+$). In other words, these aqueous PU molecules have a self-emulsified function. The reason the particle size of PU dispersion increases with the increase in solvent amount is not clear at present, but one point is certain; that is, too much solvent is unnecessary to synthesize PU resin for aqueous dispersion.[5] Thus, 20% of ethyl acetate was used in the following experiments.

Effect of DMPA Content on Polyurethane Dispersion

DMPA is widely used for providing hydrophilic groups to obtain aqueous PU dispersion in pat-

ents,[6–8] but the fundamental study on the effect of DMPA on the properties of PU resin and dispersion was very little investigated. In this study, the PU resins and their dispersions were prepared with various DMPA amounts, other parameters being equal. The number-average molecular weight (M_n), weight-average molecular weight (M_w), and viscosity of PU resins, particle size, and stability of PU dispersions were investigated and illustrated in Table III.

The data in Table III show that both average molecular weight and viscosity increase as the DMPA level increases, suggesting that the $-OH$ groups in DMPA seem to be more active than those in 1,4-butanediol and NPG, accelerating the additional polymerization between $-OH$ and $-NCO$ groups; perhaps some $-COOH$ groups might participate in the addition reaction with $-NCO$ groups, resulting in some branches. As the DMPA level increases, the particle size of PU dispersion first decreases and then increases, indicating that the content of carboxylic salt groups straightway affects the particle size. It is not difficult to understand that the particle size decreases with the increase in DMPA level because the carboxylic salt groups have a self-emulsifying function in aqueous medium. However, the reason the particle size of PU dispersion, in contrast,

Table III   The Effect of DMPA on Polyurethane Resin and Dispersion

	DMPA Content (%)[a]				
	2	4	6	8	10
M_n	1000	1200	1200	1300	1400
M_w	2600	3500	3600	4600	5500
Resin viscosity (mPa s)	300	1100	1300	2200	2800
Particle size (μm)	62.8	38.1	10.6	121.4	140.8
Stability	Slight precipitation	Slight precipitation	No precipitation	A lot of precipitation	A lot of precipitation

[a] Based on the total weight of 1,4-butanediol, NPG, DMPA, and IPDI.

Table IV The Effect of Ratio of Urethane/Acrylic on Composite Latex

|	Urethane/Acrylic (weight ratio)		
	1 : 6	1 : 3	1 : 2
Particle size of latex (μm)	0.6	1.2	2.1
Average molecular weight	ND[a]	ND	ND
Stability of latex	Stable	Stable	A little precipitation

[a] No data.

increases with the further increase in DMPA level is not utterly understood. It is postulated that as the DMPA level increases, the concentration of carboxylic salt groups in the molecular chains increases, as well as the solubility of PU molecules in aqueous medium grows, thus the particles may be formed by aggregation of hydrophilic PU molecules instead of entering emulsifier micelles. This mechanism probably reduces the stability of aqueous dispersion, resulting in a lot of precipitation after set down. Thus, 6% of DMPA was used to prepare aqueous PU dispersion for the following composite latex.

### Effect of the Ratios of Urethane/Acrylate on the Composite Latex

PU molecular chains usually contain many α-H atoms. When acrylic monomers are emulsion polymerized in the presence of aqueous PU dispersion, these α-H atoms can be abstracted by the free radicals either from the decomposition of initiators or from acrylic molecular chains containing free radicals, resulting in some graft reactions between PU molecular chains and acrylic monomers, except the normal emulsion copolymerization of acrylic monomers, just as happened in synthesis of epoxy/acrylate composite latex.[9] Thus, the composite latex is probably composed of urethane/acrylic graft copolymer, ungrafted PU, and ungrafted acrylic copolymer. The effect of the ratios of urethane/acrylate on the properties of composite latex was investigated and are summarized in Table IV. As the weight ratios of urethane/acrylate increase from 1 : 6 to 1 : 2, the average particle size of latex increases from 0.6 to 2.1 μm, which is accompanied by a little precipitation in composite latex. Certainly, both the increase in particle size and the decrease in stability of composite latex are attributed to the character of PU dispersion. What is interesting is that the particle size of the composite latex is smaller than that of PU dispersion. Recall that the average particle size of the PU dispersion used for preparing composite latex is around 10.6 μm because 6% of DMPA was used during synthesis of PU resin, whereas the maximum average particle size of composite latex is 2.1 μm, and the particle size distribution of composite latex is considerably narrower than that of PU dispersion, as shown in Figure 1. This indicates that PU dispersion has no straight effect on the composite latex in particle size and size distribution, which is different from traditional core-shell or seeded emulsion polymerization. The possible reason is that the particle growth mechanism in preparing urethane/acrylate composite latex is different from the traditional core-shell or seeded emulsion polymerization: during the synthesis of composite latex, the previously present PU dispersion is not real core or seed; the preemulsified acrylic monomers are polymerized in micelles, not in the particles of PU dispersion. As the latex particles grow, these hydrophilic PU molecules are attracted on the acrylic latex particles as stabilizers, resulting in an indirect connection in particle size between PU dispersion and composite latex; the morphology of the composite latex and their films are being under investigation and will be presented later. The average molecular weight of composite copolymers could not be determined by GPC because they did not dissolve in the suitable
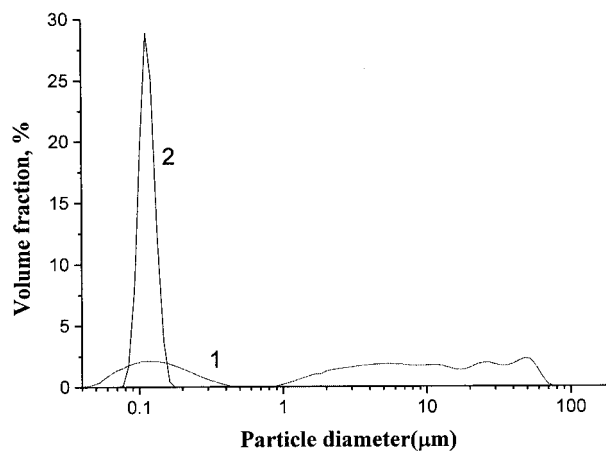
Figure 1 Particle size distribution curves for polyurethane dispersion and composite latex: (1) polyurethane dispersion; (2) composite latex.
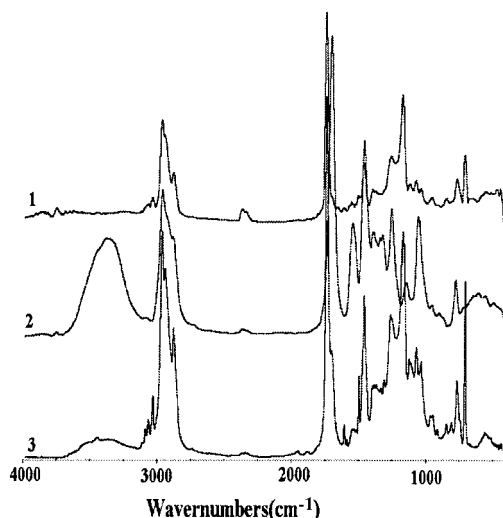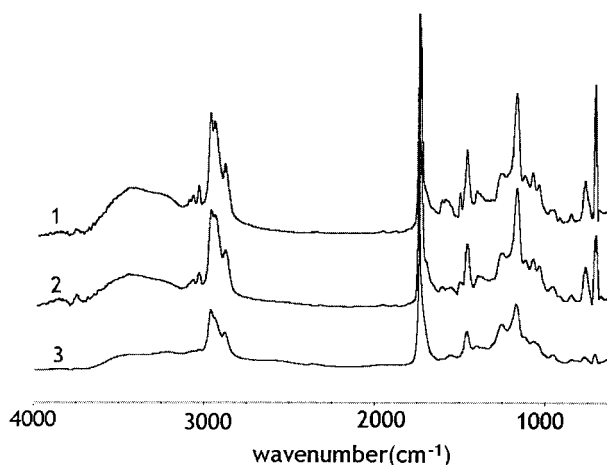
Figure 2 FTIR spectra of the dried polymer film; (1) PA; (2) PU; (3) PUA.

Figure 3 FTIR-ATR spectra of the dried polymer films; (1) air-facing surface; (2) substrate-facing surface; (3) bulk.

solvents, suggesting that some crosslink reactions had occurred.

FTIR-ATR Analysis

Figure 2 demonstrates the typical FTIR spectra of the dried films from PA, PU, and PUA. The major characteristic absorbing peaks are assigned in Table V. The representative FTIR-ATR spectra for air-facing surface and substrate-facing surface of PUA films are illustrated in Figure 3. For the

Table V   The Assignment of Characteristic Peaks

Absorption Bands (cm^{-1})	Assignment
3300	Stretching of N—H
3318	Stretching of O—H
2955	CH$_2$ stretching (asymmetric)
2876	CH$_2$ stretching (symmetric)
1650–1741	Stretching of C=O
1640	Stretching of —CONH—
1600	Vibration of aromatic ring
1550	Stretching of —CONH—
1460	Bending of CH$_2$
1415	Stretching of aromatic C—C
1365	Bending of CH$_2$
1110	Stretching of C—O—C
841	Stretching of ester —OC$_4$H$_9$
761	Vibration of aromatic C—H
700	Vibration of aromatic C—H

sake of comparison, the transmission FTIR spectrum of their bulk is also presented in Figure 3. The air-facing surface and substrate-facing surface have similar characteristic absorbing peaks to their bulk film, exhibiting that they are analogous in structure. However, if a curve-fitting technique and an iterative least-squares computer program are employed to calculate the area of absorbing peaks, it is found that the absorbing intensities of the characteristic peaks are different, implying that there are some differences in composition. Although the peaks at 3300 and 3318 cm^{-1} for stretching of N—H and O—H groups can be indicated in the content of polyurethane component, it is hard to be split and is calculated by using the curve-fitting technique and an iterative least-squares computer program. Thus, the peak at 1550 cm^{-1} for stretching vibration of the —CONH— group is used as an index for the concentration of PU component, the peaks at 761 and 841 cm^{-1} for aromatic ring and —OC$_4$H$_9$ absorbing indicate the concentration of butyl acrylate–styrene copolymer, then the relative concentration of PU component to butyl acrylate–styrene copolymer for air-facing surfaces and substrate-facing surfaces can be judged by the absorbing intensities of these characteristic peaks, as summarized in Table VI, which also lists the depth of penetration at some characteristic peaks based on the Harrick equation.[10] The relative absorbing intensities of these peaks in the transmission FTIR spectra for the corresponding composite latex bulks, as the average composition, are also calculated and shown in Table VI.

Table VI   Quantitative Analyses by FTIR and FTIR–ATR

	$A_{C_4H_9}/A_{CONH}$	$A_{-C_6H_5}/A_{CONH}$
30% solid PUA		
Bulk	1.79	8.37
Air-facing surface	0.47	1.29
Substrate-facing surface	0.12	0.47
Bulk of residua	0.089	0.31
35% solid PUA		
Bulk	2.10	9.05
Air-facing surface	0.81	4.61
Substrate-facing surface	0.21	1.09
40% solid PUA		
Bulk	2.88	10.5
Air-facing surface	0.45	3.02
Substrate-facing surface	0.20	1.03
d_p (μm)	2.38 ($841\ cm^{-1}$)	2.63, 1.29 ($761\ cm^{-1}$) ($1550\ cm^{-1}$)

The results demonstrate that all the air-facing and substrate-facing surfaces of PUA films display considerably lower ratios of $A_{C_4H_9}/A_{CONH}$ and $A_{-C_6H_5}/A_{CONH}$ than their bulk, showing that both air-facing and substrate-facing surfaces contain greatly more PU concentration than the average composition. Because the depths of penetration at 841, 761, and 1550 cm^{-1} for ATR scan are around 2.38, 2.63, and 1.29 μm, respectively, as shown in Table VI, which are two to four times of the average particle size of the composite latex, in the range of 0.6–1.2 μm, depending on the solid content of composite latex, indicating that more PU component on the surfaces than in the bulk observed by FTIR-ATR are not only from the hydrophilic PU molecules on the surface of composite latex particles as discussed above, but also from the reorientation of some PU segments after coalescence and film formation of PUA composite latex particles. This suggests that the composite latex morphology does not remain unchanged; the PU component or segments tend to move toward the surface region, whereas PA component or segments remain inside the bulk during the process of casting latex and drying films. The ratios of $A_{C_4H_9}/A_{CONH}$ and $A_{-C_6H_5}/A_{CONH}$ for all the substrate-facing surfaces are lower than their corresponding air-facing surfaces, explaining that the substrate-facing surfaces contain even more PU

than their air-facing surfaces. In another words, PU component or segments preferentially migrated into the polymer/substrate interfaces than into polymer/air interfaces because of the strong interaction via polar groups between PU molecular chains and substrates (glass plates).

From this result, it can be expected that the surface properties such as mar-resistance, adhesion, and wettability of the films prepared from PUA composite latex are comparable to those of pure PU, whereas the hardness of the films can be obtained from styrene–acrylic copolymer. This tendency is favorable from the viewpoint of the balance of cost and performance of resins for tennis court coatings, floor coatings, laminating adhesives, paper and textile finishes, and inks.

In addition, it was found that the composite copolymers did not fully dissolve in suitable solvents as mentioned above, giving us a hint that some crosslinking reactions occurred during the preparation of PUA composite latex. Here, we further chose the composite latex with 30% solid content as an example and compared this composite latex with its corresponding PU dispersion seed, partial composite latex (PUA1), acrylic latex (PA), and PU/PA blend. These latices were demulsified with methanol and then washed with deionized water and dried at room temperature for 1 week, followed by drying at 50°C in a vacuum oven for 24 h to obtain polymer samples. These polymer samples were then extracted in THF at 80°C for 24 h; the weight of residua for PU, PUA1, PUA, PA, and PU/PA was determined and listed in Table VII. The results showed that only PUA1 and PUA had residua; PU, PA, and PU/PA were completely extracted, indicating that there were some crosslinking structure in PUA1 and PUA. The FTIR spectrum of the residua for PUA (not present here) display the characteristic absorbing peaks of PA, indicating that acrylic monomers and St participated in crosslinking reactions during synthesis of composite latex. The ratios of

Table VII   The Weight of Residua

	Sample				
	PU	PUA1	PUA	PA	PU/PA
wt % of residual sample based on the initial weight	0	75	50	0	0
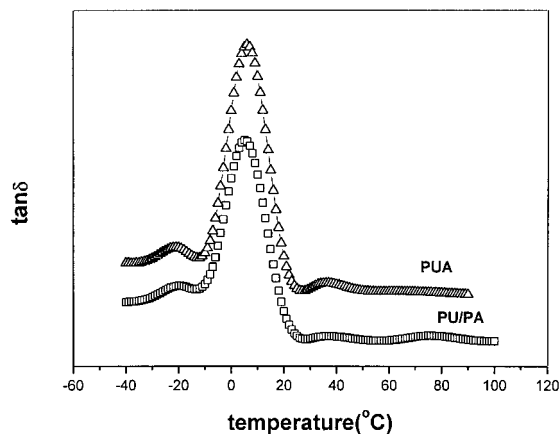
Figure 4 Dynamical mechanical analysis for the films from composite latex (PUA) and its blend latex (PU/PA).

$A_{C_4H_9}/A_{CONH}$ and $A{-}C_6H_5/A_{CONH}$ in the bulk of the residua are lower than those in the bulk of its composite latex, as indicated in Table VI, implying that more acrylic–St copolymers than polyurethane dissolve in THF, if any. In another words, more PU is not soluble in THF; 75% of residua for PUA1 and 50% of residua for PUA further confirm this point.

Dynamic Mechanical Analysis and Static Mechanical Property

Figure 4 exhibits the dynamic mechanical behavior of the polymer films obtained from the composite latex and its corresponding blend latex. The film from blend latex exhibits four transitions, in which −19.5 and 5.2°C probably arise from micro-Brownian segmental motion of acrylic–St copolymer with different compositions associated with the glass transition temperatures (T_g), 37.0 and 75.8°C from the micro-Brownian segmental motion of soft segment and hard segment of polyurethane.[11] Three transitions are observed for the polymer film from composite latex, in which −21.0 and 6.0°C probably correspond to the α-absorption from micro-Brownian segmental motion of acrylic–St copolymer with different composition; 36.3°C is from the motion of PU grafted by St and acrylic monomers. Another transition at around 75.8°C for PU is not observed, suggesting that most PU attended graft polymerization and crosslinking reaction.

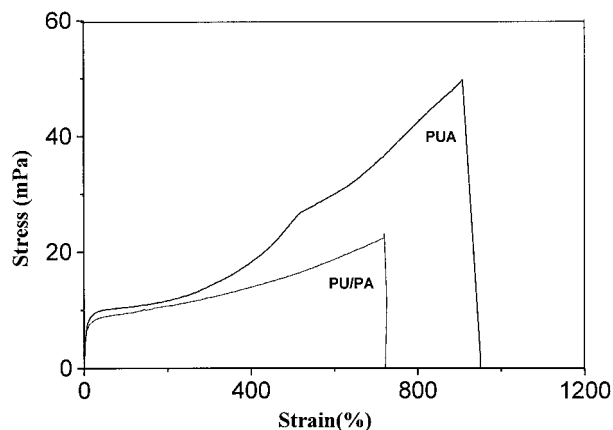Figure 5 illustrates the stress–strain behavior of the films obtained from PUA and its corre-

sponding PU/PA. The tensile strength and elongation at break are 49.9 mPa and 910%, respectively, for the film from composite latex, and 22.2 mPa and 719%, respectively, for the film from blend latex, showing that the composite latices have better film performance properties than their corresponding blend latices.

CONCLUSION

The following conclusion could be drawn from this investigation. The particle size of aqueous PU dispersion increased with the increase in solvent (ethyl acetate) level, but the stability of PU dispersion was not affected. As the DMPA concentration increased, the particle size first increased and then decreased, which was accompanied by an enhancing or weakening of the stability of PU dispersion. However, particle size of PU dispersion did not affect that of composite latex, suggesting that the preparation of urethane/acrylate composite latices has a different particle growth mechanism from traditional core-shell or seeded emulsion polymerization.

FTIR-ATR analyses displayed more PU components on both air-facing and substrate-facing surfaces than the average composition, suggesting that PU segments were inclined to migrate toward the surface layers. There were some crosslinking reactions that occurred in preparing urethane/acrylic composite latices, indicated by FTIR analyses and solvent extraction.

DMA exhibited three glass transitions for the film from composite latex and four transitions for the film from blend latex. The composite latex had

Figure 5 Stress–strain behavior of the films from composite latex (PUA) and its blend latex (PU/PA).

better film performance properties than the corresponding blend latex determined by Instron test machine.

REFERENCES

1. Min, T. I.; Klein, A.; El-Aasser, M. S.; Vanderhoff, J. W. J Polym Sci Polym Chem Ed 1983, 21, 2845.
2. Okubo, M.; Yamaguchi, S.; Matumoto, T. Kobunshi Ronbunsyu 1985, 42, 17.
3. Hegedus, C. R.; Kloiber, K. A. Proc. 21st Waterborne High Solids Coatings Symposium 1994; pp 144–156.
4. Okamoto, Y.; Hasegawa, Y.; Yoshino, F. Progress Organ Coatings 1996, 29, 175.
5. Yang, Z. Z.; Xu, Y. Z.; Zhao, D. L.; Xu, M. Colloid Polym Sci 2000, 278, 1164.
6. U.S. Pat. 4, 198,330 (1980).
7. Eur. Pat. 0189945 (1986).
8. JP59–138212 (1984), 59-210978 (1984), 1-301762 (1989), 3-195737 (1991).
9. Pan, G.; Wu, L.; Zhang, Z.; Li, D. J Appl Polym Sci 2001, 83, 1736.
10. Sung, C. S. P.; Hu, C. B. J Biomed Mater Res 1978, 27, 791–780.
11. Wu, L.; Li, D.; You, B.; Qian, F. Int J Polym Anal Charact 2000, 5, 491.