Studies on Acrylate Copolymer Soap-Free Waterborne Coatings Crosslinked by Metal Ions

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ABSTRACT: Acrylate copolymers containing hydrophobic monomers (methyl methacrylate, butyl acrylate, styrene, or divinyl benzene) and hydrophilic monomer (acrylic acid) were synthesized by solution polymerization, and neutralized to form the soap-free hydrosol. The waterborne coating was prepared from the hydrosol crosslinked by $M(NH_3)_4^{2+}$ (M^{2+} was Zn^{2+}, Cu^{2+}, Ni^{2+} or Co^{2+}). ^{13}C-NMR analysis was used to identify the copolymer. The result of GPC showed that the molecular weight of the copolymer was within the range of thermosetting resin for coating. The factors affecting the crosslinking degree of the coating films were studied by DSC and gravimetric analysis. The results indicated that the appropriate crosslinking agent was $Zn(NH_3)_4^{2+}$, and the optimum curing condition was heating at 80°C for 30 min. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 91–96, 1999

Key words: acrylate copolymer; solution polymerization; soap-free hydrosol; waterborne coating; crosslinking degree

INTRODUCTION

One of the most striking activities in the field of coating research and development today is the effort to reduce as many harmful components as possible, owing to the concern for a safe and healthy environment. The waterborne coating, with water as the main solvent or dispersion medium, has the advantage of low pollution, low price, and good quality in comparison with the traditional organic coatings. Its application in the paint industry has been flourishing rapidly in the recent years.

According to the diameter of the dispersing particles, the waterborne coating can be classified as three types: emulsion (≥ 0.1 μm), hydrosol (0.01–0.1 μm), and solution (≤ 0.01 μm), so that the hydrosol coating has better stability than the emulsion coating due to its much smaller particles size.[1] The traditional method to stabilize the hydrosol is by adding emulsifier, and the added emulsifier will be left in the coating film affecting its properties.[2] In this article, we try to prepare a new kind of acrylate copolymer hydrosol coating without added emulsifier (soap-free), and this soap-free coating will keep high stability and the coating film will keep good property.

It has been known that acrylate copolymer waterborne coatings have better luster, hardness, flexibility, weather resistance, etc.[3,4] But on the other hand, most such coatings have to be cured at temperatures higher than 120°C. This limits its application. Many studies tried to use a metal ion as the crosslinking agent, where the curing temperature could be lowered to 40–110°C, or even to room temperature, but the water resistance of the coating films had to be reduced a great deal, and the studies were limited to the emulsion coatings.[5–10] In this article, we highlight an enhancement of the water resistance of

the acrylate copolymer soap-free hydrosol coating with $Zn(NH_3)_4^{2+}$ as the crosslinking agent, and determine the optimum curing condition.

EXPERIMENTAL

Synthesis of the Acrylate Copolymers and Coatings

All monomers, methyl methacrylate (MMA), butyl acrylate (BA), styrene (St), divinyl benzene (DVB), and acrylate acid (AA), were redistilled before used. All copolymers were synthesized by solution polymerization with isopropyl alcohol (IP) and ethylene glycol butyl ester (EGBE) as the cosolvent, and benzoyl peroxide (BPO) as the initiator. The mixture of monomers, cosolvent, and initiator were slowly dropped into the four-neck 500-mL flask fitted with a stirrer, a thermometer, a reflux condenser, and a dropping funnel over a period of 5 h reaction at 120°C with agitation. Then the parent stringy solution (solid content 70%) was obtained at a refluxing temperature for the ternary copolymer system (MMA/BA/AA) or the quaternary copolymer system [MMA/BA/AA/ST(or DVB)] to complete the polymerization. When the temperature of the stringy solution dropped to about 55°C, diethylaminoethyl alcohol (DEAE) and water were added one after another until 70% of AA was finally neutralized to form the soap-free hydrosol. The hydrosol was then mixed with the crosslinking agent $M(NH_3)_4^{2+}$ (M^{2+} was Zn^{2+}, Cu^{2+}, Ni^{2+}, or Co^{2+}) to prepare the waterborne coatings.

^{13}C-NMR Analysis[11,12]

The ^{13}C-NMR analysis of acrylate copolymer was conducted by DEPT technology with Varian XL-200MHz superconductivity NMR instrument at room temperature, $CDCl_3$ as the solvent. The proton rotating angle (θ) was 135°, and the resonant frequency of ^{13}C was 50.31 MHz.

Molecular Weight Measurement

The weight average molecular weight (M_w), number-average molecular weight (M_n), and polydipersity index (DP) were measured by Waters 150-C gel permeation chromatography instrument at room temperature, $CHCl_3$ as the solvent and monodisperse polystyrene as the calibrating sample.

Water-Resistance Measurement

The coating film was prepared by curing the coating on the surface of the tetrafluoroethylene plate. The dry-cured coating film with initial weight (W_0) was soaked in water at room temperature. After some time, the film was taken out of the water, the film surface dried with the filter paper, and weighed (W_1) again; then the water-absorption ratio of the film was calculated as follows:

$$Water\ Absorption\ Ratio = (W_1 - W_0)/W_0$$

DSC Analysis

The DSC analysis of the coating film was performed on a Perkin-Elmer DSC-2C instrument from −50 to 200°C at a scanning speed of 10°C/min.

Determination of the Crosslinking Degree of Coating Film

A certain weight (w_0) of the dry-cured coating film was extracted in a Soxhlet's extractor with dilute ammonia aqueous solution (pH = 7.8) for 6 h. The extracted film was dried under vaccum at 60°C to constant weight (w_1). The crosslinking degree of the coating film was calculated as follows:

$$Crosslinking\ Degree\ (\%) = w_1/w_0 \times 100\%$$

RESULTS AND DISCUSSION

Synthesis of Acrylate Copolymer

Among the monomers for the synthesis of the acrylate copolymers in this work, MMA is the hard monomer to provide good hardness, endurance, and wear resistance, while BA is the soft monomer to provide fine flexibility and adhesion, and AA is the functional monomer to supply carboxyl to be neutralized with amine to form the stable soap-free hydrosol system. In addition, carboxyl will take part in the coordination crosslinking reaction with the metal ion to form the soap-free hydrosol coating film.[13] However, AA and the metal ion/carboxyl coordination crosslinking groups have rather strong polarity, resulting in a poor water resistance of the coating film. To improve the water resistance, we try to introduce the hydrophobic monomer DVB or St in the acry-
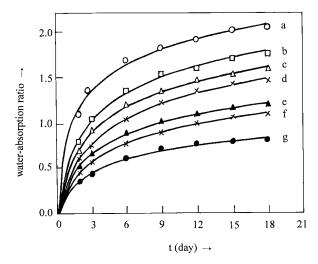
Figure 1 Influence of DVB content on water-absorption ratio: (a) I (0.00%), (b) II (0.10%), (c) III (0.15%), (d) IV (0.20%), (e) V (0.25%), (f) VI (0.30%), (g) VII (0.35%).

late copolymer to reduce the hydrophilic property of the film.

Relationship Between Water Resistance and DVB or St Content

The influences DVB and St on water resistance of the coating films crosslinked by $Zn(NH_3)_4^{2+}$ are shown in Figures 1 and 2, respectively. They illustrate that the water-absorption ratios of the coating films containing DVB or St are lower than those without DVB or St, i.e., both DVB and St have provided better water resistance. The smallest water-absorption ratio of all coating films is only 0.1 after the film was soaked for 2 days (curve i in Fig. 2), which approximately accords with the demand of the water resistance of coatings.

Why can DVB improve the water resistance? It is probably attributed to the hydrophobicity and steric hindrance of the benzene ring in DVB, and also to the inner crosslinking structures of the copolymers. Because DVB is a crosslinking agent, its content in the copolymer cannot exceed 0.35%; otherwise the polymerization reaction will be stopped due to the appearance of gel.

The reason that St can improve the water resistance is also due to the hydrophobicity and steric hindrance of the benzene ring in St. Because the St-containing copolymers have the linear molecular structures while the DVB-containing copolymers have the crosslinking net structures, it is easier to raise the water resistance of

the St-containing films just by increasing the content of St. For instance, the water resistance of the 8.00% St-containing film (curve f in Fig. 2) has exceeded that of 0.35% DVB-containing film (curve g in Fig. 1). But the content of St cannot exceed 14.87%, or else the coating film will be too fragile, owing to the too high rigidity of the copolymer macromolecule resulting from the presence of too many benzene rings.

Analysis of the Structure of St-Containing Copolymer

The ^{13}C-NMR spectra of the St-containing copolymer (XV copolymer in Fig. 2) is shown in Fig. 3. The peaks (b, e, and f) at 18.4 ppm (s), 44.8 ppm (d), and 51.6 ppm (d) are assigned to —CH_3, >C< and O—CH_3 carbons of MMA in the copolymer. The peaks (a, c, d, and g) at 13.6 ppm (s), 19.0 ppm (s), 30.4 ppm (s), and 64.4 ppm (s) are assigned to —CH_3 and three —CH_2— carbons of BA; furthermore, the closer to the high eletronegative group —COO^-, the lower field the resonant signal of —CH_2— is located, i.e., the larger will be the chemical shift. The peaks (h, i, and j) at 126.2 ppm (s), 128.2 ppm (s), and 142.8 ppm (s) are assigned to the benzene ring of St. In addition, the peaks (k) at 175.5–176.7 ppm (t) are assigned to —CO— carbon of AA, MMA, and BA. In the DEPT (Distortionless Enhancement by Polarization Transfer) spectrum (curve B), there just appear the peaks of —CH_3 and —CH_2— and —CH<, and the
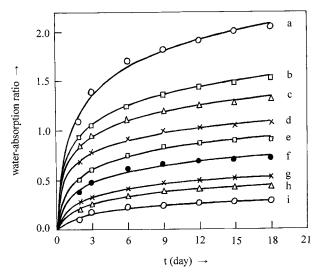

Figure 2 Influence of St content on water-absorption ratio: (a) I (0.00%), (b) VIII (0.35%), (c) IX (2.15%), (d) X (4.08%), (e) XI (6.03%), (f) XII (8.00%), (g) XIII (10.17%), (h) XIV (12.62%), (i) XV (14.87%).
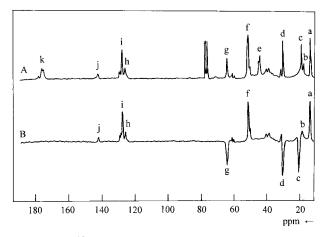
Figure 3 ^{13}C-NMR spectra of XV acrylate copolymer: (A) ^{1}H decoupled spectrum; (B) DEPT spectrum.
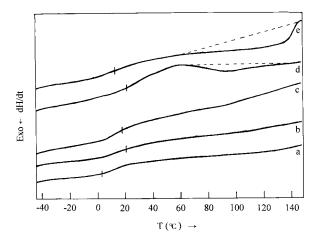

Figure 4 DSC curves of solid acrylate copolymer and M^{2+}-coating films cured at 80°C for 30 min: (a) solid acrylate copolymer, (b) Zn^{2+} film, (c) Cu^{2+} film, (d) Ni^{2+} film, (e) Co^{2+} film.

phases of —CH$_3$ (peaks a, b, and f) and —CH< (peak h, i, and j) are opposite to that of —CH$_2$— (peaks of c, d, and g). Then the analysis of ^{13}C-NMR has proven the composition of the quaternary acrylate copolymer (MMA/BA/AA/St).

The result of GPC has indicated that M_w and M_n of XV copolymer (see Fig. 2) are 1.7×10^4 and 0.9×10^4, respectively, which lie in the range of the thermosetting coating.[1] The small polydispersity index ($DP = 1.6$) illustrates the narrow distribution of molecular weights of the copolymer.

Several Critical Factors Affecting the Crosslinking Degree of the Coatings

The coating properties depend greatly on the crosslinkage of the coating film that is mainly affected by the curing agent, curing temperature, and curing time. When the crosskinking degree is more than 90%, the coating film will have the value of application.

Figure 4 shows the DSC curves of the solid copolymer (XV copolymer in Fig. 2) itself and its coating films crosslinked by $Zn(NH_3)_4^{2+}$, $Cu(NH_3)_4^{2+}$, $Ni(NH_3)_4^{2+}$, and $Co(NH_3)_4^{2+}$, respectively. It can be seen that the glass transition temperatures (T_g) of the films are higher than that of copolymer, i.e., the metal ions in the films have been crosslinked with carboxyl of acrylate copolymer. Both Zn^{2+} and Cu^{2+} films have no crosslinking exothermal peaks, while the Co^{2+} film has the crosslinking exothermal peak area larger than that of the Ni^{2+} film , i.e., the crosslinkage of Zn^{2+} and Cu^{2+} films is better than that of Ni^{2+} and Co^{2+} films, and that of Co^{2+} film is the worst.

The crosslinking degree of each coating film cured at different temperatures for 30 min shown in Figure 5 is Zn^{2+} film > Cu^{2+} film > Ni^{2+} film > Co^{2+} film. The crosslinking degrees of Zn^{2+} and Cu^{2+} films will attain 98 and 96% when they are cured at 80°C for 30 min, but those of Ni^{2+} and Co^{2+} films are below 90%. These results are consistent with those of DSC analysis (Fig. 4).

The reason why the crosslinking degrees of Zn^{2+} and Cu^{2+} films are higher than those of Ni^{2+} and Co^{2+} films may be that, in comparison with Ni^{2+} and Co^{2+}, Zn^{2+} and Cu^{2+} can be coordinated
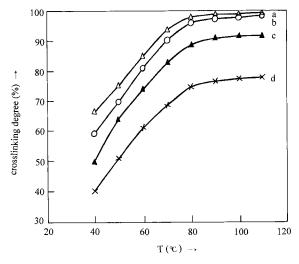

Figure 5 Dependence of crosslinking degree on curing temperature of M^{2+}-coating films cured at different temperature for 30 min: (a) Zn^{2+} film, (b) Cu^{2+} film, (c) Ni^{2+} film, (d) Co^{2+} film.

much easier with —COO$^-$ of the acrylate copolymer, and take part in a crosslinking reaction to form the coordination copolymer [(P—COO$^-$)$_n$M^{2+}].[13] It has been known that the stability constants of $(CH_3COO)_2Zn$ and $(CH_3COO)_2Cu$ are larger than 2.0, while those of $(CH_3COO)_2Ni$ and $(CH_3COO)_2Co$ are smaller than 1.6.[14]

According to the results mentioned above, $Zn(NH_3)_4^{2+}$ will be chosen as the curing agent, and the optimum curing temperature and time will be studied further.

It can be seen from Figures 6 and 7 that, first, there are different crosslinking exothermal peaks in the DSC curves of Zn^{2+}-coating films when the curing temperature is lower than 80°C and the curing time is shorter than 30 min, and second, the lower curing temperature and shorter curing time correspond to the larger crosslinking exothermal peaks (curves a–d in Fig. 6 and curves a–b in Fig. 7), i.e., correspond to the worse crosslinkage. However, there is no crosslinking peak when the temperature is higher than 80°C (curves e–h in Fig. 6), and the time is longer than 30 min (curves c–e in Fig. 7), i.e., 80°C, and 30 min is the lowest temperature and the shortest curing time for the coating. In another word, this is the optium curing condition for this soap-free waterborne coating. Moreover, the fact that the crosslinking degree of Zn^{2+} film cured at 80°C for 30 min attains 98% further proves this result (see curve a in Fig. 5).
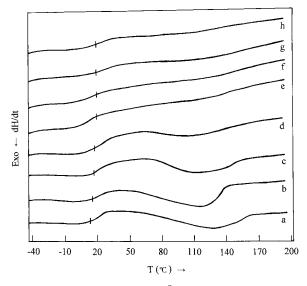

Figure 6 DSC curves of Zn^{2+}-coating films cured at different temperatures for 30 min: (a) 40°C, (b) 50°C, (c) 60°C, (d) 70°C, (e) 80°C, (f) 90°C, (g) 100°C (h) 110°C.
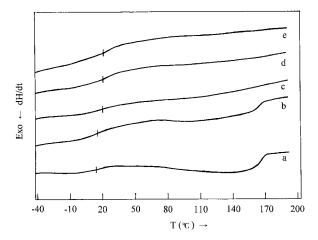

Figure 7 DSC curves of Zn^{2+}-coating films cured at 80°C for different times: (a) 10 min, (b) 20 min, (c) 30 min, (d) 40 min, (e) 50 min.

CONCLUSION

The soap-free hydrosol, which can be crosslinked with $Zn(NH_3)_4^{2+}$ to form coating film, has been prepared from the acrylate copolymer (MMA/BA/AA/St) synthesized by the solution polymerization. The results of water resistance determination indicate that this coating film has good water resistance due to the presence of the hydrophobic benzene rings in the copolymer. The component of the acrylate copolymer have been detected by ^{13}C-NMR analysis, and the molecular weight and molecular weight distribution have been studied by GPC. DSC and gravimetric analysis have been used to investigate the factors affecting the crosslinking degree of the coating films. The results indicate that the appropriate crosslinking agent is $Zn(NH_3)_4^{2+}$, and the optium curing condition is heating at 80°C for 30 min.

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