Rheological and Curing Behavior of Aqueous Ambient Self-Crosslinkable Polyacrylate Emulsion

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ABSTRACT: An aqueous ambient crosslinkable polymer acrylic (AACPA) emulsion was obtained by adding adipic acid dihydrazide (ADH) to the polyacrylate emulsion incorporating diacetone acrylamide (DAAM), and this emulsion was synthesized by two feeding materials methods. The AACPA emulsion and its paint film were characterized with rheological measurements, laser light scattering, Fourier transform infrared, torsional braid analysis (TBA), DTA, and so on. The results showed that AACPA emulsion was pseudoplastic fluid and pseudoplasticity increased with increasing of DAAM content. The results also showed that water resistance, solvent resistance, and thermotacky temperature of AACPA paint film increased with increasing of the content of DAAM. The results dealing with curing behavior of the paint film showed that adding organic swelling solvent and organic acid to the AACPA emulsion can accelerate the curing speed of the paint film. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 1448–1455, 2007

Key words: ambient crosslinkable emulsion; diacetone acrylamide; rheological behavior; curing behavior

INTRODUCTION

Aqueous acrylic polymer emulsion, which is the main component of industrial paint, has shown a number of properties, such as good film-forming property, resistance to chemicals, water, weather, and friendly environment property, lending them to a variety of industrial application. However, main disadvantages of the latex paint are poor solvent resistance, the surface tackiness at high surrounding temperature, and brittleness at low temperature caused by the thermoplastic nature of uncrosslinked latex resins; physical properties of films obtained from latex are usually susceptible to the surrounding temperature. To overcome these drawbacks, various crosslinking methods of latex paints were developed. It is well known that a carbonyl group can react readily with a hydrazide group at ambient temperature. It is a recent tendency that this reaction is applied for development of water-borne coating. For many years, a great many works in this field have focused on the novel copolymers containing diacetone acrylamide (DAAM) as functional monomer and adipic acid dihydrazide (ADH) as crosslinker. These copolymers have been synthesized by adding ADH to the polyacrylate emulsion incorporating DAAM. The most striking feature of this crosslinking reaction is that they are able to cure at ambient temperatures. Compared with uncrosslinked latex resins, the crosslinkable polyacrylate latex paint has denser surface network, higher tensile strength, better solvent and stain resistance, and has application in architectural coatings,[1,2] wood coatings,[3] water-repellent coatings,[4] ink,[5,6] hide finishes.[7]

It was reported[8] newly that this novel emulsion plays an important role for application in aqueous crosslinkable adhesives cured at ambient temperature, because it does not release formaldehyde or volatile organic solvents.

Rheological behavior is an important property of emulsion, however, this property of emulsion containing different DAAM content was not described up to now. In this article, the relationship between DAAM content and rheological behavior was investigated.

One of the interesting concerns in this study was how to accelerate the curing speed. Minimization of the energy in this industry is the most important, because enormous energy is consumed by high temperature curing. Nakauama[9–11] has studied and characterized the penetrating curing method with the two components, but the two-component method is not convenient in practice. In this article, we added film-penetrative agent directly to AACPA emulsion, namely one-component method, and characterized this emulsion. The results showed that the curing was sped up with the penetrating organic solvent and additional acids in the reaction system.

EXPERIMENTAL

Materials

Methylmethacrylate (MMA), butylacrylate (BA), and acrylic acid (AA) were purchased from Beijing East
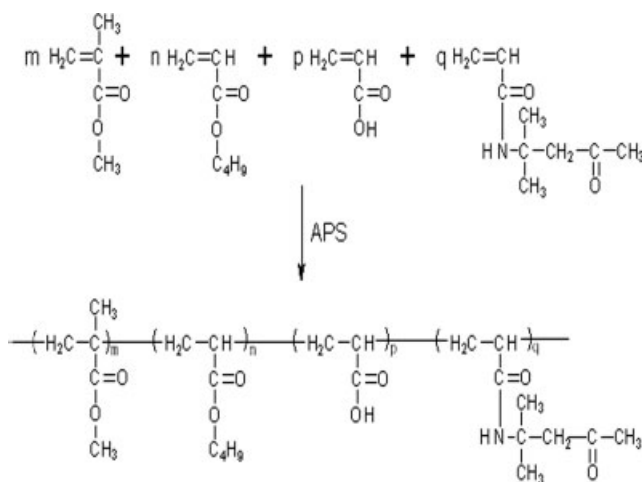
Scheme 1 Synthesis of DAAM copolymer.

Chemical Industry Factory; diacetone acrylamide (DAAM) and adipic acid dihydrazide (ADH) were supplied by Hangzhou Xinghua Chemical Ltd., Co.; polyoxyethylated octylphenol (OP-10) came from Henkel International (Germany). All of these chemicals were of industrial grade. Ammonium persulfate (APS), sodium dodecylsulfate (SDS), ethylene glycol monobutyl ether (EGBE), diacetone alcohol, n-Butanol (n-BuOH), propylene glycol monomethyl ether (PGME), ammonium hydroxide (NH$_4$OH), and acetic acid, all of these reagents were of analytical grade, supplied by Beijing Chemical Plant.

Preparation of emulsion

The emulsion was prepared by seeded-emulsion polymerization.

Preparation of seeded latex particles

30-mL MMA, 30-mL BA, 2-mL AA, 3-g OP-10, 2.5-g SDS and 60-mL H$_2$O were added to a 500-mL three-neck flask, equipped with a stirrer, a condenser, and a centigrade thermometer, and submerged in a carefully controlled water bath at 52°C. The mixture was stirred at the rate of 600 rpm and preemulsified for about 10 min, then 1/4 preemulsion was heated to 72°C in the flask and 1/2 initiator solution (SPA 0.8 g in 8-mL H$_2$0) introduced into the reaction vessel, the blend was approximately reacted for 30 min, here a slight blue-color appeared in the reaction system, and seed latex particles were obtained.

Seeded-emulsion polymerization

Preparation of the core-emulsion. Another 3/4 preemulsion was fed continuously using the dropping funnel into the seed particles and finish in 1 h. In this polymerization process, 1-mL APS solution was added every 0.5 h, and the polymerization temperature was kept at 72°C.

Preparation of the shell-emulsion. Polymerization was carried out at 72°C, 1-mL APS was dropped into the flask at the beginning, after that 3-mL APS was added every 0.5 h. The recipe is: 35-mL MMA, 35-mL BA, 2.5-mL AA, DAAM, variable, 2-mL APS, 60-mL H$_2$O, 2-g OP-10, and 1-g SDS. Two different feeding methods of monomer were used.

1. Preemulsion method of shell monomers: In this method, the method of adding the monomer was the same as in the preparation of seed latex.
2. No preemulsion method of shell monomers: surfactants OP-10 and SDS were dissolved in distilled water and added to the seed particles at the beginning, after that, the mixtures of monomers were fed continuously into core-emulsion for 1 h.

After dropping, the system was kept at 72°C for another 2 h, then, heated up to 80°C and maintained at this temperature for 1 h. At last, 10% crosslinker solution was introduced into the system and stirred for 30 min, at last neutralized with aqueous ammonium.

Finally, a kind of white fluid polyacrylate (AACPA) emulsion was obtained. The synthesis route is shown in Schemes 1 and 2. Table I shown different samples' condition obtained in my laboratory.

Characterization

1. The solid content was obtained by weighing the emulsion on an electronic balance before and after the emulsions were dried at 120°C for constant weight. The solid content was calculated by the following equation:

The solid content % $= (m_2 - m_0)/(m_1 - m_0)$

where m_0 is the weight of the vessel, m_1 is the weight of the emulsion and the vessel, and m_2 is
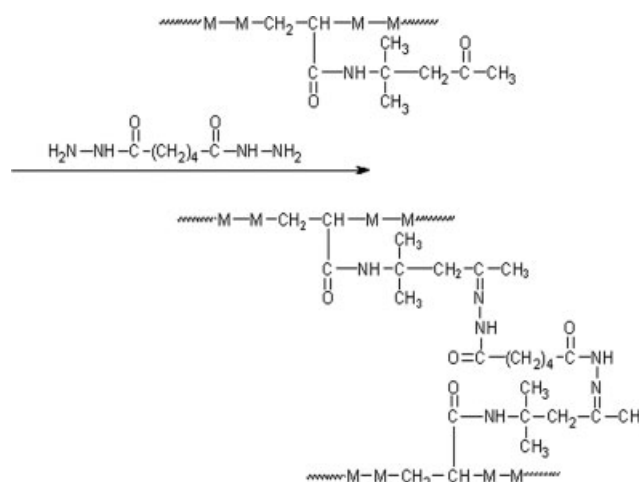
Scheme 2 Crosslinking reaction between DAAM copolymer and ADH.

TABLE I
Data for Seeded-Emulsion Polymerization

Sample	DAAM Content (%)	Shell-monomer disposal method
A	2.4	No preemulsion
B	3.2	No preemulsion
C	4.0	No preemulsion
D	2.4	Preemulsion
E	7.0	No preemulsion

TABLE II
Component of the Emulsion Used for TBA Experiment

Sample	Component of the emulsion
1	Sample E
2	E + EGBE + PGME
3	E + diacetone alcohol + PGME
4	E+ n-BuOH + PGME
5	E + EGBE + PGME + acetic acid
6	E + diacetone alcohol + PGME + acetic acid
7	E + n-BuOH + PGME + acetic acid

the weight of the vessel and dried emulsion. The solid contents of emulsion came out to be about 43%.

2. The particle size and particle size distribution (PSD) of AACPA emulsions were measured using laser scattering (Master Sizer-2000 of Malvern instruments of Worcester, UK).
3. The viscosities of AACPA emulsion were measured with a NXS-II rotational viscometer after the solid contents of emulsion were adjusted to equalize using distilled water.
4. Fourier-transform infrared spectra was obtained with a FTIR670 spectrometer. Sample A was coated on the PTFE disk and dried for 7 days at ambient temperature.
5. Methods for measurement of degree of swelling: Resin samples A, B, and C were laid on PTFE plate and dried for 7 days at ambient temperature, thickness of dried film was about 0.5 mm, these films were dipped respectively, in water and toluene for 24 h, afterwards, take them out, droplets of liquor remaining on the film surface were wiped with a filter paper, the weight of swelled film (B) was measured immediately. Swelling degree was calculated by the following equation.

$$\text{Swelling } \% = [(B - A)/A] \times 100\%$$

where A is the weight of the dried film and B is the weight of the swelled film.

6. The thermotacky temperature of the dried film was measured according to standard GB/1762-(89), China.
7. The test of torsional braid analysis (TBA): A GDP-2 polymer material dynamic TBA apparatus, made in Jilin University, China, was employed. Glass fiber braids that had been impregnated with the emulsion shown in Table II, and dried at ambient temperature for 30 min were mounted in the TBA apparatus under room-temperature condition. Curing data were recoded every 1 h.
8. The curing temperature was tested by DTA (CDR-1, Shanghai Balance Apparatus Plant) after

a wet coating film left for 5 h. Samples were heated with heating rate of 10°C/min in N_2 atmosphere.

RESULTS AND DISCUSSION

The particle size and particle size distribution of AACPA emulsion

The particle size and PSD of samples A, C, and D are shown in Figure 1. Because the emulsions exhibited a skewed distribution function, the log normal distribution was used for describing the particle size of emulsion. On the basis of the log normal distribution, the geometric mean diameter (d_g) was calculated according to eq. (1)[12]

$$d_g = \exp\left[\sum (n_i \ln d_i)/N\right] \quad (1)$$

where n_i is the number of particles in group i, having a midpoint of size d_i, and where $N = \Sigma n_i$, that is the total number of particles.

Particle size distribution breadth (B) was calculated according to eq. (2)[13]

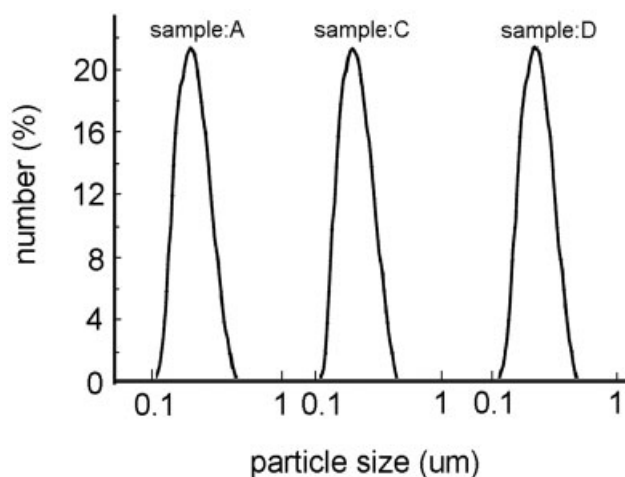$$B = (D_{90} - D_{10})/D_{50} \quad (2)$$

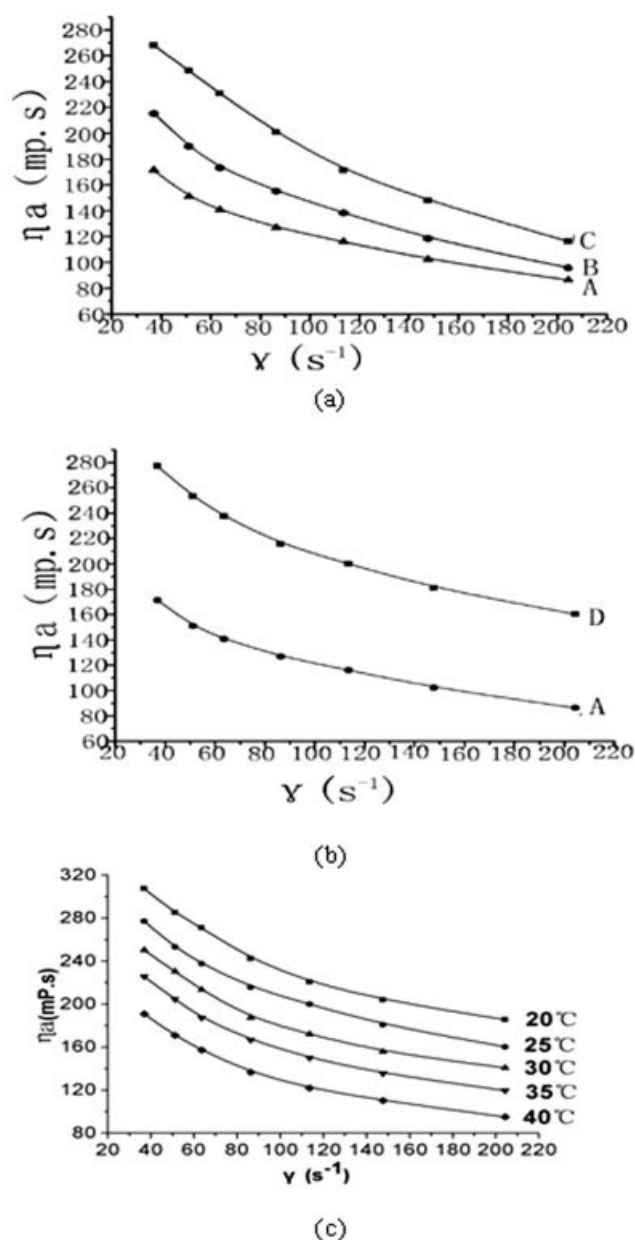**Figure 1** Laser light scattering graphs of emulsions.

Figure 2 Dependence of apparent viscosity on shear rate of emulsions. Rheological behavior curves of (a) different DAAM content, (b) different feeding method, and (c) Sample D at different temperatures.

where D_{90}, D_{50}, and D_{10} are the particle diameters for the 90th, 50th, and 10th cumulative mass percentiles, respectively.

According to Figure 1 and eqs. (1) and (2), it can be obtained that the particle size of samples A, C, and D were 0.198, 0.193, and 0.195 μm, respectively, the particle size distribution breadth was 0. 714, 0.697, and 0.689 μm, respectively. The particle size increased and PSD decreased with increasing the DAAM content. One possible explanation for this phenomenon lies in the affinity between DAAM and water, DAAM can stabilize AACPA latex particle the same as that of the surface active agent. The more DAAM that was used,

the more likely emulsoid particle that was produced, thus small and uniform particle size was observed. Whereas, all surface active agents dump into core-emulsion by the no preemulsion method of the shell-monomers, one part surfactant was adsorbed onto surfaces of core-emulsion, and another part surfactant was in the continuous phase, when shell-monomers were dropped into the flask, the concentration of the monomers in the continuous phase was very high, since DAAM is hydrophilic, a large number of subparticles or oligomers were created and a part of them was adsorbed onto surface of the polymer. So particle size was bigger and PSD was wider for the AACPA emulsion prepared by no preemulsion method of the shell-monomers, compared with that prepared by pre-emulsion method.

Rheological behavior of the AACPA emulsions

Rheological behavior is very important for the industrial paint, the plots of the apparent viscosity (η_a) versus the shear rate (γ) are given in Figure 2.

As shown in the Figure 2, the apparent viscosity η_a decreases with increasing shear rate. It is shown that the flow behavior of this emulsion is the behavior of shear thinning pseudoplastic liquid. This phenomenon is explained according to the Mooney equation.[14]

$$\ln \eta_a = \ln \eta_e + K_e V_i / (1 - V_i / \varphi)$$

where η_a is the apparent viscosity, K_e is form constant of particle, η_e is the viscosity of the continuous phase, V_i is the volume fraction of dispersed phase, and φ is the packed coefficient.

The latex particles were distorted and deformation occurred at shear action; the K_e value decreased and φ value increased after the AACPA emulsion was sheared, this caused decrease of η_a. On the other hand, this reason can be explained according to the interaction between the dispersed phase and continuous phase. The polymer molecular chain lied in a number of polar groups, such as COO—, SDS anion and initiator ion fragment and so on, which can produce the solvent effect and hydrogen bond with water. This interaction will be more and more destroyed with increasing of shear force. Accordingly, flow of the emulsion become easy and η_a decreased.

The rheological property of emulsion was analyzed in linear regress equation to know the relationship among the different DAAM content, synthesis methods, and the rheological behavior. According to Oswald–DE Waele power-law equation:[15]

$$\eta_a = K\gamma^{n-1}$$

it can be obtained that

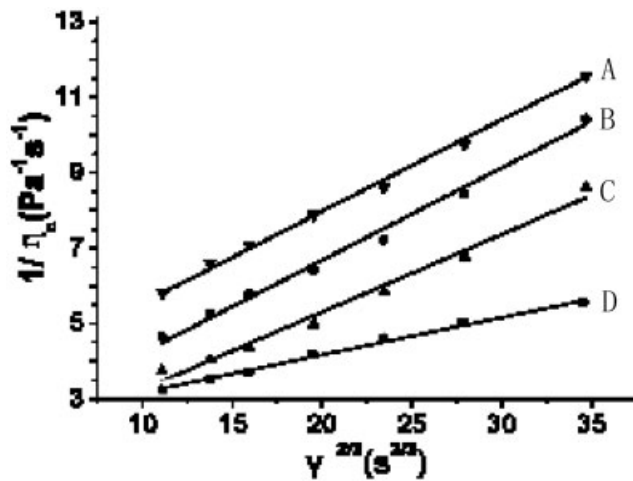$$\log \eta_a = \log K + (n - 1) \log \gamma \qquad (3)$$

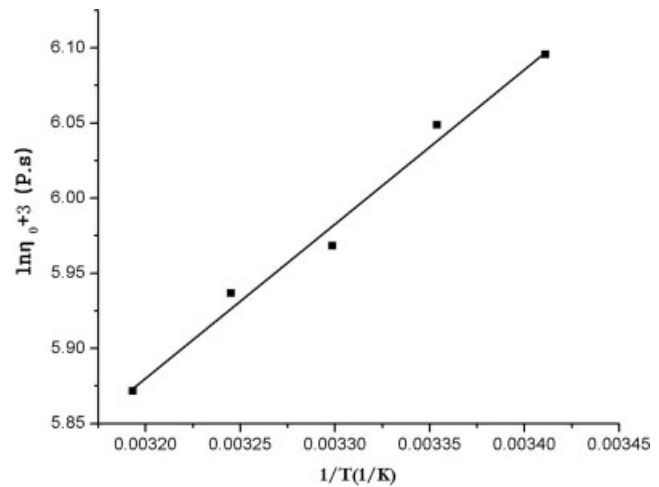**Figure 3** Dependence of $1/\eta_a$ versus $\gamma^{2/3}$.

Figure 4 Dependence of $1/\eta_a$ versus $1/T$.

where K is consistency factor, which is proportional to the apparent viscosity, n is the flow index; to non-Newtonian fluid, $n < 1$, to Newtonian fluid, $n = 1$. Values of K and n can be calculated by eq. (3) and are shown in the Table III.

The results showed that the apparent viscosity increased when DAAM content was increased, when the content of DAAM is about 4%, apparent viscosity reached the maximum. The apparent viscosity of the preemulsion method at the shell-emulsion preparation was higher than that of the no-preemulsion method. This is because the size of latex particles containing 4.0% DAAM and the size of latex particles of the preemulsion method at the shell-emulsion preparation are smaller, the interaction effect among the latex particles is stronger, and the parameter K values were higher, so the apparent viscosity was bigger.

All n values were smaller than 1 and reached the smallest when the content of DAAM was 4.0%. It can be seen that the emulsion is pseudoplastic fluid and the pseudoplastic property was the most strong in 4.0% DAAM content, this reason would be discussed as follows.

When shear rate (γ) is zero, zero shear viscosity can be obtained from Cross equation:[16]

$$1/\eta_a = 1/\eta_0 + (\alpha/\eta_0)\gamma^{2/3} \qquad (4)$$

where η_0 is the zero shear viscosity, η_0 was calculated by eq. (4) and is shown in Table III. Figure 3 showed the relationship between $1/\eta_a$ and $\gamma^{2/3}$.

DAAM containing carbonyl group has a good hydrophilic property and can form hydrogen bond with continuous phase water. This interaction between carbonyl group and water is enhanced in proportion to concentration of DAAM. Molecular chain is compelled to overcome the most strong hindrance when emulsion flow. Therefore η_0 was increased with

increasing of the content of DAAM, and the values of η_0 went up to the highest when the DAAM content was 4.0%. Zero shear viscosity of the preemulsion method at shell-emulsion preparation is bigger than that of no-preemulsion method. This phenomenon can be explained by the smaller particle size and the narrower PSD.

The molecular chain deformation appeared after the emulsion was sheared. The deformation made the apparent viscosity reduced. At that time, the interaction of the two phase too was decreased. The change in degree of interaction between carbonyl ground and continuous phase water is directly proportional to the contents of DAAM. In terms of this explanation, we draw a conclusion that pseudoplasticity of the emulsion enhanced with increasing of the DAAM content, and pseudoplasticity of emulsion containing 4.0% DAAM was the most strong.

The viscosity of masses of polymers is sensitive to the surrounding temperature. Generally speaking, the viscosity decreases with increasing of surrounding temperature, as shown in Figure 2(c). This is because free-volume of latex particles rises with increasing of temperature, which brings about reduction in the intermolecular force between latex particles. The η_0 accords approximately with Arrhenius equation: $\eta_0 = A \exp(E_a/RT)$. The equation $\ln \eta_0 = \ln A + (E_a/R)/T$ can be induced from Arrhenius equation. Viscous

TABLE III
Values of Consistency Factor (K), Flow Index (n), and Zero Shear Viscosity of Emulsion

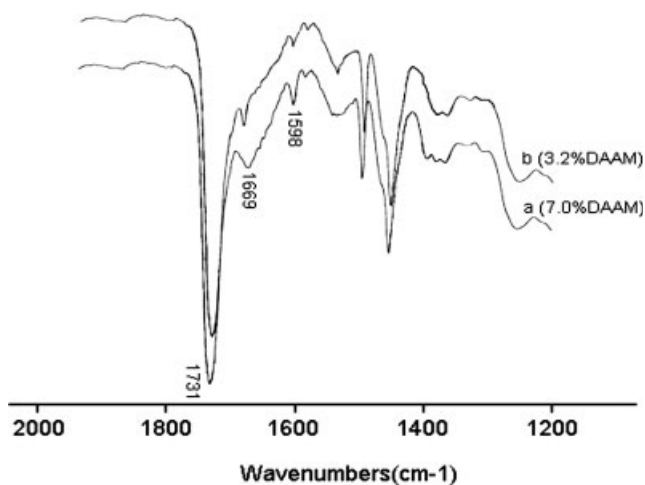| Sample	K	n	η_0 (Pa s)
A	0.6996	0.5860	0.3057
B	1.1658	0.5404	0.5296
C	1.6993	0.509	0.8769
D	0.8827	0.6826	0.4353

Figure 5 FTIR spectrum of the crosslinkable acrylate resin. FTIR spectrum of (a) Sample D (7.0% DAAM) and (b) Sample B (3.2% DAAM).

flow activation energy (E_a) can be obtained from the Figure 2(c), eq. (4), and Figure 4, $E_a = 8.542$ kJ/mol.

FTIR measurement for confirmation of crosslinking reaction

A reaction between the carbonyl group and dihydrazide crosslinker proceeds at ambient temperature in acidic conditions by the dehydration reaction shown in Scheme 2. In this article, diacetone acrylamide (DAAM) having carbonyl groups were used as the functional monomer, and adipic dihydrazide (ADH) having hydrazide groups as a crosslinker. To verify reaction of carbonyl groups and hydrazide groups, it is necessary to study the change of molecular structure during the curing process. FTIR was used for examining the room-temperature curing process of the crosslinkable acrylate resin. Figure 5 shows a change in differential FTIR spectra depending on different amount of DAAM in AACPA resin. The peak at about 1731 cm^{-1} is assigned to the ketone group of DAAM, the peak at bout 1669 cm^{-1} to the amide group, and about 1598 cm^{-1} is characteristic peak of C=N bond. Existence of the special peak of C=N verified that the reaction between carbonyl group and hydrazide group took place.

The peak height of the amide group and C=N bond in sample B decreased compared with that of the sample D. The quantitative analysis could be performed from this figure because of peak height shift. All the above clearly show that this change resulted in different content of DAAM. We conclude that the degree of the crosslinking reaction is proportional to the content of DAAM.

Degree of swelling and thermotacky temperature

Table II shows the degree of swelling of the AACPA latex film of different DAAM content, immersed in

TABLE IV
Values of Degree of Swelling and Thermotacky Temperature

Sample	Swelling degree in water (%)	Swelling degree in toluene (%)	Thermotacky temperature (°C)
A	27.38	897	120
B	21.4	390	140
C	7.8	231.6	195

water and toluene for 24 h. Three resins that contained different amounts of DAAM were used for the examination of the degree of swellings. DAAM contents of resins A, B, and C were 2.4, 3.2, and 4.0%, respectively. The results were shown in Table IV. It is evident from the measurement of the various film properties that the degree of swelling was closely related to the content of DAAM in the resins. Such a phenomenon seems to be brought about by crosslinking reaction, which change molecule structure from linear to network due to crosslinking. This network molecule structure can prevent the excessive film swelling, and this ability increased with increasing of DAAM content. Thermotacky temperature of the AACPA paint film also rose with increasing reaction, and the temperature increased with increasing the content of DAAM. That is to say, water and toluene resistance and thermotacky temperature increased in proportion to increasing amounts of DAAM. Crosslinking would be necessary to obtain good appearance.

TBA test at ambient temperature

TBA is an important method for research on curing process of latex paints. Curing behavior of some polymer material, such as polyacrylate/bloched toluene diisocyanate and polyacrylate/epoxy-amine
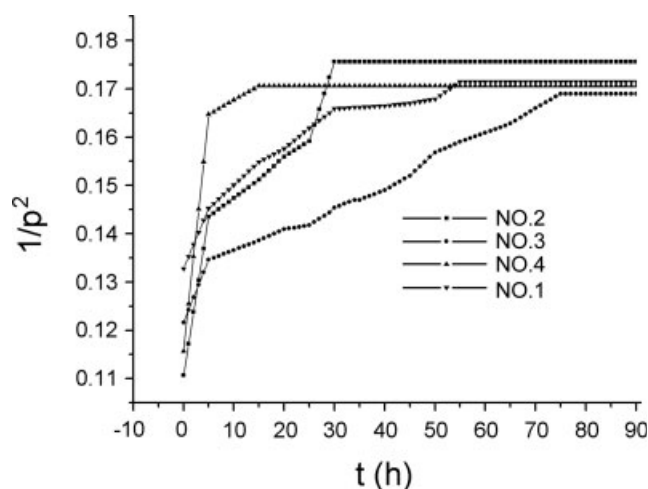

Figure 6 Dependence of relative rigidity ($1/p^2$) of the AACPA latex paint added different organic swelling agent on time (t).
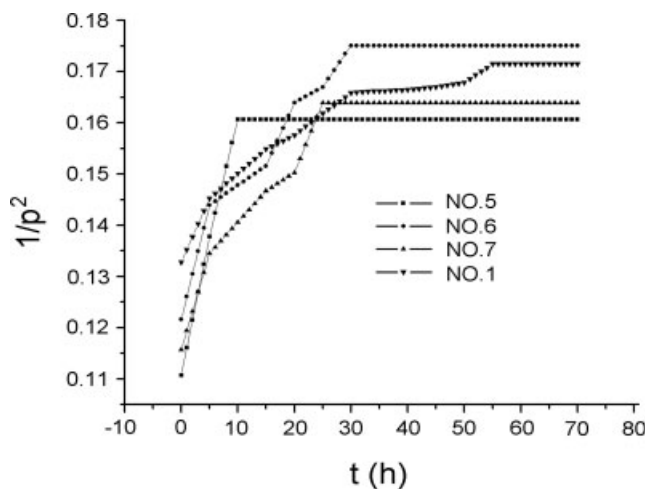
Figure 7 Dependence of relative rigidity $(1/p^2)$ of the AACPA latex paint containing organic swelling agent and additional acid on time (t).

Figure 8 Curing temperature of AACPA paint film containing different swelling agents.

adduct[17–20] has been investigated by TBA in my laboratory. In this article, we also attempt to study the curing behavior of AACPA latex film by TBA. A paint of film containing DAAM and ADH need depend several days on crosslinking completely at ambient temperature. However, the curing rate is faster by water-miscible organic solvents.

Curing processes of the samples 1–4 were investigated through the change of relative rigidity of the samples in the TBA tests at ambient temperature. We evaluated the paint film cure completely when the relative rigidity of the paint film did not change significantly. The component of the samples are shown in Table II, and the results for TBA test are indicated in Figure 6.

Figure 6 shows the relative rigidity variety of samples 1–4 added different organic swelling agent depending on time. Solvents used in this experiment can be divided into two groups, hydrophilic solvent propylene glycol mono-methyl ether(PGME) enhance the solubility of ethylene glycol mono-butyl ether (EGBE) and n-Butanol (n-BuOH), which are less soluble in aqueous media, the former solvent being poor swelling agents for the coating, do not directly accelerate the penetrative curing. The two swelling solvents accelerate effectively the penetrative curing, in particular, n-BuOH, which has good compatibility with paint resins and poor-solubility, is more effective than EGBE. The reason why the crosslinking reaction is accelerated with solvent seems to predominantly come from its affinity to the DAAM copolymer. Solvent permeates into the coating film to swell constitution and sets off an intermolecular force among copolymer molecules. So crosslinker can more easily come close to the reactive sites to form the crosslinking. However, diacetone alcohol slows curing rate, this is because diacetone alcohol is a small molecular ketone.
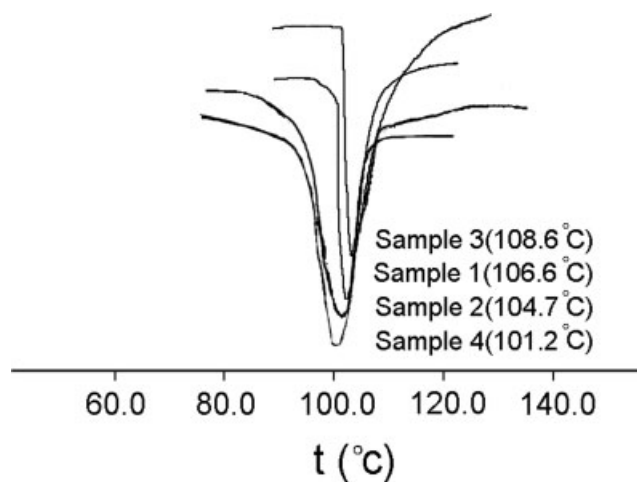
It can react readily with ADH and form small molecular weight hydrazone. This hydrazone can exchange with carbonyl group from DAAM. Though this process does not effect crosslinking degree on DAAM and ADH, it slows down the crosslinking speed.

The presence of an acidic component is indispensable to accelerate the reaction between DAAM and ADH, there, acid is an accelerant. In this article, AA, which is one of the components of the copolymer, plays an important part in supplying acidic group. Thereafter, acrylate copolymer with carbonyl groups and hydrazide group can crosslink without additional acid, however, out of question, an extraneous acid compound can accelerate curing rate.

Figure 7 shows the relative rigidity variety of samples 5–7 containing acetic acid compound depending on time at ambient temperature. Curing speed was satisfactorily improved compared with samples 1–4 without acid compounds, particularly, that of sample
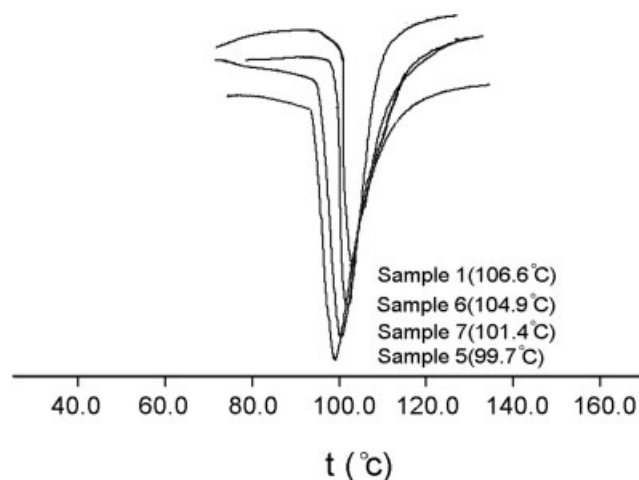

Figure 9 Curing temperature of AACPA paint film containing different swelling agents and acetic acid.

TABLE V
Values of the TBA and DTA Test

Sample	Curing time (h)	Curing temperature (°C)
1	55	106.6
2	30	104.7
3	75	108.6
4	15	101.2
5	15	99.7
6	30	104.9
7	25	101.4

5 containing EGBE and acetic acid. However, good penetrative solvent, n-BuOH and an external acid, acetic acid, involved in sample 7 did not bring out cure rate further improvement. We thought two causes were responsible for those poor results: one is that n-BuOH has very strong penetrative property, crosslinking reaction speed of the paint film is very rapid in no additional acid condition, and another is that the addition of an external acid to the emulsion containing n-BuOH has high influence on crosslinking reaction at beginning, the dent network in the molecular surface produced in the earlier stage hindered the crosslinker from penetrating further.

We must note that strong acid can not be selected as accelerant. This cause may be explained on the basis of the dense surface network, which is formed by rapid crosslinking reaction catalyzed with a strong acid and hinders the following penetration of the organic solvent.

DTA test

We attempted to accelerate curing rate making use of heating curing. DTA was employed to provide heating temperature programmed heating rate. DTA test results proved further TBA results and were shown in Figures 8 and 9, and listed in Table V. Data in Table V revealed the following results. The curing temperature of the paint film containing organic swelling agents, such as EGBE, n-BuOH, but no adding an external acid is lower than the original paint film, particularly, n-BuOH was very effective in decreasing the curing temperature. On the other hand, Table V also suggested that the addition of an acid to the AACPA

emulsion containing organic solvent made the curing temperature of all AACPA paint film containing different organic swelling agents. Furthermore, the curing temperature of AACPA emulsion combined with EGBE and acetic acid compound was influenced more greatly, while the curing temperature of the AACPA emulsion added n-BuOH solvent and acetic acid did not bring out further improvement.

CONCLUSIONS

A successful laboratory method was performed for preparing aqueous ambient self-crosslinking polyacrylate (AACPA) emulsion. This emulsion has small particle size, excellent water and solvent resistance, and high thermotacky temperature. The AACPA paint film can cure at room temperature, and the curing speed is accelerated by adding swelling solvent to the emulsion, and the curing speed is enhanced by the amount of acid in the reaction system.

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