

Research Article

Engineered Multifunctional Fluorinated Film Based on Semicontinuous Emulsion Polymerization Using Polymerizable Quaternary Ammonium Emulsifiers

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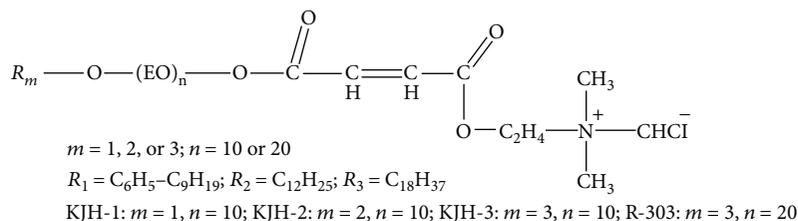
Along with society's progress, high-quality coatings are widely used. Although fluorinated polymers were successfully prepared by semicontinuous emulsion polymerization with surfactants, chlorotrifluoroethylene (CTFE), and acrylate monomers, the optimization collocation of surfactants still has room for improvement. The traditional emulsifiers are physically absorbed onto the surface of latex particles. The latex film generated by latex particles is unstable in water, which limits its application. Herein, a novel series of cationic quaternary ammonium polymerizable surfactant was selected because it can react with CTFE and acrylate monomers and can become a part of the polymers. We also studied the effects of emulsifier type on resultant emulsion properties. In addition, wonderful weatherability, water resistance, and antibacterial and antifouling of the multifunctional fluorinated films were observed, which would open up a bright future for coating industries.

1. Introduction

Fluoropolymers have recently attracted considerable attention due to their excellent chemical resistance, low dielectric constant, good hydrophobicity/oleophobic, and weatherability [1–4], which are extensively used in the fields of micro-electronic devices, coatings, optical devices, finishing agents, and biomedical implants [5–8]. Compared with traditional fluoropolymer like polytetrafluoroethylene (PTFE) [6, 9], poly(chlorotrifluoroethylene) might have a better application prospect since it is incomparably superior to gas barrier and optical transmittance. Unfortunately, the real performance achieved with pure poly(chlorotrifluoroethylene) is far from our expectations. Several factors could be responsible for

this: (1) the higher crystallinity leads to its weak organic solubility; (2) because of its high melting point (220°C), the manufacturing process will cause additional loss of energy; and (3) poor adhesion also brings about a big discount of the film forming ability. To circumvent these obstacles and cut the cost, the copolymerization of chlorotrifluoroethylene (CTFE) with other acrylate monomers seemed to be an ideal solution [1, 10–12].

Nowadays, various methods have been proposed to prepare polymers, such as suspension polymerization, solution polymerization, controlled radical polymerization, and emulsion polymerization [1, 11, 13, 14]. Among the abovementioned means, emulsion polymerization is an environment-friendly and high-efficiency technology, attributing to



SCHEME 1: The chemical structure of different cationic quaternary ammonium polymerizable surfactants.

avoiding poisonous organic solvent (e.g., 1,1,1,3,3,5-perfluorobutane), good product stability, and suitability for large-scale industrial production [15]. As we all know, the appropriate emulsifier profoundly impacts the whole emulsion polymerization. The extreme hydrophobicity of the monomers and conventional emulsifiers limits further development. Besides, even after the formation of latex particles, the force between emulsifiers and latex particles is still ordinary physical adsorption, which increases the risk of desorption from the surface of latex particles and reduces storage stability for emulsion. In addition, when the fluoropolymer film prepared by latex particles is immersed in water, the emulsifier will be easy to migrate and results in environmental pollution [16–19].

In this sense, polymerizable quaternary ammonium surfactants with vinyl groups pave a new avenue for emulsifier innovation owing to advantageously introducing direct free radical polymerization and antibacterial properties [17, 19–21]. However, the inferior activity of these polymerizable surfactants has been the main problem that limits their application [22]. Many researchers had proposed the semicontinuous emulsion polymerization to solve this problem [18, 23]. So far, there are a few reports devoted to the effect of film surface morphology, hydrophobicity, and quaternary ammonium component on the variation in antibacterial behaviour [21, 24]. For instance, Hatakeyama et al. found that the polymer-containing quaternary ammonium groups possess superb antiadhesion for BSA proteins [25]. It is a pity that the investigation has not been thoroughly discussed. If the aforementioned polymer contains fluorine, the degree of antimicrobial activity perhaps might be different. In fact, fluorine greatly influences the wettability and microstructure of polymer surface, thereby further affecting protein adsorption [26]. Without doubt, comprehensive understanding of the chemical constituents-protein adsorption relationship is essential to design new materials for medical antibacterial coating field, such as intraocular lens coatings.

Motivated by these considerations, in this paper, a series of novel fluoropolymers was successfully prepared by semicontinuous emulsion polymerization of CTFE, vinyl acetate (VAc), n-butyl acrylate (BA), versatic acid 10 esters (Veova10), and acrylic acid, using a special polymerizable quaternary ammonium salt as the emulsifier. Meanwhile, the effects of emulsifier type on conversion, particle size, and storage stability were adequately discussed. The chemical structure and latex particle size distribution were investigated by FTIR and dynamic light scattering (DLS), respectively.

Weatherability, water resistance, antibacterial properties, and protein adsorption as well as their relationship with chemical composition were also characterized.

2. Materials and Methods

2.1. Materials. CTFE, vinyl acetate (VAc), n-butyl acrylate (BA), versatic acid 10 (Veova10) esters, hexadecyltrimethylammonium bromide (CTAB), octylphenol polyoxyethylene ether (NP-10), 2,2'-azobis[2-methylpropionamide] dihydrochloride (AIBA), potassium persulfate (KPS), styrylphenol polyoxyethylene ether (600#A), and sodium dodecyl sulfate (SDS) were purchased commercially and used without further purification. The series of cationic quaternary ammonium polymerizable surfactants (KJH-1, KJH-2, KJH-3, and R-303) was supplied from Henan Titaning Chemical Technology Co., Ltd., China, and used as received. Their chemical structures are shown in Scheme 1. Deionized water was prepared by distillation.

2.2. Procedures for Fluoropolymer Synthesis

2.2.1. Pre-Emulsification of the Monomers. Pre-emulsion was fabricated by a similar recipe based on the previous report in our lab [4]. Quite simply, the prescribed amount of emulsifier was dissolved in 98.97 g deionized water. Then, 141.54 g of VAc (1.6441 mol), 47.21 g of BA (0.3683 mol), and 47.18 g of Veova10 (0.2395 mol) were added into the emulsifier solution with a stirring rate of 500 r/min and kept for 30 min to obtain the pre-emulsion. The amount of emulsifiers used in the fluoropolymer synthesis is listed in Table 1.

2.2.2. Semicontinuous Polymerization. The 10% (wt.%) resultant pre-emulsion and 80.00 g of CTFE were introduced into a 1 L autoclave at vacuum state with the assistance of agitation at 500 r/min for 30 min. Afterwards, 5% (wt.%) resultant pre-emulsion, 0.34 g of AIBA, and 176.79 g of deionized water were slowly added to the reactor. Under constant stirring, the system was heated to 75°C and kept for 25 min. The rest of the resultant pre-emulsion were mixed with AIBA (0.99 g) and deionized water (52.74 g) and injected dropwise with modest stirring for 3 h. Subsequently, AIBA (0.34 g) dissolved in the deionized water (18.26 g) was dripped into the autoclave. Finally, the polymerization was continued to maintain for an additional 3 h.

2.3. Characterization. Monomer conversion was measured by the gravimetric method. The samples were dried at

TABLE 1: Recipes for the pre-emulsion process.

Sample	KJH-1 (g)	KJH-2 (g)	KJH-3 (g)	R303 (g)	CTAB (g)	600#A (g)	NP-10 (g)	SDS (g)	Pre-emulsion stability
L1	9.39	0	0	0	0	0	0	0	Good
L2	0	9.39	0	0	0	0	0	0	Poor
L3	0	0	9.39	0	0	0	0	0	Poor
L4	0	0	0	9.39	0	0	0	0	Good
L5	0	0	0	0	9.39	0	0	0	Poor
L6	9.39	0	0	0	0	4.06	0	0	Good
L7	0	9.39	0	0	0	4.06	0	0	Good
L8	0	0	9.39	0	0	4.06	0	0	Good
L9	0	0	0	9.39	0	4.06	0	0	Good
L10	0	0	0	0	9.39	4.06	0	0	Good
L11	0	0	0	0	0	6.72	5.2	1.34	Good

120°C for 2 h, and the residual polymer was weighed. Conversion (%) was calculated as follows:

$$\text{conversion}(\%) = \frac{W_2}{W_1} \times 100\%, \quad (1)$$

where W_1 is the total weight of all monomers and emulsifiers and W_2 is the weight of the residual polymer.

In fact, the fluorine content ($F\%$) is one reflection of the CTFE proportion in the copolymer chains. Therefore, the lanthanum nitrate method is applied to investigate $F\%$ [27, 28]. Specifically, 10–25 mg of the sample was sealed with a filter paper flag and fastened to a platinum wire. Eight mL of deionized water was injected into 250 mL of Molotov cocktails, followed by bubbling with oxygen for 20 s, then filtered the light. Immediately, the sample was inserted into the abovementioned solution, ensuring complete combustion and decomposition. During this process, the mixture was constantly shaken to facilitate smoke absorption. Afterwards, 10 mL of acetone was used for rinsing the stopper. Perchlorate solution (HClO_4 , 2 mol/L) was added dropwise into the above suspension and kept at 70°C for 5 min. Subsequently, 1 g of hexamethylenetetramine, 20 mL of acetone, and four drops of hematoxylin indicator (2.5 g/L) were added with the assistance of shaking. The obtained solution was treated with titration using titrate lanthanum nitrate standard solution ($[1/3 \text{ La}(\text{NO}_3)_3] = 0.1 \text{ mol/L}$). When the solution color turned pale blue from yellow, the consumption volume (V) was recorded and blank experiment (V_0) was also monitored. $F\%$ was defined as follows:

$$F\% = \frac{\text{CL} \times (V - V_0) \times 19.00 \times 100}{m \times 1000}, \quad (2)$$

where CL (mol/L) represents the $1/3 \text{ La}(\text{NO}_3)_3$ molar concentration of the standard solution, m (g) represents the sample quality, and 19.00 (g/mol) represents the molar quality of the fluorine atoms.

The amount of coagulum was measured by collecting coagulum after filtering the latex (mesh 300) and calculating as percentage of the total added weight. The viscosity of the emulsion was recorded on a rotating viscometer

with 2# rotor (NDJ-1 style, Shanghai Jingke Instrument Company, China). For the freeze/thaw stability test, 50 g of latex (in a 100 mL plastic bottle) was kept at -5°C for 18 h. After another 6 h at room temperature, flocculation of the latex sample was observed. Next, the electrolyte stability was tested with 1 mL of CaCl_2 solution (0.25 M) added into a 10 mL test tube containing 5 mL of emulsion, with the delamination, precipitation, and flocculation observed after 24 h. Storage stability of the emulsion was carried out in 250 mL glass bottles with 200 mL of emulsion, at airtight condition and room temperature. The emulsion was examined whether there was diversion water, stratification, and precipitation phenomenon after storage of one month.

The FTIR spectrum was measured using pellets of the emulsion with an EQUINOX 55 spectrometer (Bruker Optics, Karlsruhe, Germany) in the range of 400 to 4000 cm^{-1} . The particle diameter was collected from DLS (Zetasizer 1000/DTS-5101, Malvern Instruments, UK); the polydispersity index (PDI) of the particle diameter was calculated automatically. The QUV accelerated weathering test was performed on the sample by an Accelerated Aging Tester (Q-PANEL, Q-Lab Corporation, Cleveland, OH, USA) under the conditions of 0.6 W/m^2 irradiance, 60°C base panel temperature, and wavelength of 343 nm UV.

Water resistance: latex films were obtained by placing the required amount of latex on a glass substrate and air-drying at room temperature for 24 h. Films were removed carefully, and square ($2.5 \times 2.5 \text{ cm}$) samples were prepared and dried at 40°C under vacuum for 24 h. The preweighed dry films were immersed into water for some days. At various times (approximately one time every 4 days), after careful blotting of the surface liquid with filter paper, the samples were weighed as quickly as possible.

Water absorption of films: the emulsion is put in a petri dish for uniform film and maintained dry for 7 days. Dry film thickness was about 1.0 mm, and it was cut into the size of $2 \text{ cm} \times 2 \text{ cm}$. The initial mass of film is defined as M_1 , whereafter the film was inserted into distilled water for 24 h. Prior to weighing, it was taken out and the water film surface was wiped gently with filter paper and the corresponding mass

TABLE 2: Influence of the nine stable pre-emulsions on the prepared emulsion properties.

Sample	Conversion (%)	F% (theory)	F% (test)	Coagulum (%)	Viscosity (mPa·s)	Particle size (nm)	PDI	Freeze/thaw stability	Electrolyte stability	Storage stability
L1	95.22	11.99	11.19	0.108	17.5	189.4	0.037	Pass	Pass	No change
L4	93.76	11.99	10.26	0.130	20.0	195.8	0.03	Pass	Pass	No change
L6	94.16	11.99	10.67	0.135	35	130.1	0.021	Pass	Pass	No change
L7	94.92	11.99	10.29	0.187	150	53.6	0.147	Pass	Pass	Demix
L8	86.85	11.99	9.37	8.925	173	66.4	0.17	Pass	Fail	Demix
L9	96.13	11.99	11.40	0.177	27.5	142.9	0.023	Pass	Pass	No change
L10	88.25	12.34	9.88	9.238	370	87.1	0.191	Pass	Pass	No change
L11	99.34	12.34	12.01	0.010	15.5	179.5	0.042	Pass	Pass	No change

is defined as M_2 . The water absorption ($w\%$) was calculated via the following:

$$w\% = \left[\frac{(M_2 - M_1)}{M_1} \right] \times 100\%. \quad (3)$$

Antimicrobial characteristic of the latex film was investigated according to a test method (GB/T 21866-2008) from the Technical Standard for Disinfection (2008 edition) published by the State Administration of Quality Supervision, Inspection, and Quarantine. The film was stuck on the aluminum plate twice, brushing second time after the first desiccation, which was followed by drying for 7 days at $23 \pm 2^\circ\text{C}$ and $50 \pm 5\%$ RH. The test plate was divided into $50 \text{ mm} \times 50 \text{ mm}$ in size. As for bovine serum albumin (BSA) and lysozyme solution, they were prepared in 10 mM phosphate-buffered saline (PBS), keeping an initial concentration of 1 mg/mL. Firstly, the film was incubated in BSA solution (10 mL) for 24 h with a shaker bath at 25°C . Secondly, the film was removed from the glass bottle, and the BSA equilibrium concentration was monitored by a UV-vis spectrophotometer (UL2100, GE, USA) at 526 nm. Finally, adsorption capacity (Q_e) was expressed as follows:

$$Q_e = \frac{(C_0 - C_e)V}{m}, \quad (4)$$

where C_0 (mg/mL) is the initial concentration of BSA, C_e (mg/mL) is the equilibrium concentration of BSA, V (L) is the volume of the solution, and m (g) is the dry mass of the film.

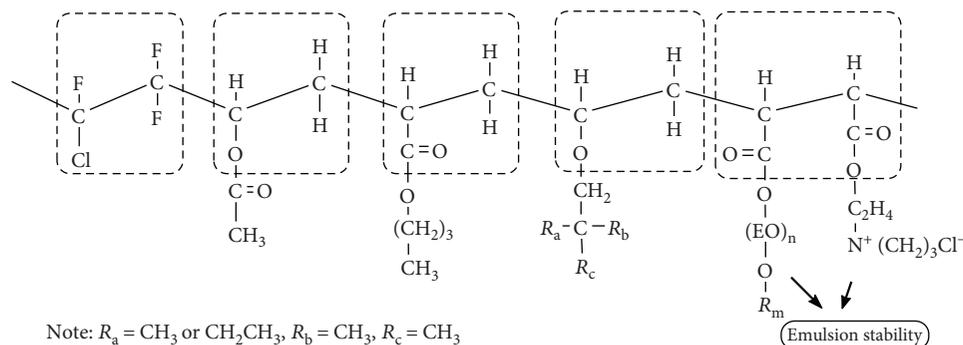
3. Results and Discussion

3.1. Influence of Different Emulsifiers on Pre-Emulsion Stability. There is no denying that pre-emulsion stability plays an important role in polymerization progress. A comparative trial was applied by using pure or mixed emulsifier systems. Table 1 illustrates the detailed components of emulsifiers and presents their respective pre-emulsion stability. Given that gaseous CTFE need to emulsify under high pressure, for safety purposes, only liquid monomers such as BA, VAc, and Veova10 were explored. It can be seen clearly that the single emulsifier of L1 and L4 exhibited better emulsifying properties: pre-emulsion can remain relatively stable for

24 h without stratification. In contrast, the pre-emulsion employing one component KJH-2, KJH-3, and CTAB (namely, L2, L3, and L5) showed inferior stability. More specifically, apparent stratification occurred just a few minutes later. The phenomenon probably ascribed to shorter hydrophilic chain segment and longer alkyl chain segment of KJH-2, KJH-3, and CTAB. Surprisingly, when combined with 600#A, pre-emulsion stability of L7, L8, and L10 had improved slightly, showing the similar stability with L1. The stabilization mechanism of cationic emulsifier (like KJH-1, KJH-2, KJH-3, R303, and CTAB) mainly depends on electrostatic repulsion. 600#A, which features nonionic and stronger hydrophilic surfactant, can enhance pre-emulsion stability via hydration mechanism. In fact, the use of surfactant mixtures, which contain the aforementioned cationic emulsifier and 600#A, is more effective than the use of single surfactant due to the synergistic effect [29]. On account of fine stability, it is wise to choose the stable pre-emulsion samples (i.e., L1, L4, L6, L7, L8, L9, L10, and L11) as analysis objects, maximally avoiding stratification and coagulation that appeared in latex emulsion.

3.2. Influence of the Nine Stable Pre-Emulsions on the Resultant Emulsion Properties. The results of polymerization using various stable pre-emulsions are listed in Table 2. Other than L8 and L10, the rest of the six emulsifier systems (L1, L4, L6, L7, L9, and L11) had attained almost complete monomer conversion and a very small coagulum rate. Perhaps influenced by KJH-2, the fluorine contents of L1, L4, L6, L9, and L11 agreed well with the calculated values, which would have an extremely profound impact on latex properties. Analogously, attributing to special chemical structure character of KJH-3, even if there was 600#A, L8 cannot guarantee ideal stability of the latex particles. With regard to L10, the presence of CTAB often made system viscosity increase [30], resulting in the decrease in latex particle size. At this point, it would bring about a relatively small microsphere surface, which may further exacerbate the shrinkage of the emulsifier's adsorbing capacity and undermine systematic stability [31, 32]. Ultimately, L10 get far more coagulum than others.

Additionally, we give a comprehensive discussion on preparative latex stability. Whether polymerizable surfactant or conventional emulsifier, all the preparative emulsion could



SCHEME 2: The chemical structure of fluorinated acrylate copolymers.

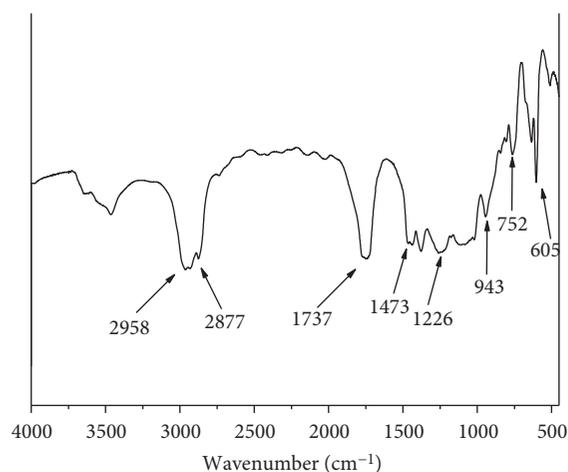


FIGURE 1: FTIR spectrum of L9.

resist these freeze/thaw cycles under -5°C . This hints that the polymerizable surfactant with long-chain nonionic groups such as ethylene oxide was of great importance for freeze/thaw stability. Apart from L8, others had wonderful stability against low concentration electrolytes, so that no visual coagulation or precipitation was detected. That is because the contents of the ethylene oxide (EO) in polymerizable quaternary ammonium surfactant were higher than those in the traditional quaternary ammonium surfactant (CTAB). In storage stability test, most of the latexes did not demix and remained in the original state. However, for L7 and L8, the latexes' stability deteriorates markedly after one month. Furthermore, other methods, for instance, increasing the amount of traditional emulsifier might be used to improve storing stability, which will be studied in the following experiments.

3.3. Characterization of Emulsion Latexes. The specific chemical structure of fluorinated acrylate copolymers is depicted in Scheme 2. Since the latex particle curves of FTIR spectrum are seriously similar, for simplicity, only L9 is described in Figure 1. As expected, the FTIR spectrum of L9 almost perfectly echoes our speculation. The peaks at 2877.27 cm^{-1} and 2958.27 cm^{-1} are designated to the stretching vibration

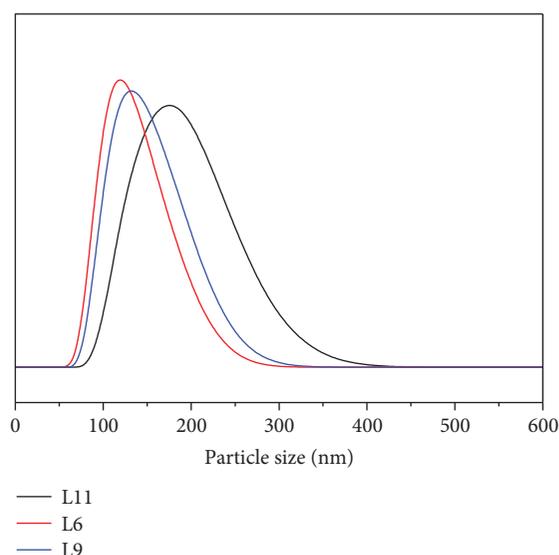


FIGURE 2: Particle size distribution of different latex particles.

of C-H on CH_2 and CH_3 . The appearance of peak located at 1737.55 cm^{-1} is assigned to carbonyl-stretching mode, arising from the adoption of VAc, BA, and Veova10. It is noteworthy that several peaks associated with the functionalized carbon groups showed up, for example, the stretching vibration absorption of C-Cl, C-F, and C-F₂ occurred severally at 605.54 cm^{-1} , 943.02 cm^{-1} , and 1226.51 cm^{-1} , respectively, suggesting CTFE was favorably brought in the latex particles as the desired monomer. Moreover, the characteristic peak of $-\text{CH}_2-\text{N}^+$ also appears at 1473 cm^{-1} and 752 cm^{-1} , which demonstrates the existence of polymerizable quaternary ammonium emulsifier (R303). Oppositely, the C=C stretching peak centered at 1650 cm^{-1} disappears entirely, proving there were no residual monomers in the sample. To probe the particle size distribution, the DLS performance was measured. As shown in Figure 2, L6, L9, and L11 have a relatively narrow monomodal distribution. We could hardly see the sign of secondary particle nucleation. Notably, the average particle diameter of L6 and L9 was about 130.1 and 142.9 nm, and the polydispersity index was less than 0.03. Compared to L9, the polydispersity index of L11 increased from 0.023 to 0.04,

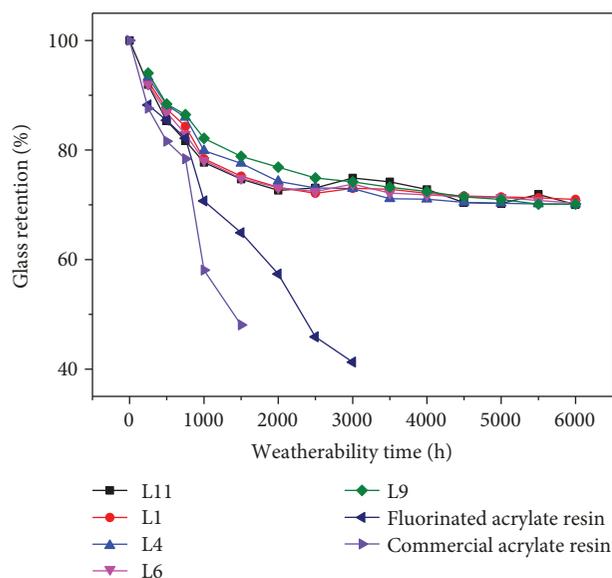


FIGURE 3: Accelerated weathering test of coatings with different polymers.

confirming that polymerizable emulsifiers have prominent emulsifying behavior [33, 34]. It is similar to the result in the literature.

3.4. Weatherability of the Waterborne Polymers. The most common use of polymers is guarding the system against exterior exposure. Therefore, the study of accelerated UV exposure onto the polymeric membranes is indispensable to evaluate their weatherability. The contrast experiment shown in Figure 3 sheds new light on the favorable antiaging properties of our own samples. It should be noted that fluorinated acrylic resin was previously reported by Zhu et al. [35], in which semicontinuous emulsion polymerization of vinyl acetate, n-butyl acrylate, Veova10, and hexafluorobutyl methacrylate was adopted. The preparation of commercial acrylic resin is almost identical with L10, except for the absence of CTFE. Generally, the original surface state of the coating film was regarded as 100%. After undergoing successive UV exposure, the film would showcase varying degrees of destruction. Once severe pulverization, bubbling, or flaking-off on the surface of the coating film happened, the surface state was deemed as 0%. Fluorine doping can endow polymers with higher chemical inertness. Conspicuously, for lack of fluoride, the weatherability test of commercial acrylic resin is far below those of fluorinated acrylic resin, L1, L4, L6, L9, and L11, which was able to stick to it for about 1600h. To some extent, accompanied by the fluorine content build-up, the performance of polymeric materials is much better [1]. By virtue of hexafluorobutyl methacrylate as a starting material, the aging resistance of fluorinated acrylic resin merely reached 3000h. With the aid of CTFE, the antiaging performances of L1, L4, L6, L9, and L11 were basically consistent with each other. What is more, they were maintaining a stable state at 6000h later.

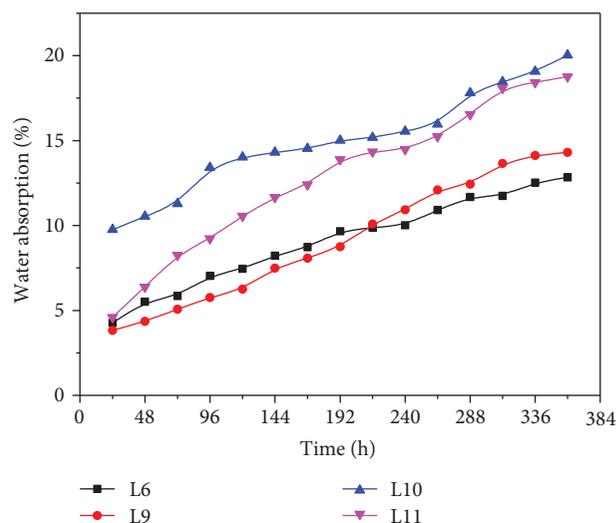


FIGURE 4: Water absorption of the films in 15 days.

3.5. Water Resistance of Latex Films. Water absorption is a vital evaluation criterion for waterproofing grade. In allusion to each latex film, individual variation of water absorption is intimately related to the selection of emulsifiers. In light of this, the results of Figure 4 are one reflection of modification effect based on polymerizable quaternary ammonium surfactant. When dry films were immersed in water up to fifteen days, the water absorption of the films prepared by L6, L9, L10, and L11 is as follows: 12.52%, 14.30%, 18.45%, and 18.77%, respectively. Unquestionably, instead of traditional emulsifiers, the emulsions (like L6 and L9) are hard for water molecules to diffuse across the bulk film on account of synergistic effect between polymerizable surfactants [36, 37]; thus, they still kept undeformed, transparent, and in stiff status. This underlines that polymerizable surfactants can effectively improve the water resistance of films.

3.6. Antibacterial Activity of Latex Films. It is well known that quaternary ammonium salts would render the obtained polymer emulsion antibacterial property. Nevertheless, some small-molecule quaternary ammonium salts are easily migrated and bring about the loss of antibacterial effect [22]. We believe that if polymerizable emulsifiers are bonded on the surface of latex particles by covalent bonds, the film will display abiding antibacterial behavior. Before the experiment began, L6 and L9 were soaked in water, and then dried for 3 h at 80°C, named as P6 and P9 separately. The selection of bacterial species was *Escherichia coli*. As listed in Table 3, the number of *Escherichia coli* decreases sharply from 2.1×10^6 cfu/piece to less than 20 cfu/piece after 24 h in contact with L6 and L9. The antibacterial ratio is as high as 99.99%, close to 100%. Similar phenomena have also been observed for P6 and P9, which indicated the high antibacterial stability of films. It is deduced that water flushing was insufficient to isolate the polymerizable emulsifier anchored in the surface of the latex film.

3.7. Protein Resistance of Latex Films. Protein fouling is a detrimental element for lengthening the lifespan of latex

TABLE 3: The antibacterial test of latex films with regard to a set number of bacteria.

Sample	The average recovery of bacteria for blank control sample after 24 h (cfu/piece)	The average recovery of bacteria for coating sample after 24 h (cfu/piece)	Antimicrobial rate (%)
L6	2.1×10^6	<20	>99.99
L9	2.1×10^6	<20	>99.99
P6	2.1×10^6	<20	>99.99
P9	2.1×10^6	<20	>99.99

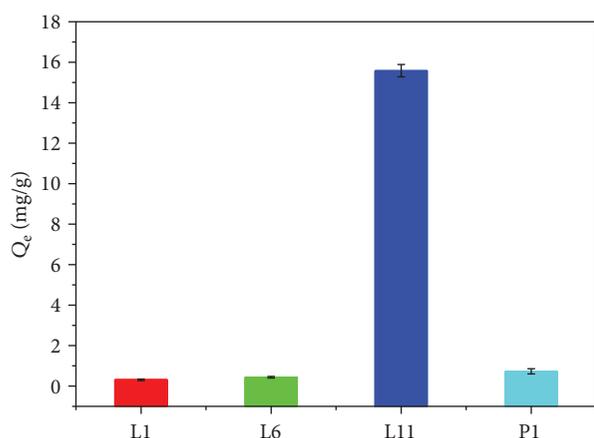


FIGURE 5: Comparison of the lysozyme adsorption levels of L1, L6, L11, and P1.

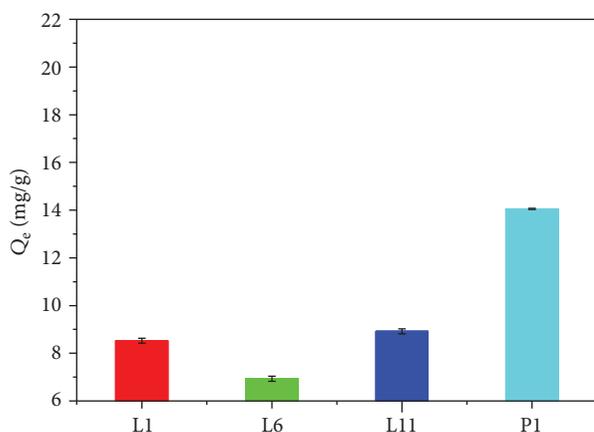


FIGURE 6: Comparison of the BSA adsorption levels of L1, L6, L11, and P1.

films. To gain an insight into the actual protein resistance of our films, lysozyme and BSA adsorption experiments were conducted. In this study, the preparation procedure of benchmark reference group (P1) is analogous to L1 except that the monomer CTFE is not employed. Figures 5 and 6 show that L6 exhibited a feeble adsorption capacity with 0.436 and 6.933 mg/g for lysozyme and BSA. Likewise, L1 merely presented a weak adsorption amount of 0.307 and 8.524 mg/g for lysozyme and BSA, respectively. On the contrary, the L11 film, because of the absence of quaternary ammonium group, was favorable for protein to approach

the surface, thereby incurring strong adsorption. It is worth mentioning that the fluorine-free P1 film has the preferable antifouling action than L11 for lysozyme, but the effect for BSA was severely restricted. It could be concluded that quaternary ammonium group and fluorine promoted the antifouling property of the film.

4. Conclusions

In summary, with the aid of cationic quaternary ammonium polymerizable surfactant and CTFE, fluoropolymers were synthesized by semicontinuous emulsion polymerization, using VAc, BA, and Veova10. Unlike exploiting conventional emulsifier or hexafluorobutyl methacrylate, the synthetic fluoropolymers exert preeminent emulsification effect and latex stability which can strengthen resistance capability for electrolytes, freezing/thawing, storage, weather, water, bacteria, and protein. Thanks to this pretty straightforward method, manufacturers would offer more practical coatings for all walks of life.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this article.

Authors' Contributions

Hongzhu Liu and Lingnan Wang contributed equally to this work.

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