Acrylic 함량이 Polyurethane/Polyacrylate 복합 에멀전의 특성에 미치는 영향

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Effect of Acrylic Content on the Properties of the Polyurethane/Polyacrylate Composite Emulsion

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Abstract: A polyurethane/polyacrylate (PUA) composite emulsion was synthesized by using polyurethane (PU) as seeds with soap-free emulsion polymerization, in which methyl methacrylate (MMA) and butyl acrylate (BA) were used as main acrylic monomers. The effect of acrylic contents and "stiff" and "soft" weight ratio of acrylic monomers on the properties of the films were investigated. The Fourier transform infrared (FTIR) results showed that acrylic monomers were involved in the emulsion copolymerization. The optimum composition of PUA composite formation was obtained when the polyacrylate (PA) content was 20%, in which the weight ratio of MMA and BA was 2/1. With the increment of PA content, the decomposition temperature increased.

Keywords: polyurethane/polyacrylate composite emulsion, acrylic content, "stiff" and "soft" weight ratio.

Introduction

Waterborne polyurethane (WPU) dispersions are considered as one of the most important commercial polymers because of its environmental benefits and tremendous usefulness when compared with conventional solvent-based polyurethanes (PUs).[1-3] Their films show excellent mechanical properties depending on their structure. Unfortunately, these kinds of polymers have high production cost and are of inferior water and temperature resistance. These drawbacks subsequently limit their applications in some fields.[4-6] Polyacrylate (PA) is the most frequently used to modify PU due to its low cost, good water resistance and proper mechanical properties. To

take advantage of the potential cost reduction and good water resistance afforded by the acrylics and maintain a greater share of the advantageous WPU properties, the composite systems were developed. The most popular strategy is to blend the WPU with a PA emulsion. In general, physical blending of the two polymers is a simple approach to integrate their individual advantages. However, in many cases the resultant blend shows poor performance properties due to incompatibility of the two polymers and because phase separation during blending renders the ideal composite polymers difficult to obtain.[7] X. Kong *et al.*, synthesized the acrylic copolymers with varying monomer contents in acetone, and the acrylic polymer aqueous dispersions were blended with the WPU in order to prepare the 2K-WPU coatings. In this experiment, acetone was used as solvent, and it was bad for the environments.[8] V. D. Athawale *et al.* prepared the PU/acrylate composite using acrylates monomers and emulsifier by semibatch emulsion polymer-

ization method and by physical blending method. The experimental results indicate better acrylic-PU compatibility in hybrid emulsions than in physical blends, resulting in improved chemical and mechanical properties. But some emulsifier was used which have negative effects on the properties of product such as confer water sensitivity.[9,10]

There is a need to introduce specific interactions and thus improve compatibility between the two different polymers.[9] Some crosslinked monomer was used to make the two systems react in some extent. The PU was prepared by using the unsaturated carbon-carbon bond monomers as the bridge of the copolymerization reactions to obtain the double bond terminated PU. Butyl acrylate (BA) and methyl methacrylate (MMA) were used as acrylic monomers since they are very common and cheaper monomers used by the polymer industry.[11] The composite systems incorporate both the urethane and acrylic polymers into the same dispersion. The formation of hybrid systems containing chemically bonded mixtures of both polymers lead to a better mixing of components, suitably combining the properties of both polymers.[12-15]

Moreover, acrylic monomers instead of solvent acetone or *N*-methyl-2-pyrrolidone (NMP) were used as a diluent to adjust the viscosity of urethane prepolymer and also to incorporate acrylic monomer into the urethane prepolymer mixture simultaneously.

This study takes an approach to find the optimum composition of PU/PA (PUA) composite formation and without external surfactant via *in situ* polymerization using a prepolymer mixing process. PU was used as seeds in the soap-free emulsion polymerization. Prepolymers containing acrylic monomer were dispersed in water environment as nanoparticles stabilized by self-emulsifying ability of urethane prepolymer anionomer, that is, no external surfactant was used.

Although there have been some references demonstrating the PUA composite emulsions,[8,9] there are a few reports concerning the synthesis and characterization of the nanograde composite PUA emulsion with no external surfactant and solvents by self-emulsifying method. In this study, PUA composite emulsions with different acrylic contents (0, 10, 20, 30 and 50 wt%) and with different "stiff" and "soft" weight ratio of acrylic monomers ("stiff" and "soft" weight ratio of MMA/BA : 1/1, 1.5/1, 2/1, 2.3/1, 3/1) were prepared through soap-free emulsion polymerization method. The effect of acrylic monomer content and different ratio of MMA and BA on the particle size distribution, the viscosity, the gel content, water resistance, the thermal stability and mechanical properties was

also investigated.

Experimental

Materials. Isophorone diisocyanate (IPDI), polycaprolactone polyol (PCL, M_n=1000), 2,2-bis(hydroxymethyl) propionic acid (DMPA) were purchased from Guangzhou Hito Trade Co., Ltd; dibutyltin dilaurate (DBTDL), triethylamine (TEA) were produced by Tianjin Hongyan Chemical Reagent Co., Ltd.; methyl methacrylate (MMA), 2-hydroxyethyl acrylate (HEA), potassium persulfate (KPS), butyl acrylate (BA) were supplied by Peking Chemical Reagent Co., Ltd.; All raw materials are laboratory grade chemicals and were used as received without further purification. PCL were dried in vacuum at 100 ℃ before use.

Preparation of Polymer Dispersions. Preparation of Aqueous PU Dispersions: The IPDI, PCL and catalyst DBTDL were added to a four-necked flask which was equipped with a thermometer, a mechanical stirrer, a condenser with a drying tube and an inlet of dry nitrogen. The reaction was carried out at 80 ℃ for 2 h to obtain an NCO-terminal hydrophilic PU prepolymer. Then, DMPA and a mixture of MMA and BA were added into the system and reacted for 1.5 h. The addition of acrylic monomers could adjust the viscosity of PU prepolymer. The terminal NCO groups of the PU prepolymer were then capped by HEA at 75 ℃ for 1.5 h. The reaction mixture was cooled to 40 ℃. TEA was added to the reaction mixture to neutralize the carboxyl group of the double bond-terminated PU prepolymer. After half hour neutralization, a calculated amount of distilled water was added to the mixture with vigorous stirring (800 rpm). The PU dispersions with a solid content of 30 wt% were obtained.

Preparation of PUA Dispersions: The preparation of PUA dispersions were carried out by using soap free polymerization, which used PU dispersions as the seed emulsions. The radical initiator (KPS: 2 wt% based on the acrylic monomer weight) was added dropwise to the emulsion in 1 h, and then the radical polymerization of acrylic monomer subsequently took place at the same time by slowly heating to 80 ℃ with the heating rate 5 ℃/min. The reaction time for the polymerization was kept for 3 h. The synthetic route is shown in Scheme 1. We prepared several PUA emulsions of different PA content and different "stiff" and "soft" weight ratio of acrylic monomers. The sample designation and composition are shown in Table 1.

Films for the tests were prepared by casting emulsions onto

Table 1. Sample Designation, Composition of Pristine PU and PUA Emulsions

Sample designation	PU composite/(wt%)					MMA	BA	Acrylic content (wt%)
	IPDI	PCL	DMPA	HEA	TEA			
WPU	34	45.4	9.9	1.8	8.9	-	-	-
PUA10	34	45.4	9.9	1.8	8.9	67	33	10
PUA20	34	45.4	9.9	1.8	8.9	67	33	20
PUA30	34	45.4	9.9	1.8	8.9	67	33	30
PUA50	34	45.4	9.9	1.8	8.9	67	33	50
PU/M1B1	34	45.4	9.9	1.8	8.9	50	50	20
PU/M1.5B1	34	45.4	9.9	1.8	8.9	60	40	20
PU/M2B1	34	45.4	9.9	1.8	8.9	67	33	20
PU/M2.3B1	34	45.4	9.9	1.8	8.9	70	30	20
PU/M3B1	34	45.4	9.9	1.8	8.9	75	25	20

[a]Weight ratio of acrylic monomers content was based on the PA content.
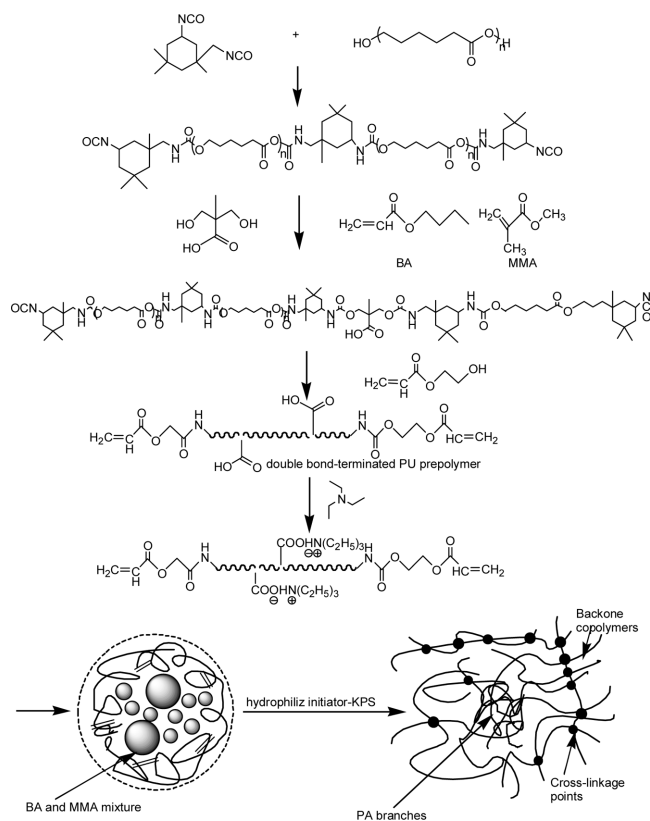
Scheme 1. Synthetic route of PUA composite emulsion.

a Teflon plate, followed by drying for 2 days at ambient temperature. The remaining moisture was removed at 60 °C for 24 h. After demoulding, the films were stored in a desiccator at room temperature.

Characterization. Particle size of dispersions was determined by using dynamic light scattering (Malvern Zetasizer Nano ZS, Malvern instruments). The samples of emulsions were diluted with diluted water to adjust the solid content to around 0.2 wt% and directly placed in the cell. The temperature of the cell was kept at around 25 °C and the equilibrium time was 120 s. The mean particle size was characterized by z-average diameter (Dz). They were automatically calculated by the computer connected to the machine.

The apparent viscosities at various shear rates were determined using an American AR2000ex rheometer (American TA company) with a concentric cylinders. The measurements were carried out at 25 °C after 60 s equilibrium time under a shear rate ranging from 0.01 to 10^3 s^{-1}.
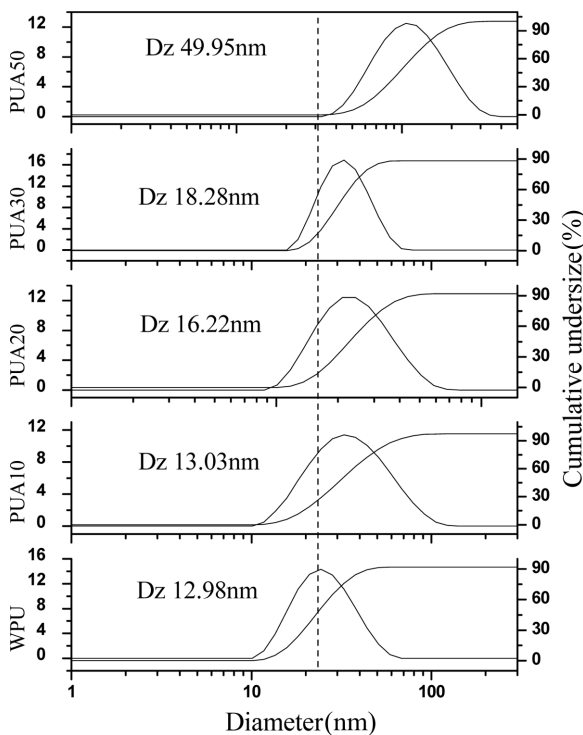
Attenuated total reflection Fourier transform infrared (ATR-FTIR) was conducted on a model V70 infrared spectrophotometer with a wavenumber resolution of 4 cm^{-1} at ambient temperature. The scanning frequency was 64 times. Pristine PU and PUA20 were coated directly on to the surface of a KBr crystal, respectively, and measured after film forming and drying.

The gel content was determined by Soxhlet extraction with acetone as a solvent at 65 °C. The dried composite polymer membranes weighed M_0 was placed in a Soxhlet extractor, then the extracted process consisted in a 24 h continuous extraction under reflux in a 250 mL round bottom flask. After the extraction, cross-linked polymer was assumed to remain in the thimble while linear polymer went down to the acetone balloon by acetone circulation, and the rest weight (M) of the membranes were obtained after drying for 72 h at 30 °C. Then the gel content (G) was calculated according to the following formula: $G(\%) = M/M_0 \times 100\%$.

The water absorption property was measured by immersing dried films (10 mm×10 mm×1 mm) weighed W_0 in deionized water at maintained at 25±0.2 °C for 24 h. The films were then taken out of the water, and after wiping off the residual water on the surfaces using filter paper, their mass was measured immediately to obtain the weight (W_1). The water absorption of the films was calculated as follows: Water absorption (%)=$(W_1−W_0)/W_0$×100%. Three runs were made for each specimen and average values were taken.

Thermogravimetric analysis (TGA) and differential thermogravimetric (DTG) analysis of the PU samples were carried out by using an American Q500 TG analyzer under a nitrogen atmosphere at a heating rate 10 °C/min. Thermal degradation temperatures were measured in the range of 30-500 °C. The samples ranged between 5 and 10 mg in weight were placed in platinum sample pans. One test was taken for each sample.

Mechanical properties of emulsion films were determined at room temperature using Tinius Olsen Series 1000 with a crosshead speed of 100 mm/min. Rectangle specimens of 100 mm ×10 mm (length×width) were used. The ultimate tensile strength and breaking elongation were investigated for all the samples. The measurements were performed according to the Chinese standard GB/T528-2009. The values quoted are the average of three measurements, and the average value was calculated.

The crystalline properties of samples were performed with Siemens D5000 X-ray diffractometer using a CuKα radiation (40 kV, 40 mA) source at room temperature. Patterns were recorded by monitoring diffractions from 5° to 60°. The scan speed was 0.02°/min.

Atomic force microscopy (AFM) observation was performed on the Seiko Instruments in tapping mode. All morphologies were acquired under ambient conditions using Nanoprobe cantilever. For AFM measurements, the emulsions were cast onto freshly cleaved monocrystalline wafer and then dried at room temperature.[16]

Results and Discussion

Effect of Acrylic Content on the Property of the Films. To investigate the properties of films with different acrylic content, the weight ratio of MMA/BA 2/1 was used.

Particle Size: The particle size of dispersions was shown in Figure 1. The curves of pristine WPU and composite emulsions containing 10, 20, 30 and 50 wt% of acrylic monomers both showed unimodal distributions. As acrylic monomers content increased from 10 to 30%, the particle size of the composite emulsions increased slightly. Further increase of PA content in composite emulsions results in a marked increase in the average particle size. The unimodal distributions ascertain the encapsulation of PU to PA. The acrylic monomers first swelled into the PU latex, and then they were initiated by the


Figure 1. Particle size and distribution of PUA dispersions with different PA content.
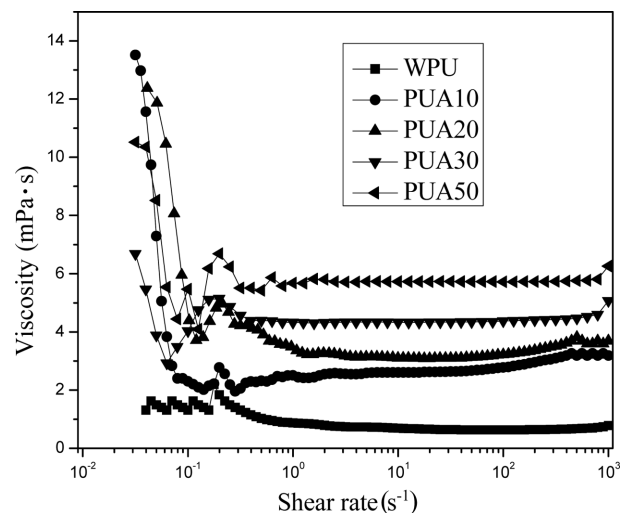
Figure 2. Viscosity *versus* shear rate of composite emulsions with different PA content.

initiator. The compatibility of the two parts was increased. The composite particles containing relatively higher hydrophobic acrylic monomers content grew bigger. This is because further introduction of acrylic monomers makes it difficult for the micelle-forming PU component to contain acrylic components. Therefore larger emulsion particles may be formed presumably by the fusion of several particles. When more acrylic components are introduced, the fusion of particles further proceeds to form much larger particles.[1,8,17]

The Viscosity: The dependencies of the viscosity on the shear rate at 25 °C are presented in Figure 2. The pristine PU emulsion displayed Newtonian behavior. No dependence of the viscosity on the applied shear rate across the shear rate range studied. In contrast to the observed rheological behavior of original PU emulsion, the PU composite emulsions containing the acrylic monomers displays non-Newtonian, shear-thinning behavior during a shear rate sweep experiment as illustrated in Figure 2. There is a decrease in viscosity by increasing the shear rate. The addition of PA could increase the cross-linking density of the system and formed a network, which made the chains integrate more closely. The original viscosity of the composite emulsions was higher than the pristine PU due to the internal structure between the systems. With the increasing shear rate, the internal structure of the composite emulsions may be disrupted. The internal structure became gradually broken, giving a sharply decrease in viscosity. With the shear rate increased gradually, the internal structure had no time to reconstruct, which led to the variation tendency become stable.[18-24]

ATR-FTIR Spectroscopy: Figure 3 demonstrates the typical ATR-FTIR spectra of the dried films from pristine PU and PUA20. The characteristic absorption band at 3320 cm^{-1} indicates the stretching of free N-H stretching vibrations. The weak absorption at 2928 cm^{-1} is assigned to C-H asymmetric stretching of the methyl group; the strong carbonyl stretching frequency near 1740 cm^{-1}, together with strong stretching bands at 1270 cm^{-1} can be attributed to the presence of an ester group.[25] All these data confirm the formation of urethane group (Figure 3(a)). The presence of acrylic component changes the hydrogen bonding interaction in composite systems and shifts the maximum N-H absorption band to higher frequencies of 3343 cm^{-1} (Figure 3(b)). Compared with the pristine PU, the presence of acrylic ester groups is evidenced by the appearance of an absorption peak at 1243 and 1166 cm^{-1} (Figure 3(b)) which are attributed to the C-O stretching vibrations of acrylic ester groups. Moreover, there are no adsorption
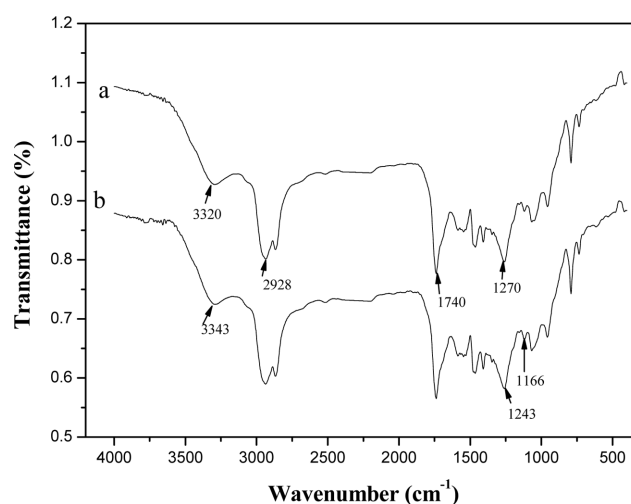
Figure 3. ATR-FTIR absorption peaks of (a) Pristine PU; (b) PUA20.

peak at 1641 cm^{-1} which is attributed to the characteristic of C=C bonds of the monomers, which suggests that the acrylic monomers have already undergone free radical polymerization. All these results of ATR-FTIR analysis indicated that PUA was prepared as desired through soap-free seeded emulsion polymerization.[8,26-28]
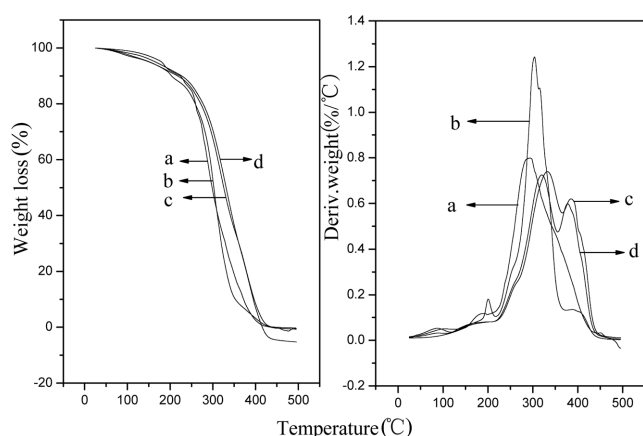
Water Absorption and Gel Content of the Films: Gel content and water absorption measurements of films with different PA content are shown in Figure 4. With the increment of PA, the water absorption of the films decreases evidently. The lowest water absorption value was obtained when the PA content was 20%. The water absorption decrease from 19% to 10.3% with w(PA) increase from 0% to 20%. PA itself has the
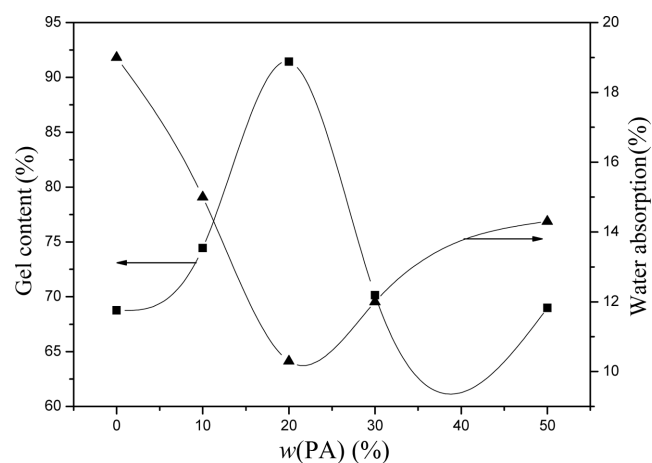
Figure 4. Gel content and water absorption of films with different PA content.

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good hydrophobicity, and good water resistance property. As the PA content increased, the PU content is relatively decreased. The more the PA content was, the better the water resistance was. And the addition of PA can increases the crosslinking density of the system, which also make the gel content increase. Besides, the particles are of a very small size and may have formed a compactly arranged structure in the films, making it difficult for water to diffuse into the film and thus decreasing water absorption. However, if the PA content is too high, the particle size may become larger, which may in turn render the particle arrangement less compact and the particle interspaces larger. Thus, more water may be retained in these interspaces, leading to increased water absorption and decreased gel content.

Thermogravimetric Analysis: TGA thermograms of different PUA films are shown in Figure 5, and the 5, 50% and maximum weight-loss temperatures of their films are listed in Table 2. The initial decomposition temperatures of all films

were almost the same. There is an obvious step of weight loss in the temperature range of 200-400 °C at TGA curves. With the increment of PA content, the T_{50} value increased from 298.24 to 330.73 °C, indicating that the decomposition temperature was higher than that of pristine PU. The temperature at maximum rate of weight loss was also higher than those of pristine PU, which shows higher stability of PUA has been obtained.

The curve in DTG indicated that there were different stages of degradation, which was not perceptible in TG curves. It has also been proved that the amount of weight loss of the first region was well correlated with the hard segment concentration, suggesting that the degradation started in the hard segment. Thus, it is generally believed that soft segments are more thermal stable than hard segments in two stages of film weight loss. The first part of the degradation corresponded to the hard segment starting at 179 °C, while the second peak corresponded to the degradation of the soft segment at 292 °C. There was also a third peak at the temperature range of 330-390 °C, which was attributed to the degradation of PA content. With the increment of the PA content, the intensity of the first degradation peak became weaker. This phenomenon could also ascertain that the increasing PA content could improve the compatibility between PU and PA.

The addition of PA can increase the crosslinking density of the films, and the miscibility of PU and PA was also improved, the copolymer can form more effective physical cross-link point, which is conductive to better physical properties of films, so the thermal stability improved relatively.[8,29]

Mechanical Properties of the Films: Influence of different PA content on the mechanical properties is shown in Figure 6.

Figure 5. TGA and DTG curves for PUA films with different PA content: (a) WPU; (b) PUA10; (c) PUA20; (d) PUA30.
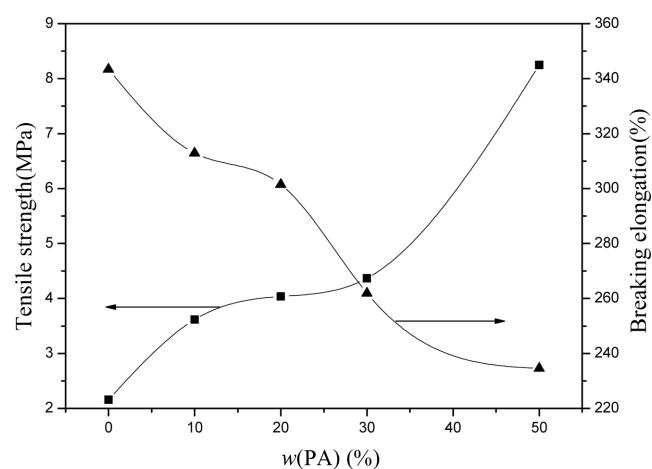
Table 2. TG Data for PUA Films with Different PA Content

| Sample	T_5 (°C)	T_{50} (°C)	T_{max} (°C)
a	165.33	298.24	179.76 292.24
b	152.41	303.28	200.49 294.85 351.12
c	165	330.73	265.65 338.43 376.09
d	150.33	325.28	261.42 315.59 388.78

Figure 6. Mechanical properties of films with different PA content.

It shows that the values of tensile strength increases continuously from 2.158 to 8.25 MPa with increasing content of PA from 0 to 50%, whereas the values of breaking elongation show the opposite tendency. This implies that the addition of PA enhances the mechanical property of the films. The increasing PA content can increase the hard segment of the films, which is good to enhance the tensile strength. The PU chains were blocked by using the unsaturated carbon-carbon bond monomer HEA, which was playing as the bridge of the copolymerization reactions. The HEA could react with the acrylate monomers initiating with KPS by radical polymerization, which can form three-dimensional network structure between the two chains as shown in Scheme 1. The miscibility of PU and PA was also improved; the copolymer can form more effective physical cross-link point, which is conducive to better physical properties of films.

Effect of Different "Stiff" and "Soft" Weight Ratio of Acrylic Monomers on the Property of the Films. The tensile strength and other properties of film with different "stiff" and "soft" weight ratio of acrylic monomers were investigated in order to get the film showed optimum properties when PA content was 20%.

Particle Size Analysis: The particle size of emulsions with different ratio of "soft" and "stiff" monomers was shown in Figure 7. The particle size analysis showed that the composite emulsions had fine particle sizes varying between 16.22 and 21.67 nm with narrow distributions. When the ratio changed, the particle size changed in some extent. Figure 7 shows that the particle size in composite emulsions increases with the increase in the MMA content. The PA in the emulsions is obtained from the BA and MMA components. Hence, if the PA content in the emulsions is constant, the BA content decreases accordingly as the MMA increases, resulting in an increase in the particle size, as shown in Figure 7. However, as the MMA content increases from 50 to 75 wt%, the particle size increases slightly.

Water Absorption and Gel Content of the Films: The gel content and water absorption property was shown in Table 3. The gel content for all the composite samples are ranged from 84 to 91%. This fact indicates that PUA composites are cross-
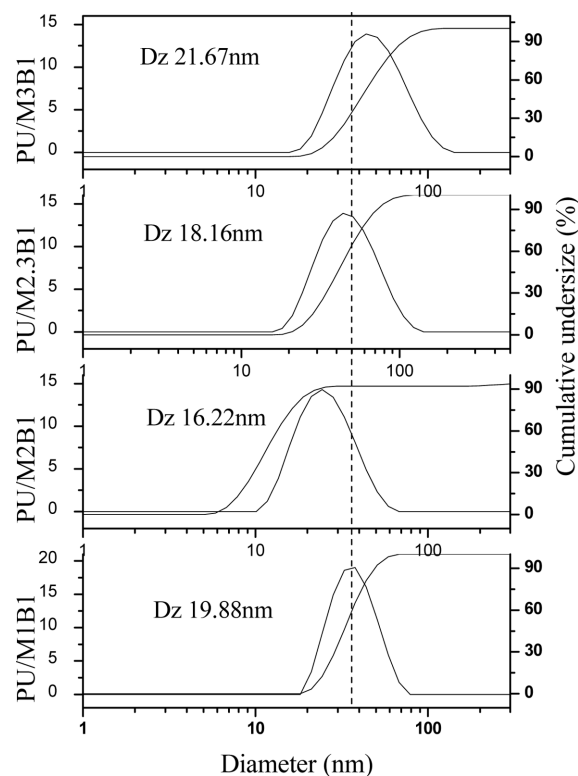

Figure 7. Particle size of emulsions with different "stiff" and "soft" weight ratio of acrylic monomers.

linked systems. With the increment of the MMA content, the gel content increased marginally. It also can be seen from the Table 3 that the water absorption value gradually declines from 11.54 to 10.3% as the MMA amount varies from 50 to 67 wt%. This is probably due to the cohesion strength between "soft" and "stiff" monomers. As the MMA content increases, the films become more compact, thus resulting in good water-resistance property. Even though the water absorption increased slightly after the MMA increased to 75%, it was still very low.[7,13]

XRD Analysis: As shown in Figure 8, all samples show similar XRD curves with a wide diffraction at around 20°. These are typical for amorphous polymeric materials. The crystallinity of the pure PU was 1.35% while the PU/M1.5B1 and PU/M2B1 was 2.15, 8.13%, which indicated that the crystalline property was enhanced gradually. The cohesion strength

Table 3. Gel Content and Water Absorption of Films with Different "Stiff" and "Soft" Weight Ratio of Acrylic Monomers

Sample	PU/M1B1	PU/M1.5B1	PU/M2B1	PU/M2.3B1	PU/M3B1
Gel content (%)	84.58	85.29	91.45	89	87.68
Water absorption (%)	11.54	11	10.3	11.6	12
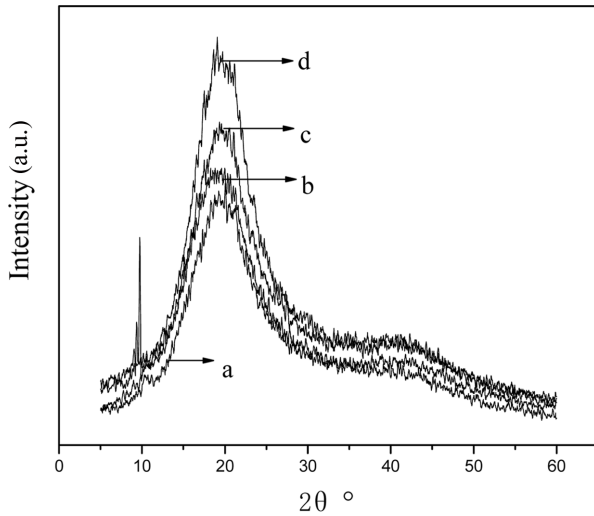
Figure 8. XRD curves of different films: (a) WPU; (b) PU/M1.5B1; (c) PU/M2B1; (d) PU/M3B1.

interaction between the "soft" and "stiff" monomer is higher, and the PA and PU also formed network structure, so the intensity and the crystallinity both increased compared with the pristine PU.[13,27,29]

Mechanical Properties of the Films: The tensile strength and breaking elongation of the samples was presented in Figure 9. It can be seen that the tensile strength of films increased from 8.455 to 11.35 MPa whereas the breaking elongation obviously decreased from 566.52 to 495.91% as the MMA content increased from 50 to 67 wt%. The copolymerization between "soft" and "stiff" monomers could produce better cohesion strength to the composite polymer. With the increment of the "stiff" monomer, the cohesion strength enhanced. The MMA content tended to make the molecular chains more rigid, thus improving the film tensile strength. BA performs as the "soft" monomer of the PA, and its existence seems to supply plasticity and elasticity to the films. Therefore, as the MMA content increases or the BA content decreases, the resultant films acquire high tensile strength and low elongation. But if the proportion of MMA content is too large, the films would
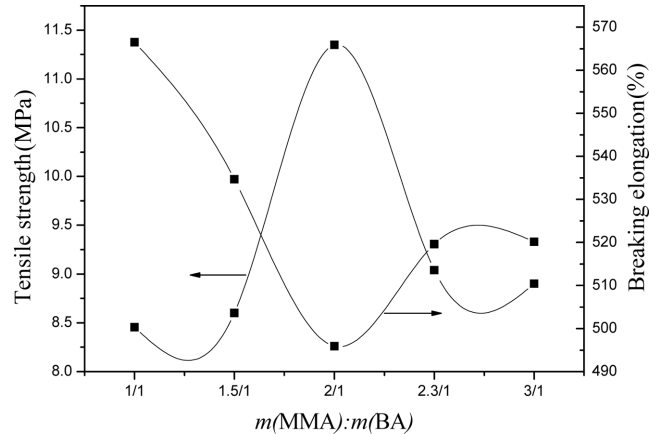

Figure 9. Mechanical properties of films with different "stiff" and "soft" weight ratio of acrylic monomers.

be too stiff and they were easy to fracture.[7,13,30]

AFM Analysis: The AFM analysis is useful for observing the topography image, and is more accurately performing the surface. The results of phase imaging with AFM in tapping-mode are shown in Figure 10. The parameters of root-mean-square (RMS), roughness average (Ra) and 10 point height (Rz)[31] were obtained from AFM software analyses as shown in Table 4. It could be seen from Figure 10 that many little protuberances or peaks appeared on a, b films surface. The topography morphologies of c and d show a flatter and smoother surface than that a, b. RMS roughness of those two films attained 10.28 and 7.447 nm, respectively. When PU prepolymer was dispersed in water, the mixture of acrylate monomers assembled in the inner of PU particles. As the PU was prepared by using the unsaturated carbon-carbon bond monomers as the bridge of the copolymerization reactions, two com-

Table 4. Various Roughness Parameters for Films of Figure 10

Factors	WPU	PU/M1.5B1	PU/M2B1	PU/M3B1
RMS (nm)	95.65	123.2	10.28	7.447
Ra (nm)	48.88	102.1	5.513	4.347
Rz (nm)	204.6	149.8	39.41	104.7
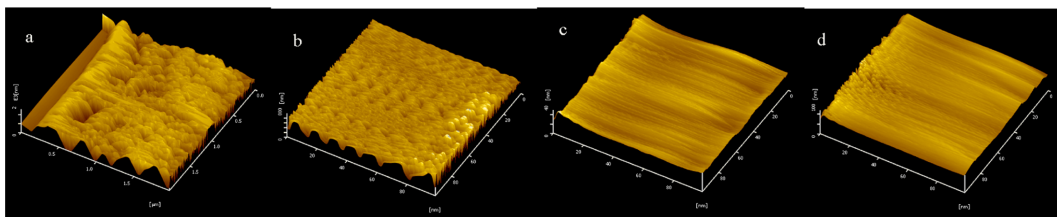
Figure 10. Topographic AFM morphologies of films with different "stiff" and "soft" weight ratio of acrylic monomers: (a) WPU; (b) PU/M1.5B1; (c) PU/M2B1; (d) PU/M3B1.

ponents of the molecular chain had good compatibility. With the increment of the MMA content, the performances of film were enhanced, and the extremely flat film was obtained.

Conclusions

PUA composite emulsions in a range of composition (10, 20, 30, 50 wt% of acrylic content), were successfully obtained by emulsion polymerization of acrylic monomers (MMA/BA) in the presence of preformed PU chain without external surfactant. The effect of acrylic content and weight ratio of acrylic monomers (MMA/BA : 1/1, 1.5/1, 2/1, 2.3/1, 3/1) on the properties of the films were evaluated. The particle size analysis ascertains the encapsulation of PU to PA. The rheology measurements indicated that addition of acrylic content increases the viscosity, imparts pseudoplasticity. The influence on viscosity is enormous: From an almost Newtonian to an strongly shear thinning behavior. ATR-FTIR analysis indicated that PUA was prepared as desired through *in situ* polymerization using a prepolymer mixing process. The optimum composition of PUA composite formation was obtained when the PA content was 20%, the weight ratio of MMA and BA was 2/1. It was found that PUA can markedly improve the water resistance and gel content. With the increment of PA content, the decomposition temperature was higher than that of pristine PU. The addition of PA can increase the crosslinking density of the films, and the miscibility of PU and PA was also improved. With increasing content of PA from 0 to 50%, the tensile strength increases continuously from 2.158 to 8.25 MPa. The addition of PA enhances the mechanical property of the films. With the increment of the MMA content, the crystalline property was enhanced gradually. The AFM measurement showed extremely flat film with the increment of the MMA content.

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