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Synthesis, modification and characterization of core–shell fluoroacrylate copolymer latexes

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ABSTRACT

Core–shell fluoroacrylate copolymer latex, typically used for the protection of ancient stone monument, was synthesized in this paper by semi-continuous seed emulsion polymerization with butyl acrylate (BA) served as the core, methyl methacrylate (MMA), BA and dodecafluoroheptyl methacrylate (DFHMA, $C_{11}H_8O_2F_{12}$) served as the shell. At the same time, the above core–shell fluoroacrylate latex was modified by hydrolysis of tetraethyl orthosilicate (TEOS, $Si(OC_2H_5)_4$) in the presence of silane coupling agent dodecyltrimethoxysilane (DTMS, $C_{12}H_{25}Si(OCH_3)_3$). The chemical component of the final latex was analyzed by FT-IR. Morphology structure and the particle size of core–shell latex were determined by TEM. The effect of DFHMA and TEOS content on the latex and film properties was characterized by SEM-EDX, AFM, TEM, DSC and UV–vis. The analysis results indicated that the copolymer latex particle presented uniform sphere core–shell structure with 40–50 nm in diameter. About 30 wt% DFHMA gave favorable characteristics both in latex and in film properties. Compared with core–shell fluoroacrylate latex, the modified fluoroacrylate copolymer displayed, when TEOS was controlled in 2.2–3.8 wt%, sound performances in hydrophobic, mechanics, thermodynamics and resistance to ultraviolet.

1. Introduction

The use of polymeric materials as protective coatings has been gradually accepted and different classes of synthetic organic coatings have been used or tried for this purpose [1–4]. Among these polymeric materials, fluoropolymer have prominent superiority [5–7] due to their extraordinary properties, such as ultralow surface tension and related hydrophobicity, well antichemical and thermostability, low flammability and low refractive index, as well as excellent mechanical behavior [8–11].

However, the relatively high market price of fluorinated monomers limits their use. Therefore, much more attention was given to the synthesis of partially fluorinated polymers. Core–shell fluoroacrylate latex, composed of fluorine-free core and fluorine-containing shell, had typical advantage in film formation compared to general emulsion [12–15]. Because of the differences in hydrophobic properties and surface tension of core and shell, fluorine-containing shell preferentially migrated to the surface during the film formation, which not only maintained the excellent physical and chemical properties but also minimized the amount of fluorine. But if the core–shell fluoroacrylate latex was recommended as the protective material for the stone monument, they must provide with higher T_g value, good adhesion towards stone substrate, enough hardness, sufficient flexibility and better aging property. It has been reported that the selection of no-fluorinated and fluorinated acrylate monomers influenced fluoropolymer' glass transition temperature (T_g), the film-forming ability and the protection feasibility [16–20]. This made it possible to prepare target polymer for the purpose of improving the stone strength and protecting the stone monument from weathering by the design of core polymer and shell polymer.

As for the shortcomings of fluoropolymer, such as poor substrate adhesion and intolerance to low temperature, it could be solved by introducing silicon-containing functional group. An appropriate method was the modification of core–shell latex by introducing silicon–oxygen bond (SiO_2) for improving core–shell fluoropolymers adhesion behavior towards stone substrate and the polymers' glass transition temperature (T_g) [21–23].

The main objective of this work was the preparation and characterization of fluoroacrylate copolymer latex typically used for the protection application to ancient buildings. Firstly, fluoroacrylate copolymer latex with core–shell structure was synthesized in this paper by semi-continuous seed emulsion polymerization in the presence of mixed emulsifier of sodium lauryl sulfate (SDS) and octylphenylpolyoxyvinyl ether (TX-10) in the ratio of SDS/TX-10 = 1:2, in which butyl acrylate (BA) served as the core, methyl methacrylate (MMA), BA and dodecafluoroheptyl methacrylate (DFHMA, $C_{11}H_8O_2F_{12}$) served as the shell. The polymeric monomers

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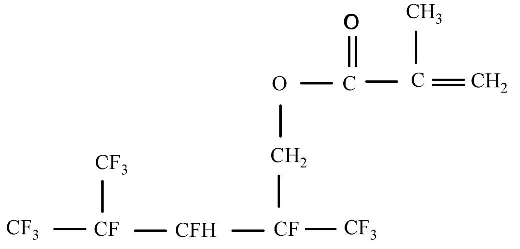
were selected based on the consideration of enough flexibility and sufficient film formation provided by BA, the higher T_g value and hardness provided by MMA, as well as lower surface energy provided by DFHMA with long fluorinated side-chain. Secondly, in order to enhance fluoroacrylate copolymer's adhesion behavior and achieve better protection performances, silica-containing fluoroacrylate copolymer was developed by the modification of above core–shell polymer with the hydrolysis of tetraethyloxysilane (TEOS, $Si(OC_2H_5)_4$) in the presence of silane coupling agent dodecyltrimethoxysilane (DTMS, $C_{12}H_{25}Si(OCH_3)_3$).

Fourier transform infrared spectrometry (FT-IR), scanning electron microscopy coupled with energy-dispersive X-ray detector (SEM-EDX), transmission electron microscopy (TEM), atomic force microscopy (AFM) as well as differential scanning calorimetry (DSC) were used not only for characterizing the morphology structure and the particle size of latexes, but also for investigating the effect of DFHMA and TEOS content on the properties of latexes and films. Ultraviolet spectrometer was used to detect the absorption of films to ultraviolet light.

2. Experimental

2.1. Materials

MMA and BA monomers, supplied by Aldrich, were washed first by 10 wt% aqueous solution of sodium hydroxide, and then by water, until pH value of the washings became neutral. The purified monomers were dried over anhydrous magnesium sulfate and stored at −5 °C. Dodecafluoroheptyl methacrylate (DFHMA, $C_{11}H_8O_2F_{12}$), shown in structure 1, was supplied by XUEJIA Fluorine–Silicon Chemical Co. Ltd. (China).



Structure 1 Dodecafluoroheptyl m ethacrylate (DFHMA, $C_{11}H_8O_2F_{12}$)

SDS and octylphenylpolyoxyvinyl ether (TX-10) were both of chemical purity and mixed in the ratio of SDS/TX-10 = 1:2. Tetraethyl orthosilicate (TEOS, $Si(OC_2H_5)_4$) and dodecyltrimethoxysilane [DTMS, $C_{12}H_{25}Si(OCH_3)_3$)] were provided by Silicone Company of Wu Han University (China). Ammonium persulfate (APS) was of analytical purity.

2.2. Synthesis of core–shell fluoroacrylate copolymer latex

The core–shell fluoroacrylate copolymer latex was prepared by two-stage semi-continuous seed emulsion polymerization. All the polymerization steps were carried out under the protection of nitrogen atmosphere in a 250-ml four-neck flask equipped with reflux condenser, mechanical stirrer, separating funnel and inlet for nitrogen gas. Detail recipes of core–shell fluoroacrylate copolymer were shown in Table 1.

Firstly, BA was emulsified in a mixed emulsifier (SDS/TX-10) at 50 °C for 0.5 h, a part of initiator (APS) was added when temperature was increased to 80 °C. Keep this temperature for 0.5 h for the production of core polymer. Secondly, the mixture of BA/MMA/DFHMA for the shell and another part of APS were added drop-by-drop during 3–4 h. After the addition of all these materials, the temperature was increased additionally 5 °C and lasted for 0.5 h. When the reaction was over, the temperature was reduced to 25 °C and the reaction was terminated by the addition of $NaHCO_3$ (pH 6–7).

2.3. Synthesis of silica-containing fluoroacrylate copolymer latex

The silica-containing fluoroacrylate copolymer latex was prepared by two steps. The first step was the preparation of the core–shell fluorinated acrylate copolymer latex as described above. The second step was the hydrolysis of TEOS in the presence of DTMS. In the second step, 2.20–4.68 wt% TEOS and 0.02–0.11 wt% DTMS were added by drops into the prepared core–shell latex. The hydrolysis of TEOS was maintained at 75 °C for 6 h with HCl as catalyst. The pH value was controlled in the range 3–5 during the hydrolysis reaction.

2.4. Characterization of latexes and films

Fourier transmission infrared spectra of core–shell fluoroacrylate copolymer and silica-containing fluoroacrylate latex were obtained by an AVATER-360B FT-IR spectrometer. The film formed by latex was cast from chloroform solutions and dried under vacuum at 60 °C for 5 h after purified by precipitation in excess methanol and by washing in deionized water. A JEM-3010 TEM, performed in an ultrahigh vacuum chamber equipped with a hemispherical electron energy analyzer, was used to observe the configuration particles and the morphology structure. The particle morphology of core–shell latex was obtained after staining latex particle by phosphotungstic acid solution pH = 6.4.

Table 1

The detailed recipe for the synthesis of core–shell fluoroacrylate copolymer latex

	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
Seed (batch) (0.5 h, 80 °C)					
BA (g)	10	10	10	10	10
MMA (g)	0	0	0	0	0
SDS/TX-10 (g)	1.800	1.800	1.800	1.800	1.800
APS (g)	0.050	0.050	0.050	0.050	0.050
Water (g)	50	50	50	50	50
Shell (drop-by-drop) (3–4 h, 80 °C)					
BA (g)	5	5	5	5	5
MMA (g)	10	10	10	10	10
DFHMA (g)	4	6	10	12	14
APS (g)	0.095	0.1050	0.1250	0.1350	0.1450
Water (g)	0	4	10	13	17

The monomer conversion and solids content were measured by gravimetric analysis. A certain quantity of emulsion (m_1) was cast onto a Petri dish (m_0), and dried to a constant weigh (m_2) in a dry oven at 110 °C. The solids content and final conversion, respectively, were calculated by the following formulas:

$$\text{solids content}\,(\%) = \frac{m_2 - m_0}{m_1}$$

$$\text{monomer conservation}\,(\%) = \frac{[m_3 \times \text{solids content}\,(\%)] - m_4}{m_5} \times 100$$

where m_3 is the total weight of all the materials put in the flask in each polymerization, m_4 is the weight of emulsifier, and m_5 is the weight of total monomers.

The coagulum content was measured using gravimetric method by determining the dry mass of coagulum (m_g), latex mass (m_e), and calculated as follows:

$$\text{coagulum content}\,(\%) = \frac{m_\mathrm{g}}{m_\mathrm{e}} \times 100$$

The storage stability of latex was symbolized by storing the latexes at room temperature for a year or at 50 °C for 2 months.

The tested films were prepared on a cleaned glass panel by drying for 7 days at room temperature or drying at 50–60 °C for 5 h.

A NETZCH DSC-200 was used to measure the glass transition temperatures of films from the tested curves recorded at 10 °C/min as the range of −100 to 100 °C.

JSM-6460 scanning electron microscopy coupled with electron beam microprobe analysis using an SEM-EDX was employed to characterize the morphology of films and to determine the elementary composition on the film surface. The determination of elementary composition was carried out at an acceleration voltage of 25–30 keV, lifetime >50 s, CPS ≈ 2000 and working distance 34 mm. AFM was used for analysis the film surface evenness. Ultraviolet spectrometer UV-240 was used to detect the absorption of films to ultraviolet light.

Water absorption of films was measured by gravimetric variation before and after immerging the films into deionized water for 24 h. The hardness of films was tested by pencil sclerometer. The acid and alkali resistance of films was calculated by the film size variation in 5% (v/v) HCl and 5 wt% NaOH for 7 h.

3. Results and discussions

3.1. Analysis of chemical component of latexes

Fig. 1 shows the FT-IR spectra of the core–shell fluoroacrylate copolymer latex (a) and silica-containing fluoroacrylate copolymer latex (b). Both (a) and (b) exhibited the characteristic stretching peaks of C–H (CH_2) at 2958 and 2874 cm^{-1}, stretching vibration of C=O at 1734 cm^{-1}, and distortion vibration of CH_2 at 1454 and 1388 cm^{-1}. Absorption at 970 cm^{-1} was the characteristic peak of BA. The typical stretching vibration and wagging vibration of C–F bonds were at 1246 and 690 cm^{-1}. Fig. 1 revealed that BA, MMA and DFHMA have taken part in the polymerization. Compared with core–shell fluoroacrylate copolymer latex (Fig. 1(a)), dissymmetry flexible vibration of Si–O–Si at 1100–1140 and 476 cm^{-1} was detected in Fig. 1(b) for silica-containing fluoroacrylate copolymer latex. Stretching vibration of O–H at 3444 cm^{-1} in Fig. 1(b) was intensified because of the hydrolysis of Si–O–R. Due to the abundance of CH_2 in DTMS, absorption peaks of CH_2 were strengthened, especially at 842 and 750 cm^{-1} in the fingerprint region of Fig. 1(b). FT-IR spectra of Fig. 1(b) confirmed the silica-containing fluoroacrylate copolymer latex.

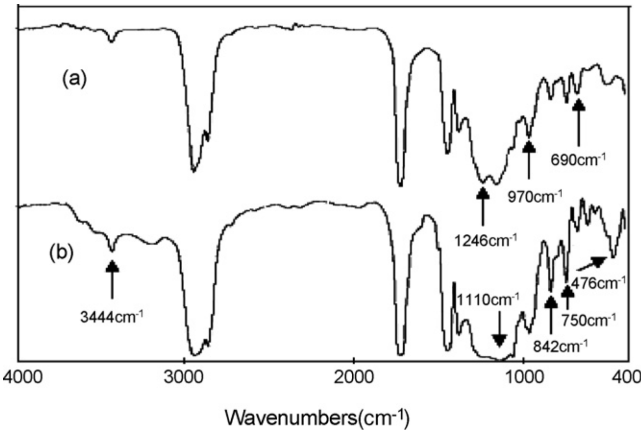


Fig. 1. FT-IR spectra of fluoroacrylate copolymer latex (a) and silica-containing fluoroacrylate copolymer latex (b).

3.2. The effect of DFHMA content on the properties of latex and film

Table 2 listed the effect of DFHMA content on the mechanical stability, solid content and the monomer conversion of core–shell fluoroacrylate copolymer latexes. The latexes had proper mechanical stability and the solid content was 34–39 wt%. The monomer conversion was in nonlinear relationship with the increase of DFHMA amount, but a tendency decreased at first and then increased (Table 2). This phenomenon was dependent on the polymerization process and the properties of monomers. The lower activity of DFHMA made it easy to polymerize at low content. On the other hand, when the polymerization was started, the seed of latex was produced promptly; after the seed of latex was formed, there was very little possibility in forming new seed due to both the insoluble mixture in water and the monomers adding method by drops. Therefore, the core was completely covered by poly(BA/MMA/DFHMA) shell. This led to higher monomer conversion (Table 2). But when the latex was hydrophobic, DFHMA was difficult to satisfy further polymerization, so that the monomer conversion would be lower which led to lower monomer conversion.

Table 3 listed the effect of DFHMA content on the film properties. The optical observation of films formed by core–shell fluoroacrylate copolymers were colorless and transparent when DFHMA amount was controlled less than 30 wt%, but a semitransparent film when DFHMA amount was over 30 wt%. It was because of the decrease of reflectivity resulting from the increase of F element on the film surface with the increasing in DFHMA amount in shell. SEM images displayed that continuous and evenness film was obtained by 30 wt% DFHMA (Fig. 2a), corrugation film when DFHMA content was more than 30 wt%, such as agglomerate phenomenon in 36 wt% DFHMA (Fig. 2b).

EDX analysis indicated that the amount of fluorine in the film surface was proportional to the DFHMA content, but a little higher

Table 2
Effect of DFHMA content on the properties of core–shell fluoroacrylate latex

	DFHMA content (g)				
	4.00	6.00	10.00	12.00	14.00
DFHMA content (wt%)	13.79	19.35	28.57	32.43	35.90
Monomer conversion (wt%)	95.88	95.33	98.03	94.73	87.12
Solid content (wt%)	34.62	34.78	38.14	39.02	38.89
Mechanical stability	Stable	Stable	Stable	Stable	Stable

Table 3
Characteristics of the film formed by core–shell fluoroacrylate latex

	DFHMA content (wt%)				
	13.79	19.35	28.57	32.43	35.90
w(F) on the film surface (%, by EDX)	7.99 (1.65)*	12.02 (8.24)	21.76 (33.58)	23.46 (26.88)	24.28 (18.67)
w(F) on the film surface (%, theoretical)	7.86	11.03	16.29	18.49	20.46
Film appearance	Colorless, transparent	Colorless, transparent	Colorless, transparent	Colorless, semitransparent	Colorless, semitransparent
Film SEM characteristic	Smoothness	Smoothness	Smoothness	Agglomerated	Agglomerated
Water absorption (wt%)	17.57	14.88	11.21	10.50	9.14
Film hardness (pencil nick)	1H	2B	2B	4B	5B
Size change in NaOH (%)	0.98	0.55	0.24	0.23	1.61
Size change in HCl (%)	0.89	0.61	0.67	0.49	0.40
Xylene rubbing (100 returns)	No defects	No defects	No defects	No defects	Small scratch
Resistance to hot water	No defects	No defects	No defects	No defects	No defects
Storage stability	No coagulation	No coagulation	No coagulation	No coagulation	No coagulation

Where * represents increased percent of F content, it was calculated by the ratio of the difference of experimental value and theoretical value by theoretical value.

than theoretical value (Table 3). When DFHMA was controlled in 14–30 wt%, the experimental value was higher 1.65–33.58% than the theoretical value, but when DFHMA was controlled in 32–36 wt%, the experimental value was higher 26.88–18.67% than the theoretical value, which was in agreement with the monomer conversion (Table 2). It implied that fluorine-containing groups were collected onto the film surface and gradually reached a saturation state with the increase of DFHMA content.

According to the effect of DFHMA content on the properties of core–shell fluoroacrylate copolymer latexes and films, it was impracticable to improve copolymer properties only depending on increasing fluorinated acrylate monomers amount. For this core–shell fluoroacrylate copolymer, the appropriate DFHMA content should be controlled in about 30 wt% in order to obtain the higher monomer conversion (98 wt%) and better film properties.

3.3. The modification of latex by TEOS

During the modification of the synthesized core–shell fluoroacrylate latex by the hydrolysis of TEOS, namely the formation of silica-containing fluoroacrylate copolymer latex, the main chemical reactions were shown in Fig. 3. The deduced interaction between SiO_2 and latex included three steps. Firstly, TEOS hydrolyzed and formed SiO_2 sol in nano-particle. Secondly, nano-SiO_2 was chemically modified by DTMS. Finally, the modified SiO_2 gel particles were coated by core–shell latex.

In the second step, in order to stabilize latex and let nano-SiO_2 be easily coated with latex, a small amount of silane coupling agent DTMS was very necessary to embellish nano-SiO_2. However, excess DTMS made latex higher viscosity and over cross-linked, which lead to much coagulum (Fig. 4). The analysis revealed that the

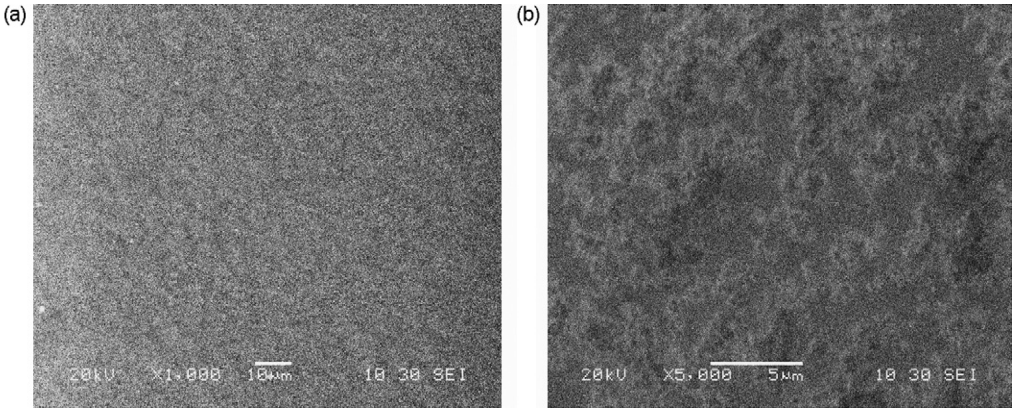


Fig. 2. SEM micrograph of film surface in 30 wt% DFHMA (a) and 36 wt% DFHMA (b).

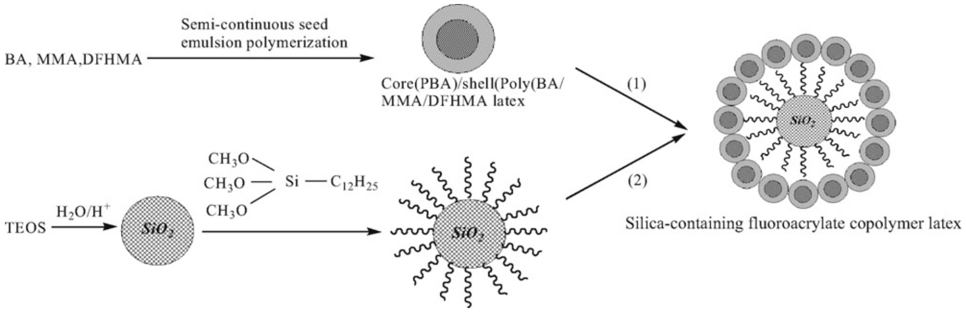


Fig. 3. Schematic diagram of the formation of silica-containing fluoroacrylate copolymer latex and deduced interaction between nano-SiO_2 and core–shell latex.

Table 4
Effect of TEOS content on the silica-containing fluoroacrylate copolymer latex properties

	TEOS content (wt%)					
	0	2.20	3.10	3.80	4.40	4.68
Solid content (wt%)	35.30	49.20	36.10	45.90	38.50	36.90
Centrifugal stability	Stable	Stable	Stable	Stable	Little of deposit	Little of deposit
Coagulum content (wt%)	0	0.50	0.80	1.40	13.60	40.50

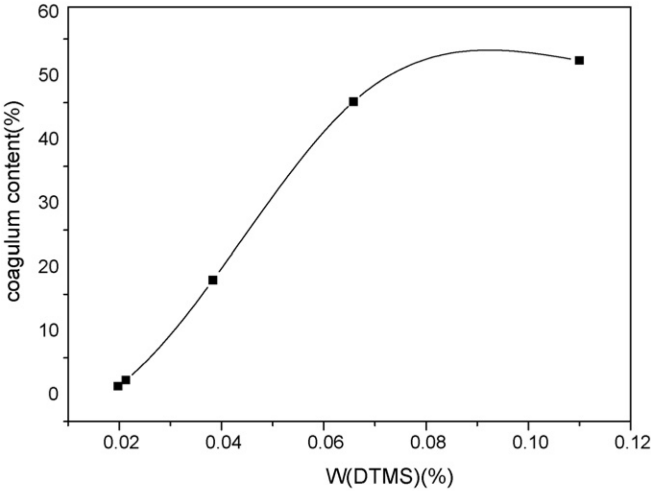


Fig. 4. Effect of DTMS content on the coagulum amount.

amount of DTMS should be controlled in 0.02–0.022 wt% for avoiding much coagulum formation.

3.4. *The effect of TEOS content on the latex and film properties*

Table 4 listed the interrelation between TEOS content and the properties of latex when DFHMA content was controlled in 30 wt%. Coagulum content was increased when TEOS content increased. It was difficult for fluoroacrylate copolymer latex to coat much SiO_2 sol particle produced by excess TEOS. In this study, the amount of TEOS was controlled in 2.2–3.8 wt% to assure less coagulum formation and sufficient dispersion of latex, and at the same time to exert the characteristics of nano-SiO_2.

The TEM micrograph was shown in Fig. 5. Uniform spherical core–shell structure was presented due to the difference of electron penetrability to the core and shell. In both latexes, TEM micrographs showed that the core–shell particles were uniform in sphere shape with the diameter of about 40–50 nm and the shell was about 6 nm in thickness. In Fig. 5b, the light and dark regions in the particles corresponded to PBA core and poly(BA/MAA/DFHMA) shell, respectively.

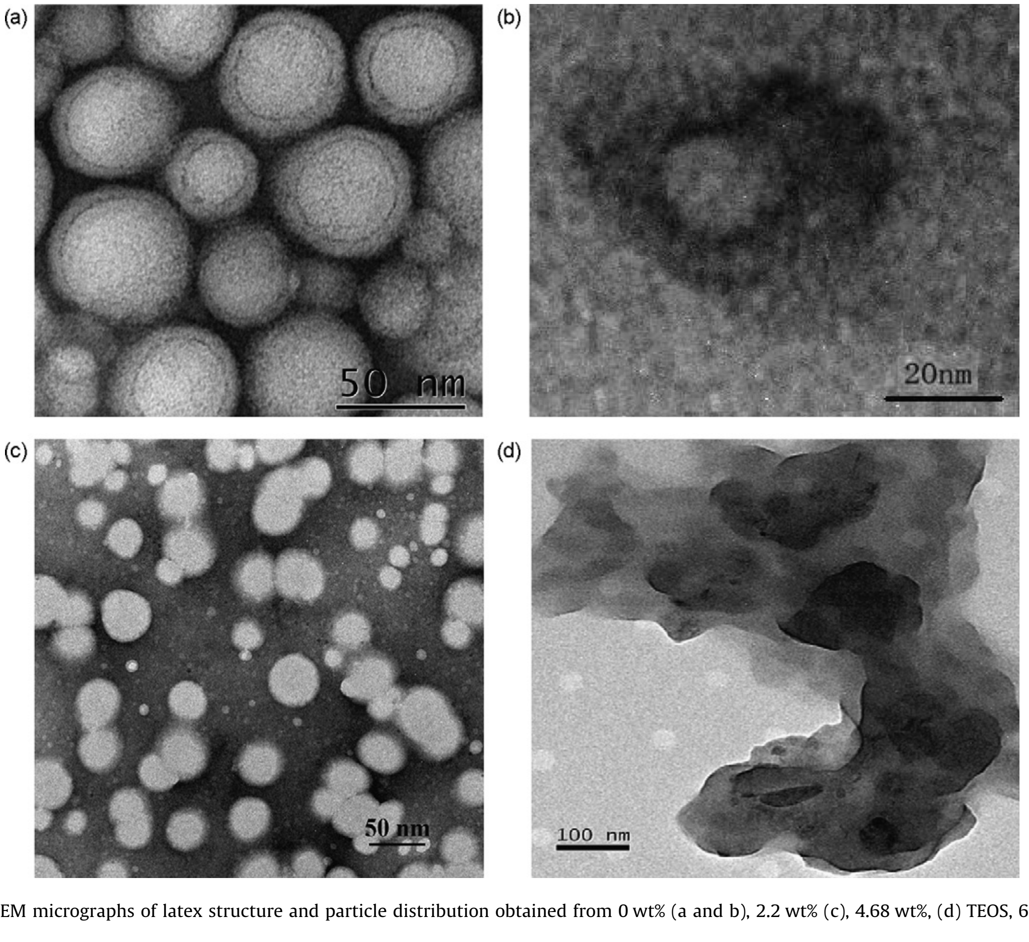


Fig. 5. TEM micrographs of latex structure and particle distribution obtained from 0 wt% (a and b), 2.2 wt% (c), 4.68 wt%, (d) TEOS, 60,000×.

Table 5
Properties of the films formed by silica-containing fluoroacrylate copolymers

	TEOS content (wt%)					
	0	2.20	3.10	3.80	4.40	4.68
w(F) on the film surface (%, by EDX)	21.76	23.47	23.32	23.74	23.93	23.79
w(F) on the film surface (%, theoretical)	16.29	14.62	14.32	14.10	13.90	13.68
w(Si) on the film surface (%, by EDX)	0	0.41	0.80	1.48	1.74	2.23
w(Si) on the film surface (%, theoretical)	0	0.95	1.30	1.56	1.78	1.88
Tensile strength (MPa)	110	174	224	130	380	272
Rupture protraction (%)	472	302	120	300	148	96
Water absorption (%)	11.21	10.05	9.88	9.64	8.75	7.02
Size change in NaOH (%)	0.24	0.24	0.21	0.17	0.13	0.13
Size change in HCl (%)	0.67	0.59	0.34	0.07	0.19	0.18
Xylene rubbing (100 returns)	No defects	No defects	No defects	No defects	Small scratch	Small scratch
Resistance to hot water	No defects	No defects	No defects	No defects	No defects	No defects
Storage stability	No coagulation	No coagulation	No coagulation	No coagulation	No coagulation	No coagulation
T_g (°C) (shell)	30.3	45.5	37.5	38.6	39.7	40.9

The modification by TEOS and DTMS made the particles much more uniform and tight distribution (Fig. 5c) in water solution than unmodified one (Fig. 5a). But excess TEOS, such as 4.68 wt%, converted the particle size abnormal and in a tangle shape, which made no obvious limit between particles (Fig. 5d).

Table 5 listed the effect of TEOS content on films properties obtained from the silica-containing fluoroacrylate copolymer latex when DFHMA content was in 30 wt%. SEM-EDX analysis showed that fluorine-containing groups in silica-containing fluoroacrylate copolymer latex was much easier to migrate to the surface during film formation. However, silicon content was a little less than theoretical value (Table 5). It can be inferred that there were a few silica particles protruding from the surface and that most silica particles lay under a covering of polymer during film forming. This indicated the difference of self-migration and orientation between fluorine-containing groups and silica particles. The orientation of F and Si played a key role for the product properties, which was not only suitable for the combination of latex with stone substrate but also favorable to embody extraordinary surface properties of fluoroacrylate. It was the enrichment of F element on the film surface that made the film suitable for size stability in acid and alkali and lower water absorption compared with core–shell fluoroacrylate copolymer (Table 5).

A comparison of film surface topography between core–shell fluoroacrylate copolymer and silica-containing fluoroacrylate copolymer latex was carried out using SEM and AFM. SEM analysis showed that SiO_2 produced by the hydrolysis of TEOS really improved the film appearance (Fig. 6a), but excess TEOS brought about agglomeration on the surface (Fig. 6b). The observation in cross-section of films revealed that the presence of SiO_2 reduced the lacuna of film (Fig. 5c and d) and caused the film continuum

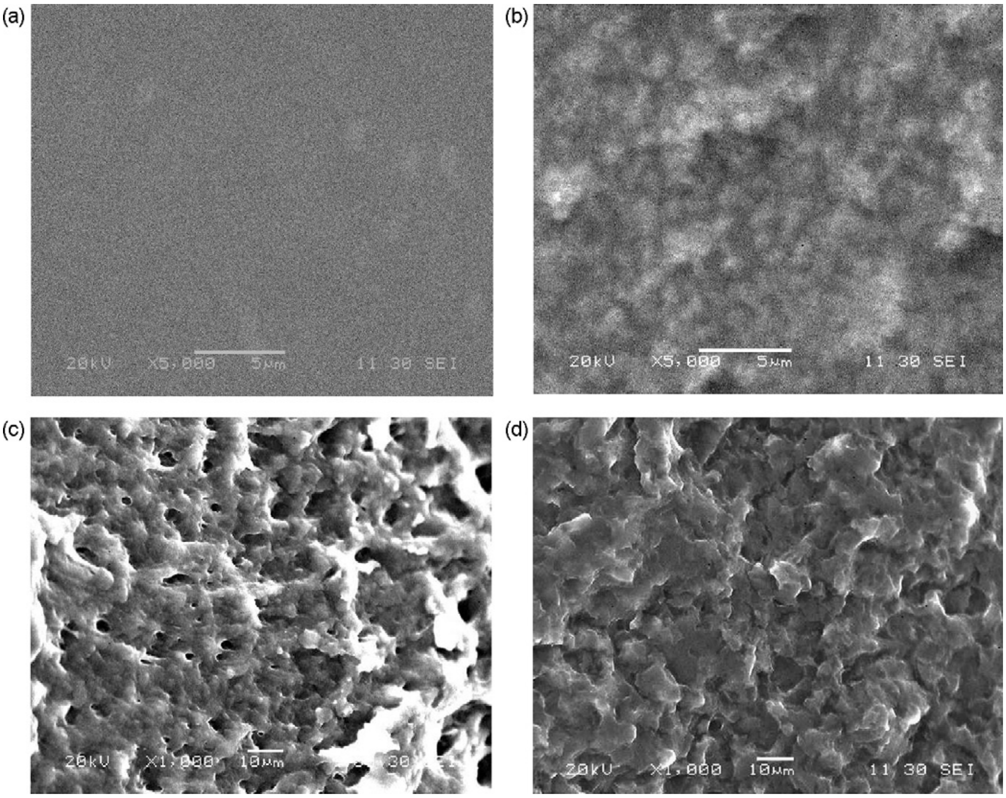


Fig. 6. SEM micrograph of film surface in 2.2 wt% TEOS (a), 4.4 wt% TEOS (b) and cross-section before (c) and after (d) modification by TEOS.

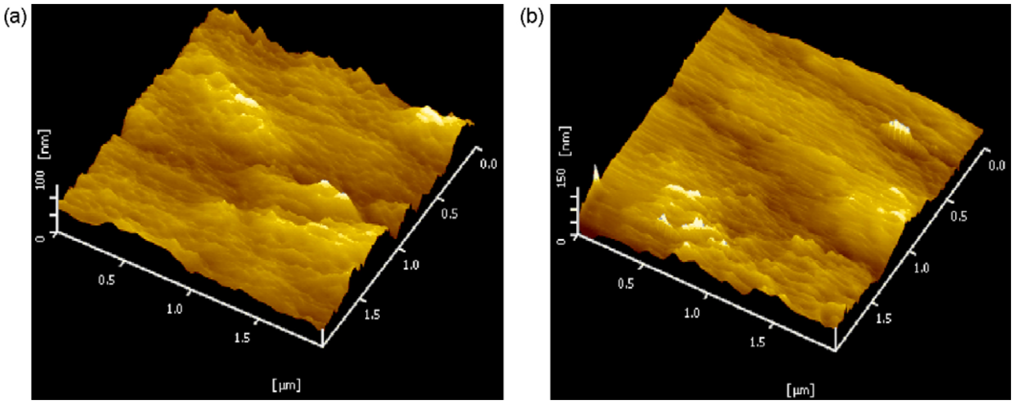


Fig. 7. AFM image of films in 30 wt% DFHMA (a) and modified by TEOS (b).

and compactness, which illustrated the effect of nano-SiO_2. AFM analysis in Fig. 7 also indicated that the film surface obtained from silica-containing fluoroacrylate copolymer latex was much more smooth and homogeneous.

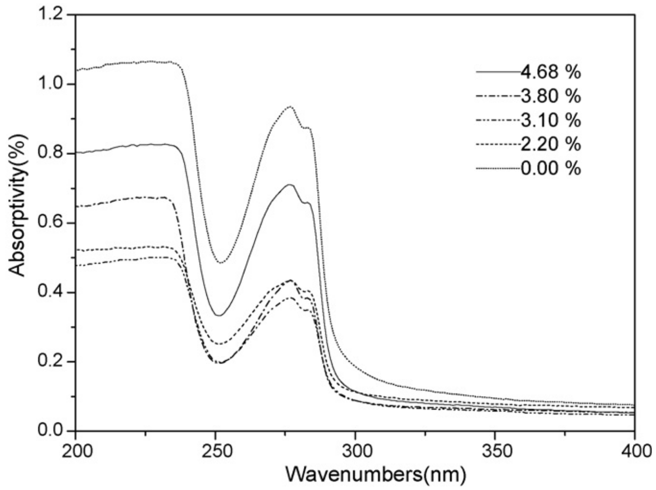


Fig. 8. UV-Vis spectra of films obtained from 0 wt/%, 2.20 wt/%, 3.10 wt/%, 3.80 wt/%, 4.68wt/% TEOS.

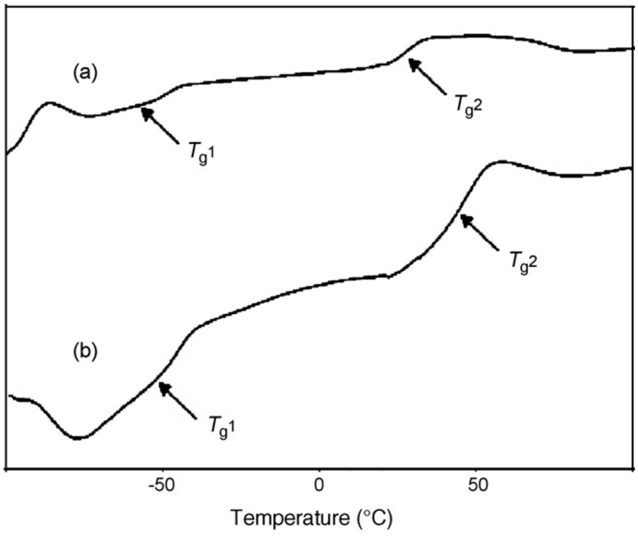


Fig. 9. DSC curve before modification with 30 wt% DFHMA (a) and after modification with 2.2 wt% TEOS (b).

The film absorption to UV light (Fig. 8) reached its maximum in 275 nm, which was assigned to carbonyl band ultraviolet absorption peak. The higher reflection of nano-SiO_2 to UV light reduced the absorption and ensured the film the ability of anti-aging from light. When TEOS was 4.68 wt%, the absorbance was decreased by 25%, and 2.20–3.10 wt% TEOS decreased by 58–60%.

Glass transition temperature (T_g) was obtained by DSC curves on films. Two T_g values in core–shell fluoroacrylate copolymer with 30 wt% DFHMA and silica-containing fluoroacrylate copolymer with 2.2 wt% TEOS were clearly displayed in Fig. 9(a) and (b), respectively, which indicated that the core–shell structure latex was formed and modified latex increased shell T_g values. The shell T_g values for fluoroacrylate copolymer were listed in (Table 5). The modified latex with 30 wt% DFHMA obviously increased T_g value from 30 to 45 °C when TEOS content was in 2.2 wt% due to the entanglements and strong interaction between silica particles and polymer which resulted in low polymer fluidity, but descend with the increase of TEOS content maybe due to facility of Si–O–Si bond.

4. Conclusions

The core–shell fluoroacrylate copolymers latex and silica-containing fluoroacrylate copolymer latex were obtained by semi-continuous seed emulsion polymerization, in which BA served as the core, and BA/MMA/DFHMA as the shell. The latexes particles presented uniform spherical core–shell structure with the particle size 40–50 nm in diameter. The effect of DFHMA content on the properties of latexes and films indicated that the latex in about 30 wt% DFHMA performed favorable characteristics. The stability of the final latex was good enough.

Modification of the latex by TEOS and DTMS facilitated to increase the latex's T_g value and to perform better film-forming ability because of the production of SiO_2 by the hydrolysis of TEOS. But the amount of TEOS were limited in 2.2–3.8 wt% and DTMS in 0.02–0.022 wt% in order to assure sufficient dispersion in emulsion and to play the characteristics of nano-SiO_2. The fluoro-silica-containing latexes performed suitable properties in hydrophobicity, mechanics, optics, thermodynamics and resistance to ultraviolet.

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