Preparation of Acrylic Copolymer Latex Modified by Fluorine, Silicon, and Epoxy Resin

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ABSTRACT: A series of modified acrylic copolymer latices have been prepared through a semicontinuous emulsion copolymerization process with a variety of hydrocarbon monomers and (perfluoroalkyl) methyl methacrylate, vinyltriethoxysilicone, and phenol-formaldehyde epoxy resin. The composition of copolymer was analyzed by fluoride ion selective electrode analysis, ^{19}F NMR, FTIR, crosslinking degree determination, and epoxy-acetone method. The results showed that the fluorine monomer, silicon monomer and epoxy resin had copolymerized with acrylic monomers. The optimum mass ratio between the curing agent TEA and epoxy resin was 1.36 : 6. The determination results of stabilities (electrolyte stability, freeze-thaw stability, high temperature stability and mechanical stability) of latices showed that the incorporation of fluorine monomer and silicon monomer improved freeze-thaw stability and mechanical stability, whereas the epoxy resin did not have obvious effect on the stabilities. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 112: 181–187, 2009

Key words: latices; copolymerization; fluoropolymers; silicons; epoxy resin

INTRODUCTION

Among recently developed heavy duty coatings, acrylic coatings modified by fluorine, silicon, and epoxy resin have a special place. Fluoropolymers, having the atom of fluorine in the polymer chains with high electronegativity and small atomic radius, which compasses to better hydrogen than other heteroatoms and allows for replacement of C—H with C—F bonds, with only minor changes in conformational mobility and steric hindrance of the resulting molecule due to its nonbulkiness,[1–3] offer the potential advantages of high mechanical and thermal stability, chemical inertness (to solvents, chemicals, acids, and bases), low friction coefficients, low flammability, excellent weatherability, good resistance to oxidation, extremely low surface energy and related unwettability, and relatively low permeability for most gases.[4,5] Silicon-containing polymers represent attractive surface properties coupled with an exceptionally low glass transition temperature, low elastic modulus, and high thermal and chemical stability.[6–8] Epoxy resins play a dominant role in protective coatings mostly due to their outstanding performance in terms of corrosion resistance and chemical resistance.[9–16]

New polymer architectures combining the unique properties of fluorinated, silicated polymers, and epoxy resin in a single polymer might provide new interesting materials, particularly with regard to potential application for heavy duty coatings.[17] However, most of the open literatures, focusing on the modification of acrylic latices, have only adapted either one or two of the above modifying agents, and the analogical reports in the coating area are very few. Some innovative investigation into modified acrylic copolymer latices is provided in our work.

In this article, we described the preparation procedure of acrylic copolymer latices modified by fluorine, silicon, and epoxy resin. The chemical composition of copolymer was characterized by fluoride ion selective electrode analysis, ^{19}F NMR, FTIR, crosslinking degree determination, and epoxy-acetone method. Some application properties such as stabilities (electrolyte stability, freeze-thaw stability, high temperature stability, and mechanical stability) were also studied.
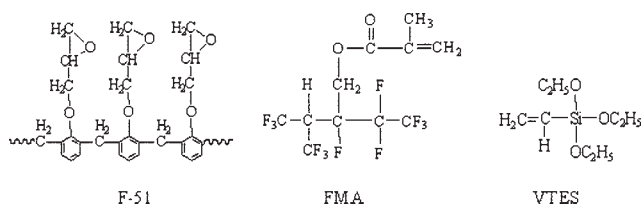
EXPERIMENTAL

Materials

Phenol-formaldehyde epoxy resin (F-51), dodeca-fluoroheptyl methacrylate (FMA) (99.5+%), and

Scheme 1 The basic structures of F-51, FMA, and VTES.

vinyltriethoxysilicone (VTES) (98+%) were used as received. Styrene (St) (99+%), methyl methacrylate (MMA) (99.5+%), and butyl acrylate (BA) (99+%) were all used as received, too. The crosslinking agent acetoacetic ethyl methacrylate (AAEM) (99.8+%) and initiator ammonium persulfate (APS) were used without further purification. The mixed emulsifier systems were composed of sodium 3-allyloxy-2-hydroxy-propane sulfonate (COPS-1) (40+%) and ammonium *p*-nonyl phenoxy polyoxyethylene(4) sulfate (CO-436) (58+%), which were both purchased from Rhodia France (Hubei, China) and used as received. Curing agent triethanol amine (TEA) was used as received. The structural formulae of F-51, FMA, and VTES were presented in Scheme 1.

1,1,2-Trifluorotrichloroethane, *n*-hexane, and acetone were used as the solvents for selective extraction. Sodium fluoride (NaF) was dried before use.

Preparation of acrylic copolymer latex

The synthesis was carried out in a four-neck round-bottom flask equipped with an electromechanical stirrer, thermometer, addition funnel, and reflux condenser. When the temperature of water bath reached $82 \pm 2°C$, a complex solution containing 45% amount of initiator, 28% amount of CO-436, 42% amount of COPS-1, and 30 g water was injected into the reaction kettle. Three minutes later, half of the preemulsion composed of all the St, BA, MMA, part of the FMA, 72% amount of CO-436, 58% amount of COPS-1, 18% amount of APS, and 25 g water was added to the reactor over a period of 1 h. The remaining preemulsion with FMA, VTES, and F-51 were fed continuously over a period of 75 min, and the rest initiator solution was fed over a period of 80 min simultaneously. Upon the completion of the initiator feeding, polymerization was allowed to continue for an additional 1.5 h at $82 \pm 2°C$. After that, a certain amount of triethanol amine (TEA) was added into the reaction system, and the agitating speed was raised to enable the complete curing reaction. Then the temperature was allowed to reduce naturally to room temperature. In this way, the coagulate-free and long-time stable latex with a solid content of about 43% was obtained.

Characterization

The acrylic copolymer latex was deemulsified with acetone and washed several times. The resulting powder was dried and then extracted with 1,1,2-trifluorotrichloroethane for 24 h to eliminate the residual FMA and its oligomer in the latex, and finally dried in a vacuum oven. ^{19}F (versus CF_3CO_2H) NMR spectra was obtained on a Varian Unity Inova 600 NMR spectrometer using chloroform-d ($CDCl_3$) as the solvent if not otherwise specified.

The fluorine content of polymer was determined by ion-selective electrode analysis. A standard curve was created through examining standard NaF solutions with different concentrations (from 10^{-1} to 10^{-6} mol/L). According to the mathematical analysis of the standard curve, a linear regression [eq. (1)] was obtained, as follows:

$$E \text{ (mV)} = -6.067 - 55.114 \log[F^-] \text{ (mol/L)} \quad (1)$$

The latex films for characterization were prepared by casting the modified acrylic copolymer latices onto petri dishes and drying them at room temperature for several days until the weights of latex films reached constant values.

The latex films were extracted with 1,1,2-trifluorotrichloroethane for 24 h. The residual film was dried in vacuum at room temperature. Next, a certain amount of the residual film (about 20–30 mg) was burned in an oxygen bomb with 10 mL 10% of NaOH solution as absorption liquid. After degradation, the value of pH was adjusted to 6–7 with 0.1 mol/L of HCl solution. Then, the absorbing solution was detected with fluoride ion selection electrode to obtain a response E. According to the linear regression eq. (1) and the response E, the concentration of fluorine ion in the solution could be calculated. The fluorine content of the copolymer was calculated by the following equation:

$$C_f \text{ (wt \%)} = \frac{0.05 \times [F^-] \times M_F}{W_o} \times 100\% \quad (2)$$

where $[F^-]$ is the concentration of fluorine ion in the absorbing solution; M_F is the atomic weight of fluorine; and W_0 is the weight of the film before burning.

The copolymerization ratio of fluorine monomer can be calculated according to the eq. (3):

$$F_{cp}\% = \frac{C_f}{F_{theory}} \times 100\% \quad (3)$$

where F_{theory} is the theory concentration of fluorine in the copolymer.

Before the FTIR analysis, the latex was also deemulsified with acetone and washed. Then the powder was dried and extracted with *n*-hexane for 48 h
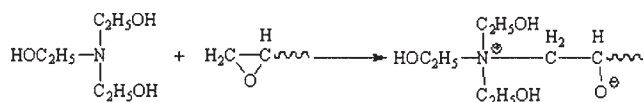
Scheme 2 The reaction formula between TEA and F-51.

and acetone for 24 h, respectively. FTIR spectrum analysis for the residual product was recorded with a Perkin–Elmer one FTIR spectrophotometer, and the crosslinking degree can be calculated by the following equation:

$$\text{Crosslinking degree} = \frac{W_1}{W_2} \times 100\% \qquad (4)$$

where W_1 and W_2 are the weights of the latex before and after extraction, respectively.

The unreacted epoxy group content was determined by the method of epoxy-acetone. An excess of hydrochloric acid was added in the acetone to react with epoxy group and generate chlorhydrin, and then the unreacted hydrochloric acid was titrated with alkali.

The latex films without curing agent were dried to constant weight exactly and put into a 150 mL taper bottle, added 20 mL hydrochloric acid-acetone solution (1 mL strong hydrochloric acid was dissolved in 40 mL acetone, used as formulated), rocked till uniform, put in a shady and cool place for 1 h, and then added 2–3 drops methyl red indicator, titrated with 0.1 mol/L of NaOH standard solution. When the solution color changed from red to yellow, the titration reached the end point. At the same time, a blank experiment was carried out.

The value of epoxy group was calculated as follows:

$$M = \frac{(V_0 - V_1) \times N_{\text{NaOH}}}{10\,W} \qquad (5)$$

where M is the value of epoxy (mol/100 g); V_0 is the volume of NaOH solution consumed by the blank sample (ml); V_1 is the volume of NaOH solution consumed by test sample (mL); W is the mass of test sample (g); N_{NaOH} is the concentration of NaOH solution (mol/L).

The stability to electrolyte of latex was represented by critical coagulation concentration (C.C.C). The testing process was as follows: 10 test tubes were firstly filled with the latex sample having equal volume and then with NaCl aqueous solutions having the same volume but different concentrations (1.0, 0.9, 0.8, …, 0.1 mol/L). The mixture was joggled until uniform and stood still for several minutes. Thus, the concentration at which coagulation appeared was defined as approximate C.C.C (X). Consequently, analogical tests in the tubes were carried out by adding the NaCl solutions having con-

centration as 0.9X, 0.8X,…, 0.1X into the latex sample. The critical concentration when coagulation appeared was the true C.C.C.

Latex sample (10 g) was filled into a sealed glass bottle and stored at −5°C for 18 h and then at 20°C for 6 h. The operation was repeated five times. Mass of coagulation and viscosity of latex was measured after five freeze-thaw cycle, and freeze-thaw stability of latex was represented by the coagulation mass and variation of latex viscosity.

High temperature stability was measured by sealing 10 g of the obtained latices in a glass bottle and storing it at 60°C for 48 h. Then the state of latices was recorded.

Mechanical stability was determined by observing the state of latices at high shear rate. A small amount of latex was injected into a 1 mL centrifugation tube and centrifuged at the rate of 12,000 r/min for 15, 45, and 100 min.

RESULTS AND DISCUSSION

The definition of the amount of curing agent

TEA is a conventional curing agent of epoxy resin. In the reaction system composed of TEA and epoxy resin, TEA has two active groups: hydroxyl group and tertiary amine group. The reaction between hydroxyl group and epoxy group is difficult to occur, and generally needs a very high temperature (above 200°C) to promote it. Although there is no active hydrogen in tertiary amine group, the isolated electron in the nitrogen atom can still combine with the carbon atom of epoxy group and let ring open, as shown in Scheme 2.

The newly formed oxygen negative ion is a stronger nucleophilic reagent than TEA that can react with epoxy group continuously (Scheme 3).

Theoretically, the reaction is likely to repeat as above and form reticulated structure among F-51 molecules eventually. However, TEA is a mild curing agent of epoxy resin, which opens epoxy groups in a step-by-step way especially in the polymer system in question. F-51 mostly locates in particle phase due to its solubility in silicon monomer whereas TEA mostly locates in water phase, thus, the effective contact area contributing to curing reaction is not large and a diffusion process of TEA into
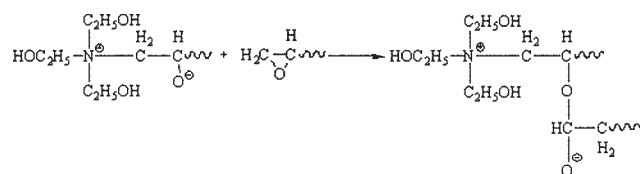
Scheme 3 The further reaction formula between TEA and F-51.

TABLE I
The Influence of Amount of TEA on the System Stability

Amount of TEA (g/6 g F-51)	Ring opening ratio (%)	Storage stability	State
0.69	15	1 month, bad	Opaline, have insoluble matter
0.91	20	3 months, bad	Opaline, have insoluble matter
1.14	25	4 months, sound	Opaline, have blue light
1.36	30	>6 months, excellent	Blue, uniform, transparent
1.60	35	>6 months, excellent	Blue, uniform, transparent
1.83	40	>6 months, excellent	Blue, uniform, transparent

particle phase is also indispensable to further cure the epoxy resin. As a result, the rate of curing reaction in the dispersion is quite slow, enabling the retention of epoxy groups in F-51 to crosslink with silicon monomer.

Because the curing rate significantly depends on the concentration of curing agent, it is possible to control the extent of curing reaction by changing the ratio of TEA to epoxy. In our experiments, a series of modified acrylic resins with different ring opening ratios were synthesized using the curing system consisting of 6 g epoxy resin and certain amount of TEA.

From the data listed in Table I, it can be seen that as the amount of TEA increased, the storage stability of the system was improved significantly. When the amount of TEA was above 1.36 g, the system formed a uniform, transparent, and stable solution; and when the amount of TEA was lower than 1.36 g, some insoluble matter appeared.

The reason is that the average functionality of F-51 is 3.3, the mass ratio between TEA and F-51 is 1.36 : 6, and the molar ratio between TEA and epoxy group in F-51 is 1 : 3, so each epoxy group ring-opening reaction has led the hydrophilic TEA molecule into F-51. Thus, the modified F-51 with two epoxy groups in each molecule is enough hydrophilic, and the release of epoxy resin from water can be avoided. When the mass ratio between TEA and epoxy resin is above 1.36 : 6, more than one epoxy group ring is opened in every epoxy resin molecule. And when the mass ratio between TEA and epoxy resin is less than 1.36 : 6, there would be certain amount of the residual epoxy group rings unopened. As the residual epoxy groups increase, the amount of F-51 remaining uncured will increase, which may

release from the water, aggregate, and precipitate. Therefore, the mass ratio between TEA and F-51 should be above 1.36 : 6 to have the latices with good storage stability.

Preparation and characterization of modified latex

Modified acrylic copolymers have been prepared with high monomer conversion (>95%), and the basic recipes were presented in Table II. Synthetically, the parameters varied including amounts of FMA, VTES, and F-51. The incorporation of the FMA in the copolymers was confirmed by ^{19}F NMR (Fig. 1) and fluoride ion selective electrode analysis. The incorporation of VTES and F-51 in the copolymers was confirmed by FTIR and the measurements of crosslinking degree.

In emulsion polymerization, the readily hydrolysis reaction of ethoxy groups in silicon monomer and the resulted self condensation reaction of silanol causing rapid self crosslinking are always challenges to obtain stable silicon-containing latices. In our experiments, however, two effective methods were used to reserve the functional groups in VTES. First, a pH buffer sodium bicarbonate solution was added into the system to keep the pH of reaction media at 6–7; second, the delayed addition profile of VTES was adopted to minimize the retention time of VTES. Stable latices were obtained eventually, indicating that the hydrolysis of ethoxy groups was effectively restrained.

The ^{19}F NMR spectrum of copolymers extracted by 1,1,2-trifluorotrichloroethane was shown in Figure 1. In the ^{19}F NMR spectrum of modified acrylic latex, the peaks between −73 and −77 ppm were assigned to the trifluoromethyl group, indicating that FMA has participated in copolymerization. The

TABLE II
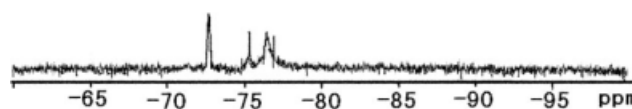**The Basic Recipe of Modified Acrylic Copolymer**

Fixed factor	Variable
Monomer	42 g
Emulsifier	4%
Initiator	0.7%
Deionized water	60 mL

Figure 1 ^{19}F NMR spectrum of copolymer with FMA content of 18%.

FMA (%)	3	6	9	12	15	18
F_{theory} (%)	1.72	3.40	5.10	6.81	8.51	10.21
E (mV)	200	183	164	159	150	147
Log [F^-]	−3.734	−3.430	−3.086	−2.995	−2.832	−2.777
[F^-] × 10^{-4} (mol/L^{-1})	1.824	3.711	8.209	10.116	14.733	16.70
F_{fact} (%)	0.866	1.765	3.897	4.796	6.749	7.912
Efficiency (%)	50.35	51.91	76.42	70.43	79.31	77.49

fact that the other two peaks did not appear may be due to the low content of FMA.

The fluoride ion selective electrode analysis of copolymers provided further information. The latex extracted by 1,1,2-trifluorotrichloroethane was burned in oxygen bottles, and absorbed by NaOH solution to transform the fluorine atom in copolymer into fluoride ion. The electrode voltage of NaF standard solutions, with concentration in 10^{-1} to 10^{-6} mol/L, was linear to the concentration of fluoride ion, so we chose NaF solution as standard solution and used fluoride ion selection electrode to measure the fluorine content in copolymer. From eq. (1), the fluorine content was obtained and the test results were listed in Table III.

From Table III, it can be seen that the copolymer latex extracted by 1,1,2-trifluorotrichloroethane still contain fluorine, which can further certify that FMA has participated in copolymerization, although the copolymerization ratio was not very high.

Figure 2 shows the FTIR spectrum of the latex film extracted by *n*-hexane and acetone. It can be seen that the characteristic absorption of the C=C bond at 1640 cm^{-1} has disappeared, indicating that the monomers have copolymerized into polymer chains. Compared with unmodified acrylic latex, the absorption peak of modified acrylic latex at about 950 cm^{-1} was assigned to the characteristic absorp-

tion band of Si —O— Si and Si—O—C bonds. The absorption peaks at 770 cm^{-1} and 843 cm^{-1} were assigned to the characteristic absorption band of Si—C bond. The absorption peak at about 3500 cm^{-1} was assigned to the characteristic absorption band of hydroxyl group generated by ring-open reaction of epoxy groups. All of these showed that VTES and F-51 have copolymerized with acrylic monomers.

From the crosslinking degree data listed in Table IV, it can be seen that as the amount of VTES and F-51 increased, the crosslinking degree increased and enhanced largely even with a very small increasing amount of VTES. This is because F-51 contains many epoxy groups, which could open their rings spontaneously but not extensively in weak acidic media, and generate hydroxyl groups responsible for the formation of crosslinking reticular structure during polymerization. In addition, VTES is a multifunctional monomer containing a C=C bond, which enables the incorporation of silicon monomer into acrylic copolymer main chains, and three ethoxy groups, which can readily hydrolyze and generate hydroxyl groups to condensate with the hydroxyl groups in epoxy resin. It is likely that the hydroxyl groups yielded from hydrolysis reaction of VTES will self condensate and form networks among copolymer chains contributing to the crosslinking degree to some extent. It is known that the
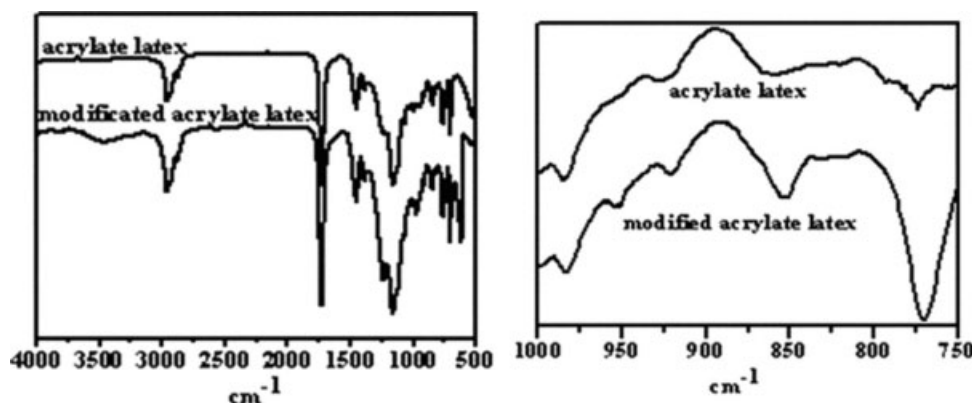

Figure 2 (a) FTIR spectrum of modified and unmodified acrylic copolymers; (b) the amplified section of image (a) from 1000 cm^{-1} to 750 cm^{-1}.

TABLE IV
The Influence of Amount of VTES and F-51 on Cross-Linking Degree of Acrylic Copolymer

VTES (%)	0	1	2	3	4	5	6
Cross-linking degree (%)	52.64	84.08	88.94	90.31	93.62	93.76	93.86
F-51 (%)	0	1	3	5	7	9	11
Cross-linking degree (%)	61.34	62.07	63.17	64.36	65.09	65.23	65.58

probability of self condensation increases largely with increasing the concentration of silanol, thus crosslinking degree increases largely as the amount of VTES increases. However, with increasing F-51, the probability of ring-opening reaction of epoxy groups in F-51 will not increase much due to the limitation of acidity of media controlled by adding a pH buffer sodium bicarbonate solution in our experiments, causing an indistinctive increase of crosslinking degree. During polymerization, the crosslinking reaction allows some linear macromolecules to link and form networks among molecular chains. Moreover, the crosslinking degree increased as the amount of VTES and F-51 increased, which further indicates that VTES and F-51 have copolymerized with acrylic monomers.

Stability of latex

Table V (the annotations a, b, and c represent three different latex samples: [a]FMA = 9%, VTES = 0%, GMA = 0%; [b]FMA = 0%, VTES = 3%, GMA = 0%; and [c]FMA = 0%, VTES = 0%, GMA = 5%) shows the C.C.C, freeze-thaw stability, high temperature stability, and mechanical stability of unmodified and modified acrylic latices.

Critical coagulation concentration (C.C.C) is a criterion of the ability of counter ions to coagulating the latex. It can be seen that the copolymerization of fluorine and silicon monomer caused a reduction in C.C.C of acrylic copolymer latex, i.e., a reduction in the electrolyte stability, whereas the epoxy resin did not have a significant effect on the electrolyte stability.

In addition, all the modified acrylic latices displayed excellent stability to high temperature. Moreover, compared with the unmodified acrylic latex, the freeze-thaw stability and mechanical stability were enhanced by incorporation of fluorine monomer and silicon monomer.

CONCLUSIONS

A series of novel acrylic latices modified with fluorine monomer, silicon monomer, and epoxy resin for waterborne heavy duty coating applications were synthesized through a semicontinuous emulsion polymerization process. The optimum amount of curing agent TEA to obtain modified latices with excellent storage stability was 1.36 g of every 6 g epoxy resin. The incorporation of the FMA in the copolymers was confirmed by ^{19}F NMR and fluoride ion selective electrode analysis, although the copolymerization ratio was not very high. The incorporation of VTES and F-51 in the copolymers was confirmed by FTIR and the crosslinking degree. It can be inferred from the results of composition study that the modified acrylic latices have potential ability to combine the unique properties of fluorinated, silicated polymers, and epoxy resin. The stabilities (electrolyte stability, freeze-thaw stability, high temperature stability, and mechanical stability) of latices were investigated. The results showed that the fluorine and silicon monomers improved the freeze-thaw stability and mechanical stability but had negative effect on the electrolyte stability, whereas the epoxy resin did not affect the stabilities obviously.

TABLE V
The Information of Stabilities of Unmodified and Modified Latices

Latex	C.C.C (mol/L)	Freeze-thaw stability	High temperature stability	Mechanical stability		
				15 (min)	45 (min)	100 (min)
Unmodified acrylic latex	1.42	Little coagulation	No coagulation	No coagulation	Little coagulation	Much coagulation
[a]Fluorine-containing latex	0.74	No coagulation, viscosity increase	No coagulation	No coagulation	No coagulation	Little coagulation
[b]Silicon-containing latex	0.96	No coagulation, viscosity increase	No coagulation	No coagulation	No coagulation	Little coagulation
[c]Epoxy-containing latex	1.33	Little coagulation	No coagulation	No coagulation	Little coagulation	Much coagulation

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