Soap-Free Seeded Emulsion Copolymerization of MMA onto PU-A and Their Properties

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ABSTRACT: The polyurethane acrylate (PU-A) containing double bond and COOH group was synthesized by stepwise reaction of 2,4-toluene diisocyanate (TDI), polyetherdiol (PPG), dimethylolpropionic acid (DMPA), and 2-hydroxpropyl acrylate (HPA), and the PU-A was neutralized with triethylamine (TEA) and self-emulsified in water to form the PU-A emulsion seed. Adding methyl methacrylate (MMA) into PU-A seed, the seeded emulsion copolymerization of MMA onto PU-A seed had been carried out at 80°C under the soap-free condition to obtain anionic latex of P(UA-MMA). The kinetic behavior of the seeded emulsion copolymerization, the MMA grafting ratio, and the crosslinking copolymer were investigated. IR spectra showed that it did form the P(UA-MMA) copolymer. The measurements revealed that the structure of the P(UA-MMA) copolymer, its latex properties and the cast film were significantly influenced by the amounts of HPA, DMPA, and MMA. The experimental results indicated that with DMPA increased, the particle size of P(UA-MMA) latex decreased, but the tensile strength of its cast film increased. Adding a small amount of HPA, it could improve the tensile strength of the cast film. With MMA content increased, the distribution of the particle size of P(UA-MMA) latex became narrow, whereas under certain amount of MMA, the tensile strength of the cast film was enhanced. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 82: 941–947, 2001

Key words: polyurethane; methyl methacrylate; PU-A seed emulsion; soap-free emulsion copolymerization; property

INTRODUCTION

Combination of two kinds of polymers with different chemical component and performance is one of the important methods of preparing new polymer materials and extending their uses.[1–4] Two kinds of polymers can be made into composite by blending and copolymerizing etc. In the polyurethane (PU) and polyacrylate (PA) composite (PU/PA) polymer, as it contains PU and PA segments, this widens the PU/PA properties and usage. Because the PU/PA composite polymers have many advantages, such as solvent resistance, abrasive resistance, and flexibility of PU polymer as well as water resistance, brilliant, and aging resistance of PA polymer, the latexes of PU/PA have been widely used as coating, adhesive, sealing of buildings, as well as coatings of fabric and leather.[5,6]

The PU/PA composite polymers were mostly prepared by the solution polymerization methods.[7–9] To eliminating solvent toxicity and environment pollution, the aqueous latexes of PU/PA composite polymers have become into important topics.[10–15] The latexes of PU/PA composite polymers have various preparation methods such as the latexes blending,[16] polymerization of composite emulsion,[17,18] emulsion copolymerization, etc.[19,20]

To increase the compatibility, aging resistance, and other performances of the PU/PA composite polymers, the latexes of P(UA-MMA)composite polymers were synthesized by seeded emulsion copolymerization under the soap-free condition.

The synthesis of PU-A containing double bond and COOH group was carried out by two-stage reaction. First, TDI, PPG, and DMPA were reacted together, then adding HPA with a double bond and hydroxyl group. Here DMPA acted both as hydrophilic monomer and chain extender, and HPA is an end-capping monomer. After the PU-A seed had been neutralized with TEA and self-emulsified in water, MMA monomer was added into the emulsion; thus, the PU-A/MMA seed emulsion was prepared. The PU-A seed containing the MMA monomer was copolymerized without adding any emulsifier, and we obtained the latex of P (UA-MMA) composite polymer. Here, PU-A was used as the seed and as a dispersing agent for stabilizing the latex particle in the condition of no any other added emulsifier. Therefore, the performances of the composite polymers as adhesive and coating without interface weakening effects have been enhanced.

In the emulsion copolymerization of PU-A/MMA under the soap-free condition, the COOH group, double bond, MMA, and initiator amount extensively affects polymerization kinetics of MMA, stability, and the particle size of the latex as well as the properties of the cast film. IR spectra of the PU-A polymer, the conversion time during the copolymerization process, the size and dispersity of the latex particles, and the mechanical property of the cast film were investigated. The multiple steps of solvent extraction measured the content of graft and crosslinking copolymer in the cast film. Effects of the amount of DMPA, HPA, and MMA on the copolymerization and properties of the latexes were also discussed.

EXPERIMENTAL

Material

2,4-Toluene diisocyanate (TDI), polyetherdiol (PPG), 2-hydroxypropyl acrylate (HPA), dimethylolpropionic acid (DMPA), triethylamine (TEA), dibutyltin dilaurate (DBTD), and ethanediol (ED) were used as received. Methyl methacrylate (MMA) was distilled under reduced pressure. Potassium persulfate (KPS) was recrystallized and dried at room temperature under a vacuum. The water was deionized.

Table I   The PU-A Seed Recipes

Reagents	Mole Ratio	Weight
TDI	0.12	21.0 g
PPG	0.048	53.8 g
DMPA	0.024–0.04	3.7–6.4%PU
HPA	0.01–0.04	25–100%-NCO
ED	0.005–0.200	0.35–1.40 g
TEA	0.024–0.040	2.4–4.0 g

Synthesis of PU-A

The synthesis of the PU-A seed was carried out in a four-neck glass reactor equipped with a stirrer, thermometer, reflux condenser, and inlet system for N_2. First, TDI, PPG, DMPA, and DBTD were poured into the reactor, after 3 h reaction at 80°C, HPA and ED were added into the system and allowed to react for another 3 h. Then the system was neutralized with TEA, and water was added into the system to forming emulsion under vigorous stirring. The recipes are summarized in Table I. The scheme of formulation of the chemical reaction of the PU-A/MMA latex is illustrated in Figure 1.

Copolymerization of PU-A/MMA

After the PU-A seed was neutralized with TEA and self-emulsified in water, sequentially the MMA monomer was added into the emulsion and the PU-A particle was swelled at room temperature for 12 h. Then the seeded emulsion copolymerized of MMA onto PU-A was conducted with $K_2S_2O_8$ initiator at 80°C for 4 h.

Measurement and Characterization

The IR spectra of the PU-A seed were gained on an IR-400 spectrograph instrument. The conversion was determined with the gravymetric method. The size and its polydispersity of the latex particles were measured on a Malvern Auto Sizer LoC-FC963 apparatus. Here polydispersity was represented with "poly" (the deviation of average diameter in particles). The tensile strength and elongation at break of the cast film were measured on AG-A type all-purpose tester at room temperature using a crosshead speed of 10 cm/min.

To investigate the content of graft and crosslinking copolymers in the P(UA-MMA) composite latex, we referred to the literature.[21] Two-stage extraction was used to remove PMMA and
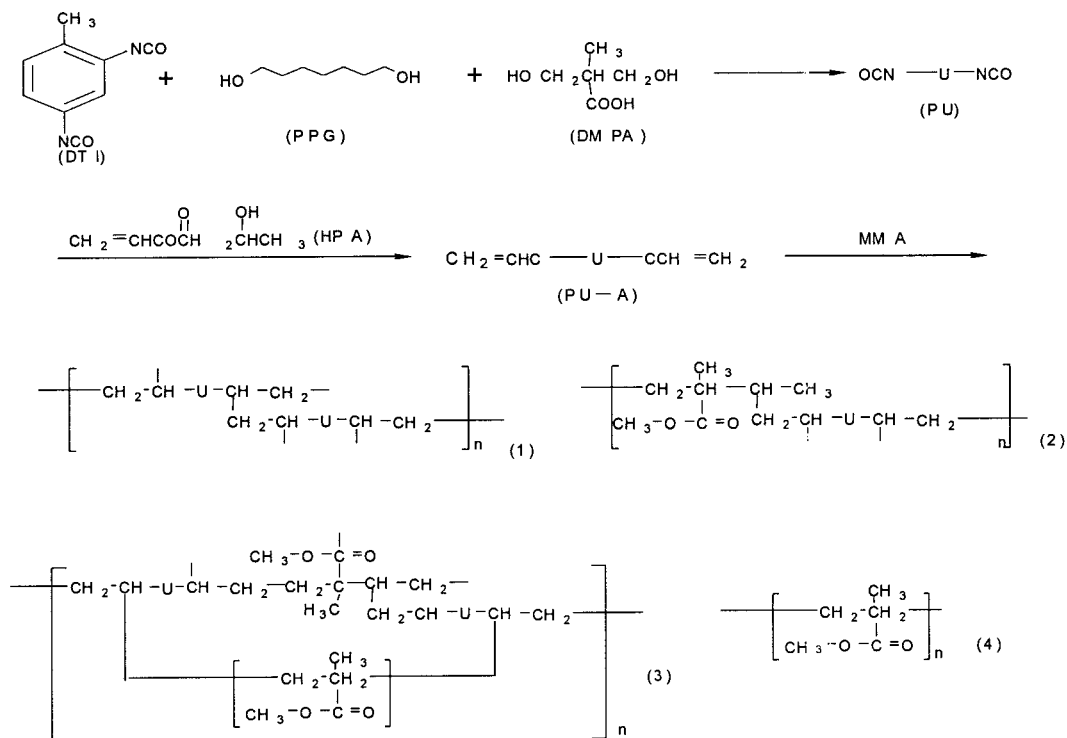
Figure 1 Scheme of the reaction products of P (UA-MMA) synthesis: (1) P (UA) seed; (2) P(UA-MMA) graft copolymer; (3) P (UA-MMA) crosslinking copolymer; (4) PMMA homopolymer.

linear PU-A with the Soxhlet apparatus. The bits of the cast film were weighed out at an accurate quantity (W_1), and then was extracted by toluene for 24 h to remove the MMA homopolymer. The remainder material was dried, and was extracted using *N,N*-dimethylformaminde for 24 h to remove the PU-A linear polymer. Then the solid left was extracted again with chloroform for 48 h, and then was dried to remove the solvent; thus, we got the graft P (UA-MMA) (W_2). Therefore, the left residue was the crosslinking P (UA-MMA) (W_3). Content of the graft and crosslinking copolymer is calculated according to the following equations respectively: Graft copolymer % = (W_2/W_1) × 100. Crosslinking copolymer % = W_3/W_1 × 100.

RESULTS AND DISCUSSION

Analysis of IR Spectra

To confirm that the PU-A seed has been prepared, that is, the copolymerization has happened between PU and HPA (2-hdroxypropyl acrylate), FTIR spectrometer was used to monitor the progress of the copolymerization. Figure 2 shows the FTIR spectra in the copolymerization process,

which is before, 10 min, and after 3 h of PU-A by adding the HPA monomer. The curve "a" is symbolized as a PU curve without any COOH group because HPA has not been added into the system; we can clearly observe the sharp and strong NCO peak around 2270 cm^{-1}. After adding the HPA monomer 10 min later, it can be seen that the NCO peak in the curve "b" decreases its strength; 3 h later, the NCO peak in the curve "c" is completely disappeared, indicating that the NCO group in PU has reacted with the OH group in HPA to form the —NH—COO— group, and the seed synthesis is completed. Therefore, it has been proven that we have successfully made the PU-A seed.

Relation of Conversion Time

The recipes of the seeded emulsion copolymerization of MMA onto the PU-A seed under the soap-free condition are presented in Table II. The effects of the initiator ($K_2S_2O_8$) and MMA amount on the copolymerization rate are shown in Figures 3 and 4, respectively. It can be observed that the copolymerization rate increases with increasing the initiator amount. When the initiator ($K_2S_2O_8$) is in the amount of 0.3 g, the conversion
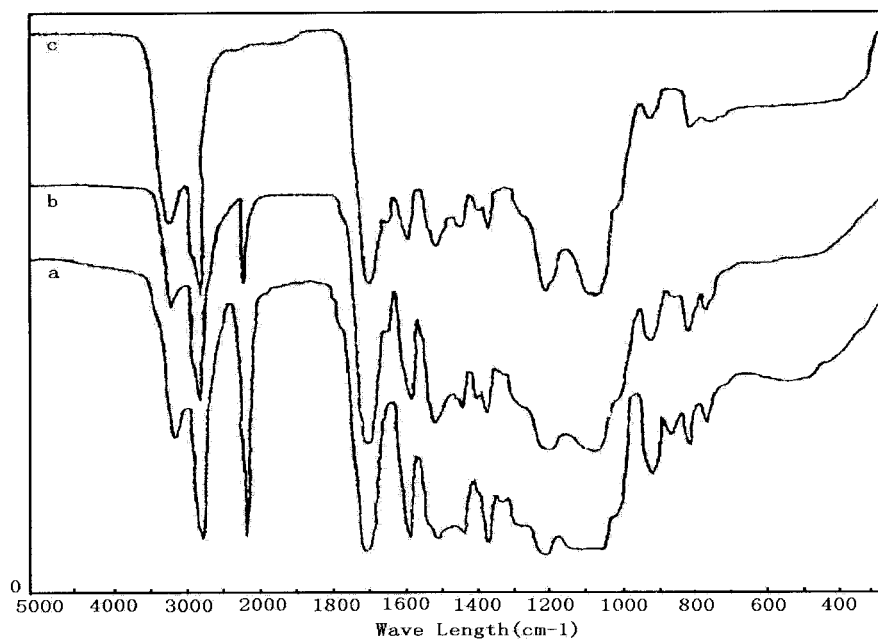
Figure 2   IR spectra of the PU-A seed during the copolymerization process of PU with HPA. (a) Before adding HPA; (b) 10 min after adding HPA; (c) 3 h after adding HPA.

of the seed emulsion copolymerizatin is nearly reached 100% after 4 h copolymerization. This is accord with the conventional polymerization theory.

From Figure 4 it can be seen that the polymerization rate increases with increasing the MMA monomer or the MMA/PU-A ratio. However, the MMA/PU-A ratio has a certain limit that it cannot be too larger, because if a large amount of MMA is added, it will make the emulsion particle size larger and decrease the emulsion stability.

Size and Distribution of P(UA-MMA) Particles

Because the stability and rheological properties of the latex are strongly influenced by the particle size and its distribution, whereas the COOH and —OH groups might affect the particle size largely due to their polar and hydrophilic effects, the

Table II   The Major Content in the Recipes[a] of Copolymerization of PU-A and MMA

Component	Weight (g)
PU-A emulsion	
(solid content 20%)	200
MMA	15, 30, 45, 60
$K_2S_2O_8$	0.075, 0.15, 0.225, 0.3

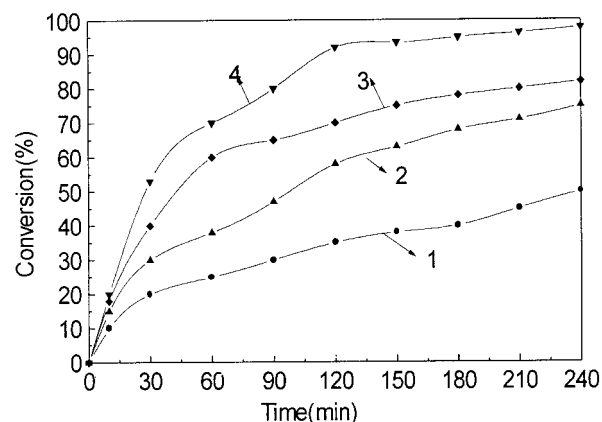[a] The detailed recipe is listed under the relative figure.

effects of DMPA, HPA, and MMA on the particle size of P(UA-MMA) latex are investigated. From Figure 5, it can be seen that with increasing the level of DMPA(based on PU level), which contains the COOH group, the P(UA-MMA) particle size decreases.

Figure 6 shows that with the content of HPA(based on the —NCO level) increasing, the P(UA-MMA) particle size only has a small decreases. Because HPA that contains OH group is an end-capping monomer when copolymerizing with
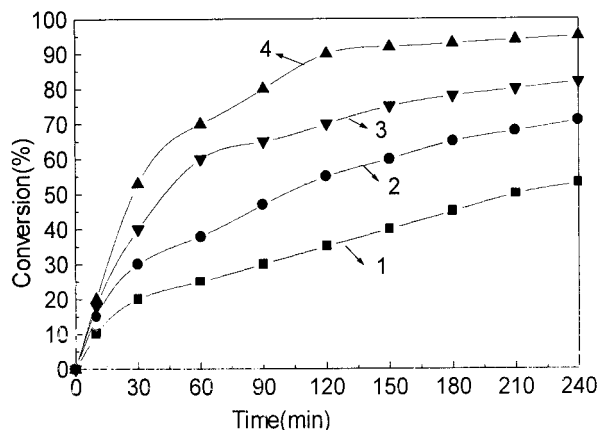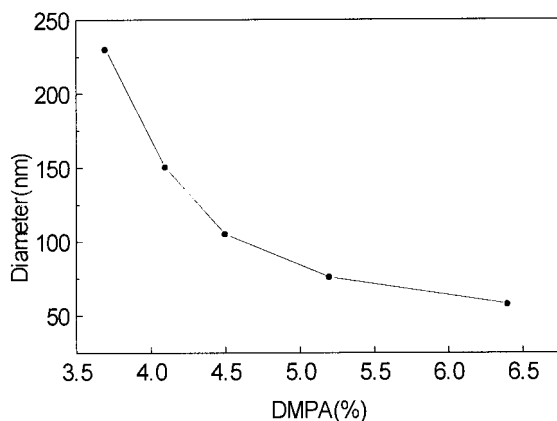

Figure 3   The effect of initiator $K_2S_2O_8$ on copolymerization rate: KPS (1) 0.075 g, (2) 0.15 g, (3) 0.225 g, (4) 0.3 g. [PU-A 200 g, DMPA, 5% PU(wt.), HPA 50%-NCO(mol), MMA 60 g; 80°C, 4 h].
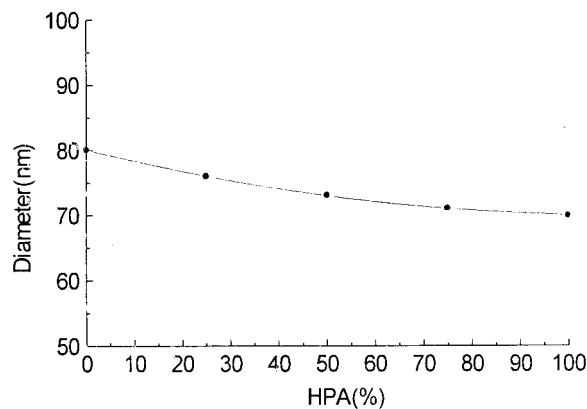
Figure 4 The effect of MMA on copolymerizaion rate: MMA (1) 15 g, (2) 30 g, (3) 45 g, (4) 60 g, [PU-A 200 g, DMPA 5% PU(wt.), HPA 50%-NCO(mol), KPS 0.3 g; 80°C, 4 h].

Figure 6 The effect of HPA content on particle size. [PU-A 200 g, DMPA 5% PU(wt.), MMA 60 g, KPS 0.3 g; 80°C, 4 h].

MMA, it is merely used as a crosslinking agent to lead to a small shrinkage of the particle volume, which may be the reason why HPA has a small effect on the P(UA-MMA) particle size.

The results (Fig. 7) exhibit that with MMA monomer increasing, the P(UA-MMA) particle size obviously increases, while its dispersity decreases. Because the numbers of the PU-A seed is constant, the MMA monomer is copolymerized mainly onto the seed; the more MMA monomer, the larger the P(UA-MMA) particle size is. Besides, during the swelling and copolymerization process of MMA onto the PU-A seed, there might have some repartition and mass balance among the different sizes of particles, which makes the particle size distribution become narrow. Because the emulsion copolymerization in this article was

carried out under no any other added emulsifier, the possibility of forming the pure PMMA particles is relatively small.

Graft and Crosslinking Copolymer

Because polymerization reaction between the PU-A seed and MMA are very complex, the composite polymers with different kinds of molecule structure can be obtained, such as the graft and the crosslinking of P(UA-MMA), PMMA homopolymer, as well as PU-A seed (see Fig. 1). From the results shown in Figures 8 and 9, it can be seen that with the MMA content increasing, the crosslinking polymer increases, but the graft ratio decreases.

Where with HPA content (based on —NCO level) increases, that is, the numbers of molecule containing double bonds in the PU-A seed in-

Figure 5 The effect of DMPA content on particle size. [PU-A 200 g, HPA 50%-NCO(mol), MMA 60 g, KPS 0.3 g; 80°C, 4 h].
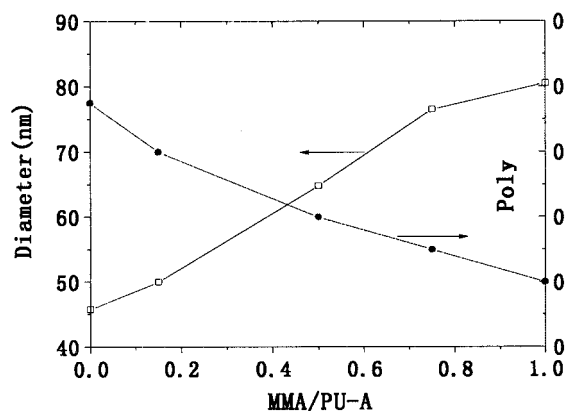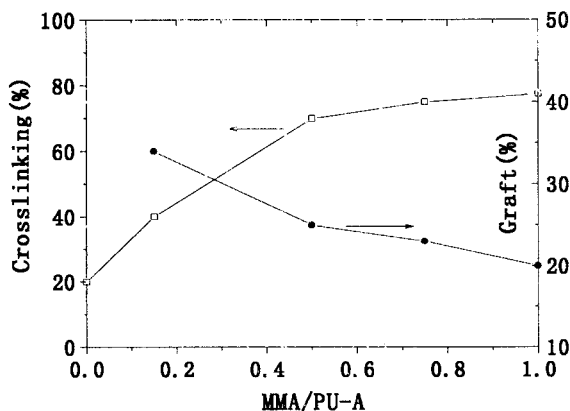

Figure 7 The effects of MMA/PU-A ratio on particle size and dispersity. [PU-A 200 g, DMPA 5% PU(wt.), HPA 50%-NCO(mol), KPS 0.3 g; 80°C, 4 h].
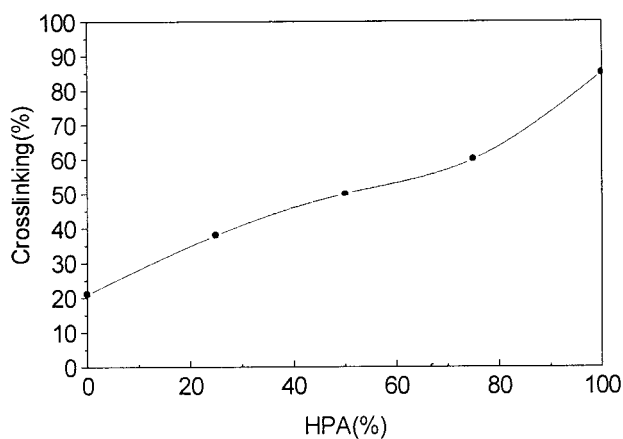
Figure 8 The effect of MMA content on crosslinking and graft ratio. [PU-A 200 g, DMPA 5% PU(wt.), HPA 50%-NCO (mol), KPS 0.3 g; 80°C, 4 h].

creases, the amount of the crosslinking agent increases, where it can be expected that the crosslinking copolymer is increased. Hence, we can take advantage of HPA to adjust the amount of it to obtain the different latexes with variable properties to be used in the suitable places.

Mechanical Properties of the Cast Film

The stress–strain curves of the P(UA-MMA) cast films with the different contents of DMPA and HPA are shown in Figures 10 and 11. It is found that with the DMPA content increasing within the range of 4.5–6.4%, the stress of the cast films increase. This is probably because higher amounts of DMPA produce the smaller latex particles (Fig. 5), which are packed closely to form better quality cast film, and have the higher tensile strength. In Figure 11,


Figure 9 The effect of HPA content on crosslinking ratio. [PU-A 200 g, DMPA 5% PU(wt.), MMA 40 g, KPS 0.3 g; 80°C, 4 h].
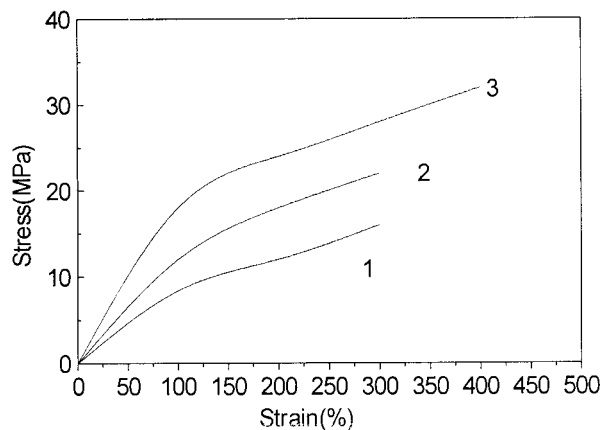

Figure 10 Stress–strain curve with different contents of DMPA: (1) 4.5%; (2) 5.2%; (3) 6.4% (based on PU level) [PU-A 200 g, HPA 50% —NCO(mol), MMA 40 g, KPS 0.3 g; 80°C, 4 h].

when the HPA content increases from 0.01 to 0.04 mol, the tensile strength of the P(UA-MMA) latex cast film increases, but the elongation at break decreases duo to HPA's crosslinking effect, so the HPA content cannot be too large; otherwise, the cast film may become brittle.

The effect of MMA content on the mechanical properties is shown in Figure 12. It is evident that when the MMA/PU-A ratio is below 80%, the tensile strength of the cast film increases with MMA increasing; when the MMA/PU-A ratio is over than 80%, the tensile strength decreases with increasing the MMA content, whereas the elongation at break of the cast film decreases all the process with increasing the MMA/PU-A ratio. The
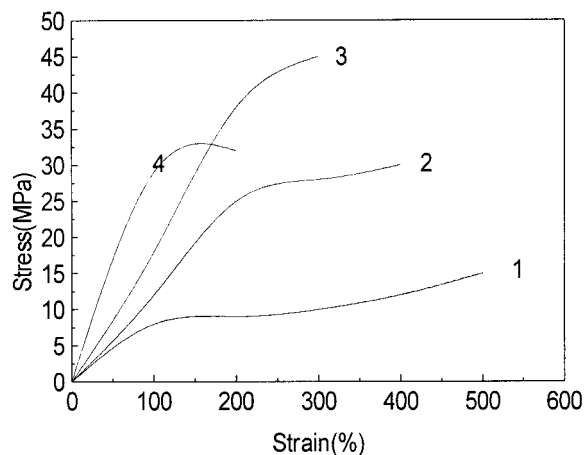
Figure 11 Stress–strain curves of the films with different content of HPA: (1) 0.01 mol; (2) 0.02 mol; (3) 0.03 mol; (4) 0.04 mol. [PU-A 200 g, DMPA 5% PU(wt.), MMA 40 g, KPS 0.3 g; 80°C, 4 h].
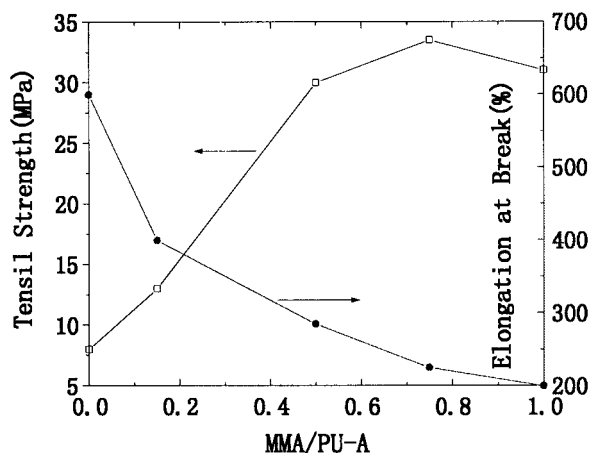
Figure 12 The effects of MMA/PU-A ratio on mechanical properties of the cast films [PU-A 200 g, DMPA 5% PU (wt.), HPA 50% —NCO(mol), KPS 0.3 g; 80°C, 4 h].

reason is that MMA belongs to a hard segment that would increase the rigidity and strength and reduce the toughness of the copolymer. When the MMA content is more than a certain value, such as 80% in this article, it will even reduce the strength of the copolymer, so it is necessary to control the amount of MMA used.

CONCLUSIONS

The PU-A seed containing the double bond and COOH group were synthesized by the two-step method, and this reaction was confirmed by IR spectra. The seeded emulsion copolymerization of MMA onto the PU-A seed was successfully conducted under the soap-free condition. These kinds of emulsions are expected to be useful in the binding, sealing, and coating industry, as the interface weak effect resulted from the emulsifiers having a lower molecular weight has been avoided. Also, the PU-A/MMA composite latex can be expected to be useful in the plastics industry as a compatibilizer.

In accord with the polymerization theory, increasing the initiator KPS and MMA monomer levels leads to the increasing of the conversion and polymerization rate. And in a certain amounts of KPS and MMA, the conversion can be as large as over 90%. Considering the emulsion stability and other factors, the MMA content must be limited under a certain scope.

Due to containing the different functional groups in their molecular chains, the different acrylate monomers used in this article have the different effects on the composite latex. DMPA (containing the —OH group) and HPA (containing the —COOH group) decrease the particle size and the elongation at break, and increase the tensile strength of the composite latex when their contents increase, whereas MMA increases the particle size and the tensile strength and decreases the elongation at break. With the crosslinking agent HPA and MMA monomer increase, the crosslinking copolymer in the P(UA-MMA) latex increase, but increasing MMA leads to the graft ratio decrease.

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