Effects of Carboxyl Group on the Ambient Self-Crosslinkable Polyacrylate Latices

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ABSTRACT: Ambient curable carbonyl functional acrylic latices were synthesized by incorporating diacetone acrylamide as functional monomer into acrylic copolymer, adipic acid dihydrazide (ADH) was used as curing agent. In this work acrylic acid (AA) and acrylic acid homopolymer (PAA) were used to facilitate the crosslinking reaction. We found that the properties of latex film were different when use AA and PAA as the source of the carboxyl groups separately. The results from the characterization of carboxyl groups of the latex particles demonstrated that the distribution of the carboxyl group on the latex particle surface is optimal for the crosslinking reaction. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 3948–3953, 2007

Key words: ambient self-cross-linking; acrylic acid; emulsion polymerization; polyacrylate latex

INTRODUCTION

Since ambient self-curable latex can get crosslinked at room temperature and do not need additional crosslinker to be added before use, this kind of latex is of great interest for coatings, adhesives, and elastomers.[1] However they must meet some requirements: functional groups bounded on the polymer must be stable during emulsion polymerization and storage period, and have sufficient reactivity during film formation under ambient conditions. Several ambient crosslinking reaction systems based on the following functional monomers and cure agents have been studied by now: (1) siloxane,[2] (2) glycydle (meth) acrylate and acrylic acid,[3] (3) acetoacetoxyethyl methacylate (AAEMA) and diamine,[4,5] (4) dimethyl *meta*-isopropenyl benzyl isocyanine (TMI) and methyl acrylic acid,[6] (5) TMI and amnio-telechelic polybutadiene,[7–9] (6) N-(4,4-Diethoxy-butyl) methacrylamide (MABEA) under acidic conditions,[10] (7) chloromethylstyrene (CMS)-functionalized polymer and a tertiary-amine- functionalized polymer,[11] (8) polymer incorporated diacetone acrylamide and dihydrazide.[12]

The reaction between the carbonyl group and hydrazine proceeds rapidly at ambient temperature in acidic conditions.[12] The self-cross-linking system of diacetone acrylamide (DAAM) as the functional monomer containing carbonyl group has been studied extensively. Nakayama[13] studied the effect of solution of the carbohydrazide as the film-penetrative crosslinker to cure the latex film containing DAAM. They found that the content of organic solvent, cure temperature and acid amount in the carbohydrazide solution affect the crosslinking reaction remarkably. Hasegawa and Yoshino[14] prepared polyacrylate (incorporated DAAM) and polyurethane (terminated with ADH) latices to get urethane/acrylic composite polymer latex through the reaction between carbonyl group and carbohydrazide. Kan et al.[15] observed the morphologies of the p (Styrene-butyl acrylate-acrylic acid -DAAM) latex particles and studied the effects of different preparation methods of the latices and the DAAM amount used in the emulsion polymerization on the morphologies of the latices particles. Zhang et al.[16] prepared ambient crosslinkable latex using DAAM as functional monomer in soap-free emulsion polymerization, microemulsion polymerization and traditional emulsion polymerization respectively, and studied effect of different preparation methods on the latex properties.

Acid condition is indispensable for the crosslinking reaction between diacetone acrylamide and adipic acid dihydrazide. Acrylic acid is usually incorporated into copolymer to give an acid condition to facilitate the crosslinking reaction. In our present work, attention was focus on the effect of different introduction styles of the carboxyl group on the crosslinking reaction. In carboxylated latex

the carboxylic acid group may be available distributed in three forms: (a) in acrylic acid homopolymer, free in water phase and adsorbed on the particle surface; (b) in copolymer, bounded on the particle surface; (c) in copolymer, buried in the particle. As we know there is less reports on the effect of the carboxyl group distribution styles on the crosslinking reaction between active carbonyl group and dihydrazide. In this work acrylic acid and acrylic acid homopolymer were used as sources of the carboxyl group separately to achieve an understanding of the role of different forms of carboxyl groups in the crosslinking reaction. The preparation and characterization for acrylate-DAAM copolymer latices was discussed, in particular different introduction styles of carboxyl groups.

EXPERIMENTAL

Materials

AEROSOL 501 (35% aqueous solution of disodium isodecyl sulfosuccinate) was purchased from Special Chemical Reagent Company (Shanghai, China). Methyl methacrylate (MMA), n-butyl acrylate (BA) and (meth) acrylic acid were purchased from Tianjin Chemical Reagent Factory (Tianjin, China), analytical reagents and the inhibitor was removed by vacuum distillation before use. Ammonium persulfate (APS) was recrystallized using deionized water. Ddiacetone acrylamide (DAAM) (98%), adipic acid dihydrazide (ADH) (98%) (Chemidea Chemical R and D Co., Shandong China) used as received. Anionic (001 × 1) and cationic (201 × 4) exchange resins were supported by Nankai University Chemical Factory (Tianjin, China). De-ionized water was purchased from Nankai University Chemical Factory.

Latex preparation

The emulsion copolymerization was carried out in a 500 mL four-necked glass reactor equipped with stirrer, thermometer, dropping channel and nitrogen gas inlet. Comonomers (containing MMA,BA,AA, DAAM) were mixed in a 100 mL beaker and the emulsifier A-501 was dissolved in 80 mL de-ionized water. Ten gram of the mixed monomers and all the emulsifier solution were charged into the reactor and stirred at 400 rpm for 30 min at 45°C under bubbled N_2. Then the temperature was elevated and kept at 75°C and APS was added into the reactor. After the latex became faint blue, the left mixed monomers was added into the flask drop by drop in 5 h. The reaction was kept for additional 3 h under 75°C. Finally the latex was cool down below 35°C and pH value was adjusted to about 8 with ammonia and then added the curing agent ADH. Stirring for another 20 min and the final latex was obtained.

TABLE I
Recipes for Emulsion Polymerizations

	Runs					
	1	2	3	4	5	6
AA (wt %)	0	0.5	1.0	1.5	2.0	0
PAA (wt%)	0	0	0	0	0	1.5

Other reagents kept constant: MMA, 35.37 g, BA, 34.64 g, DAAM 2.22 g, ADH 1.14 g, H_2O 80 g, $(NH_4)_2S_2O_8$ 0.37 g, A-501 0.74 g

The recipes for emulsion polymerizations were shown in Table I.

Purity of latex

Anionic (001 × 1) and cationic (201 × 4) exchange resins were conditioned using 0.1 mol/L HCl and 0.1 mol/L NaOH aqueous solution alternately. Finally the resins were washed to an unchanged conductance value with de-ionized water. Latex was cleaned use the method that reported by Vander Hoff.[17] The original latex was diluted out to2.8 wt % with de-ionized water. Ten gram wet Anionic (001 × 1) and cationic (201 × 4) exchange resins were added to 100 mL diluted latex and stirring for 24 h and the cleaned latex was obtained.

Film formation

The lattices were cast on plate glass molds at and dried at room temperature for 7 days. The obtained dried films in thickness of 0.4–0.6 mm were further dried in the vacuum oven for additional 3 days at room temperature.

Characterization

The measurement of transmission electron microscopy (TEM) was performed on a Jeol TEM-100 (Japan). Before TEM measurement, the latex samples were diluted to 2 wt % solid content with deionized water. Then a drop of latex was placed onto the copper grill covered with carbon membrane and dried by IR lamp.

The latex viscosity was determined by RHEO-TEST-2 viscosimeter (Germany). The tested latex volume was 25 mL and the testing temperature was at (25 ± 0.5)°C.

The distribution of carboxyl groups on the surface of particles was determined by conductimetric alkali (NaOH)/acid (HCl)-back titration for the previously cleaned latex. The conductimetric titration was carried out under a N_2 atmosphere at 25°C. Excess alkali was added to adjust the pH value to about 11 and kept for 10 min before titration for the full neutralization of the carboxyl groups on the particle surface.

In water absorption test, latex films which had been dried for 72 h in vacuum at room-temperature
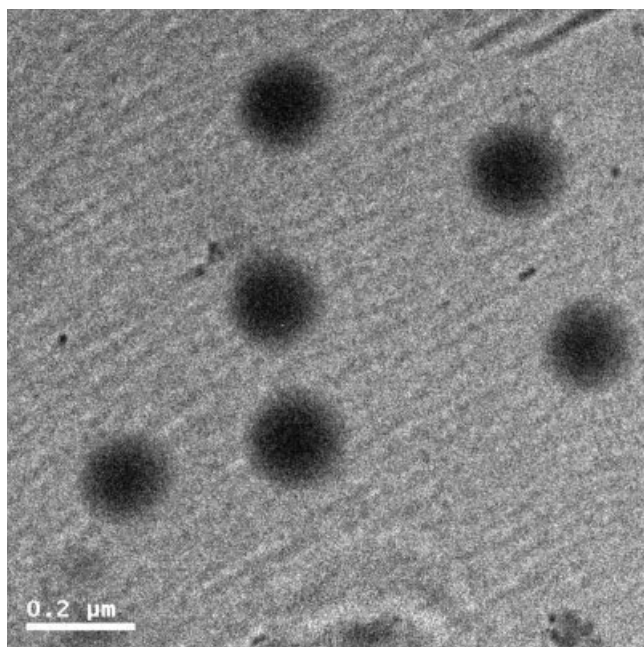
Figure 1 TEM micrograph of latex particles (Run 4).

were immersed in deionized water at 25°C. The films were weighed for every 24 h. The water absorption ratio (R) was obtained from the difference of the weights of the film before (W_0) and after water immersion (W_1), $R = [(W_1) - (W_0)]/(W_0)$.

The swelling test was performed by placing dried latex films in tetrahydrofuran at room temperature for 24 h. The swelling ratios of films were calculated as W_s/W_0, W_0, and W_s are the weight of the film before and after being swollen respectively.

Stress/strain tests were done on Testometric M500-25kN universal material tester (UK) at a tension rate of 20 mm/min at 23°C.

RESULTS AND DISCUSSION

Latex preparation

Latices containing 0–2 wt % AA (based on monomers) were prepared. There was almost not coagulation during emulsion polymerization and more than 98% conversion was obtained. These latices stored stably for 6 months at ambient and no coagulation was observed. All the latex samples have similar morphology, typically the morphology of the latex particle of Run 4 (contain AA 1.5 wt % and DAAM 3 wt %) was shown in the Figure 1. From Figure 1, it can be seen that the latex particle size distribution is homogeneous and the mean particle diameter is about 180 nm (statistical sample content was 100). The variation of the latex viscosity and AA content is shown in Figure 2. Figure 2 shows that the latex viscosity increased with the increase of AA amount

but the relationship is not linear, that is, there is a turning point at which the AA content is between 1.5 and 2% and after this point the viscosity of the latex increase rapidly. This phenomenon indicates that a lot of AA homopolymer formed during the copolymerization with the increase of AA amount and PAA dissolved in water act as a thickener after neutralization with ammonia in the final latex.

Carboxyl group distribution

The amount of carboxyl groups on the surface of the latex particles was tested by conductimetric titration of latex. DAAM is a hydrophilic monomer and has a trend to distribute on the surface of the latex particles. And since ADH cannot penetrate into the polymer particle to react with the carbonyl group buried in the latex particle without the help of organic solvent,[12] the reaction between carbonyl and hydrazine is an intraparticle surface reaction. The interactions between hydrazine and carbonyl residues on the surface of latex particles were illustrate in Scheme 1. Thus the surface carboxyl group bounded on the latex particle surface is very important. The conductimetric titration result was shown in the Figure 3. Figure 3 shows that the first stage represents the titration of excess alkali with HCl. The negative slope arises from the great loss of mobility from the consumption of OH$^-$ ions despite of the gain in conductance from less mobile chloride ions. The second stage involves the neutralization of ''surface bound'' acid radical by HCl. The third stage represents an increase of conductance from excess HCl.[18] From the curve we got the carboxyl group percentage on the surface is 22.8 mol % (to the whole AA) through the HCl volume used in stage two with the following function, $P_c = \frac{V_{HCl}*C_{HCl}*M_{AA}}{w_{latex}*S*W_{AA}}$,, P_c is
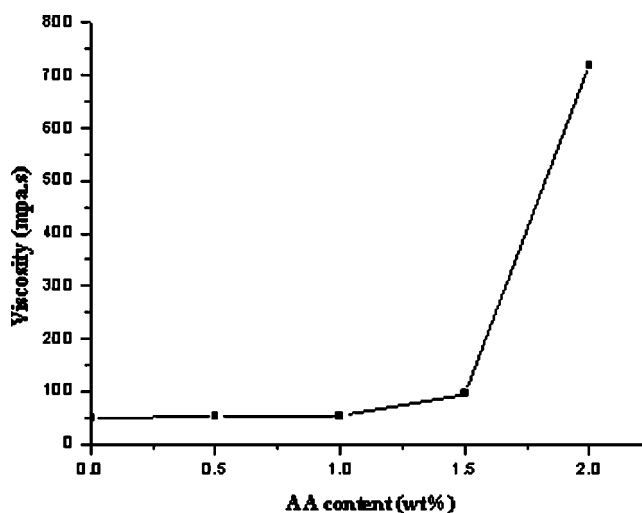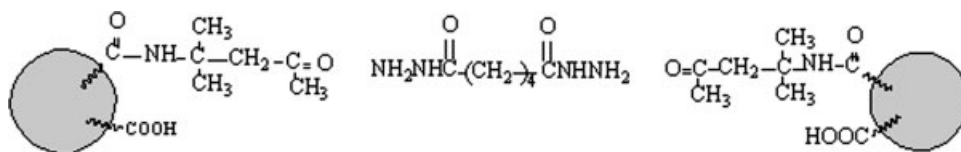

Figure 2 The relationship curve of latex viscosity and AA content.

Scheme 1 The interaction illustration between hydrazine and carbonyl residues on the surface of latex particles.

the mole fraction of carboxyl group on the particle surface, V_{Hcl} is HCl aqueous solution volume used in the stage two, C_{Hcl} is the mole concentration of HCl solution, M_{AA} is the molecular weight of AA, w_{latex} is latex weight used in the titration, S is the latex solid content, W_{AA} is AA percentage by weight used in the copolymerization.

Stress/strain behaviors of cured films

The stress-strain curves for samples with different addition amount of AA were shown in Figure 4. At the higher AA content, the yield stress and tensile strength increased, as compared with the blank sample (Run 1), however, the ultimate strain at fracture decreased somewhat. This indicates that an increase in the crosslinking density makes the polymer stronger and more rigid. Figure 4 also shows that the rate of tensile strength development decreased with the AA amount increased. There is no remarkable difference between 1.5 and 2 wt % AA amount relative to other samples, so a much higher AA amount is not required for significantly improving the mechanical properties. In the fact a higher amount may result in a more hydrophilic latex film.

To understand the role of different carboxyl group introduced styles, we compared tensile behaviors of the AA copolymerized latex films and PAA post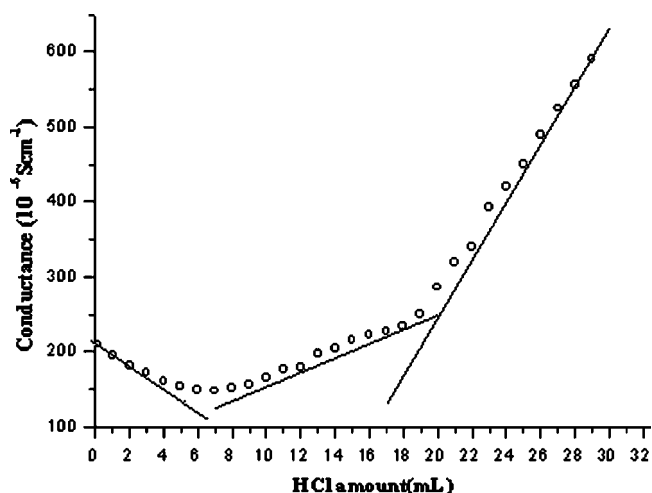 added latex film, both containing the same amount carboxyl group (1.5 wt % weight to all monomers). Figure 5 is the tensile behavior of the latex films with different carboxyl group introduced styles. Figure 5 shows that the latex film incorporated AA by copolymerization obviously has a higher yield stress and tensile strength than the latex film with PAA post added despite PAA also enhanced yield stress and tensile strength of the latex film at some extent. But both AA copolymerized and PAA post added latex films have less elongation at break than the blank sample (Run 1). The reaction between carbonyl and hydrazine is an interfacial reaction. It is easy to understand the tensile test result combining the conductimetric titration result, that the carboxyl group on the latex particle surface can improve the miscibility between the ADH and polymer latex particle surface, make ADH react with carbonyl group readily. For the PAA post added latex, the reason of improvement of the mechanical properties may be that the added PAA gave an acid condition and partial PAA absorbed on the latex particle also improve the miscibility between ADH and latex particle surface, then also facilitated the crosslinking reaction.

Water absorption ratio

The water absorption ratio is sensitive to the changes in the polarity and crosslinking density of polymeric material. The results for water absorption of the
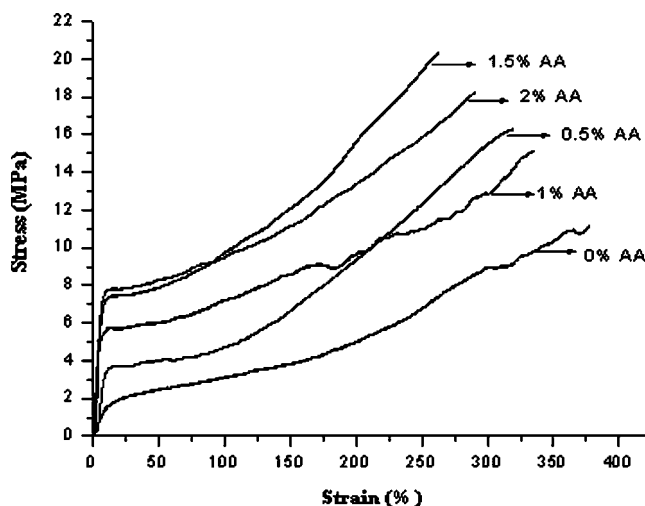

Figure 3 Conductimetric titration curve of 1.5 wt % AA copolymerized latex purified with the mixed-bed ion exchange resin. Total time contact with resin: 24 h.

Figure 4 The stress-strain behaviors of the latex films with different AA content.

Figure 5 Latex film stress-stain behaviors of different introduction style of carboxyl group.

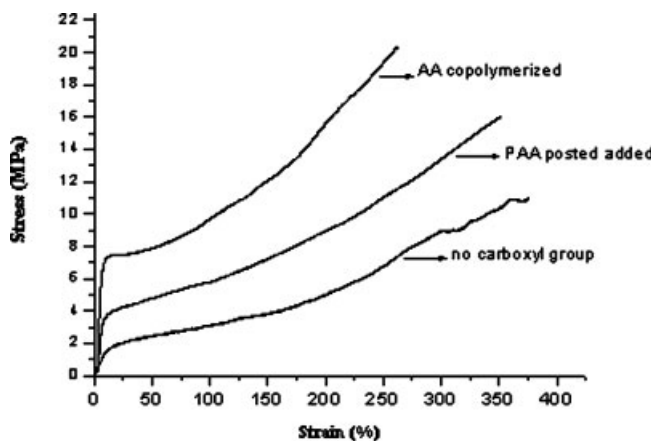**Figure 7** The variations of water absorption ratios of the latex films with the different introduction style of carboxyl group.

latex films with different AA content were shown in the Figure 6. From Figure 6 it can be seen that the water absorption of blank sample is the lowest in all the latex film in the first day. This is due to it is a more hydrophobic composition than the others samples. When the amount of AA was 0.5 wt %, the water absorption is higher than the blank sample for the former 10 days, but lower after 10 days. This can be attributed to the formation of a more hydrophilic and lower crosslinking density film. When the AA content reached 1 and 1.5%, the water absorptions were obviously lower than blank sample. From Comparing the Figure 4 and the Figure 6, the Run 4(1.5 wt % AA) and Run 5(2 wt % AA) have almost the same stress/strain behavior and water absorption ratio. It demonstrated that the crosslinking density enhanced with the AA content increased, but
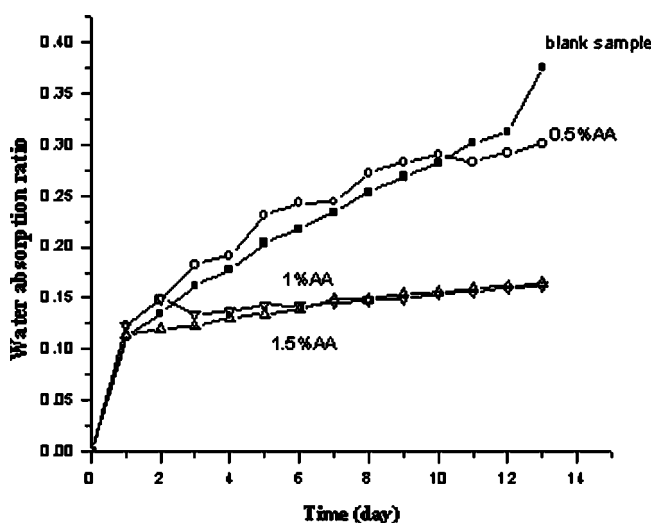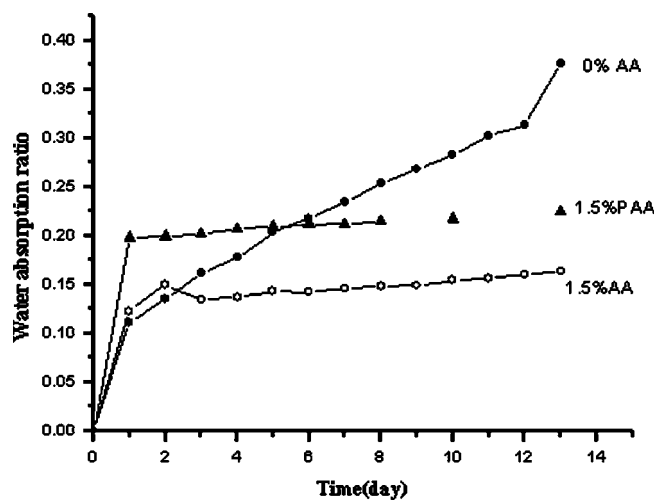
there is an optimal AA content for good water-resistance and mechanical properties.

The water absorption ratios of the latex films with carboxyl groups from different introduction styles were shown in Figure 7. It can be seen that compared with the blank sample the water absorption of the latex films containing carboxyl groups show a faster growth at first days. But the crosslinking density is the dominant factor on the water absorption at last. AA copolymerized latex film exhibit better water resistance property than the PAA post added latex film. This result is consistent with the tensile test that the location of the carboxyl group on the particle surface is optimal for the crosslinking reaction and gives a higher crosslinking density.

Solvent test

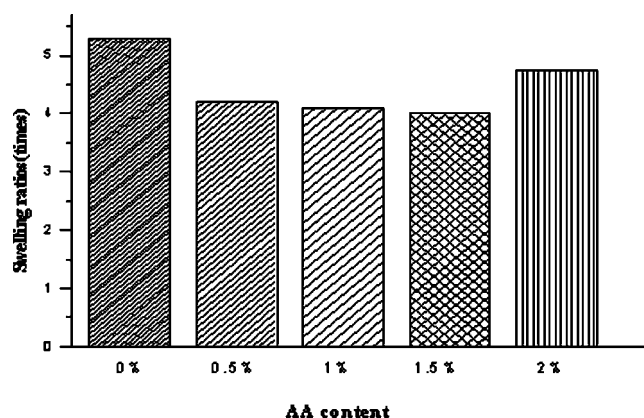Swelling ratios of the latex film with different AA content were shown in the Figure 8. Figure 8 shows

Figure 6 The relationships of water absorption ratios with AA content.

Figure 8 Solvent swelling ratios of the latex films with different AA content.
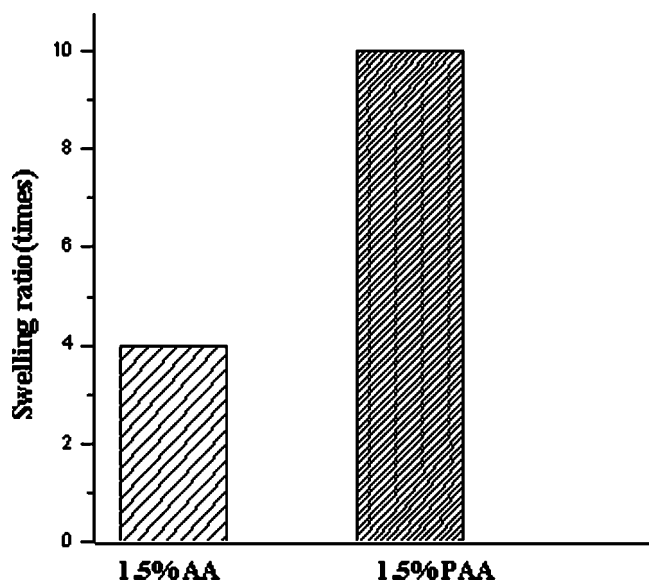
Figure 9 Solvent swelling ratios of the latex films with different introduction style of carboxyl group.

that the swelling ratio of latex films decreased with the increase of AA content when the AA content is not more than 1.5 wt %. When AA content reached 2 wt % the swelling ratio is higher than all the latex films except the blank sample. It can be considered that the development rate of the crosslinking density decreased when the AA content is more than 1.5 wt %. The latex film of Run 1 that no AA copolymerized was only swelled not dissolved; this may be due to the slight crosslinking reaction occurred even at the absence of AA. But the crosslinking density is far lower than the others latex films.

Swelling ratios of the latex films with different introduction style of carboxyl groups were shown in the Figure 9. From Figure 9 shows that the swelling ratios of the latex film of different carboxyl group introduction styles have marked differences. Swelling ratio of the latex film incorporating carboxyl group by copolymerized obviously less than the latex film incorporating carboxyl group by the post added method. This result is consistent with relevant result of tensile test and water absorption test that

AA copolymerized latex films have a higher crosslinking density than the PAA post added latex film.

CONCLUSIONS

Ambient crosslinkable acrylic polymer latices were prepared with different introduction styles of carboxyl group. AA and PAA were used as donors of the carboxyl groups, which is indispensable to the crosslinking reaction. It was found that AA naturally copolymerized latex film has better properties in tensile strength, solvent resistance and water resistance than the PAA post added latex system. Combine the result of Conductometric titration and the others test the conclusion can be made that the carboxyl groups distributed on the particle surface is optimal for facilitating the reaction between ADH and DAAM.

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