

Application of Low Surface Energy Fluorinated Polymer in Leather Finishing

Zhengjun Li, Qinhuang Yang, Tingyou Zhang*

National Engineering Laboratory for Clean Technology of Leather Manufacture, Sichuan University,
Chengdu 610015, Sichuan, P.R. China

Abstract: A lower fluorine-content core-shell latex copolymer with fluorinated polyacrylate rich in shell was manufactured by seeded emulsion polymerization and its morphology was confirmed by TEM and particle size analysis. The results indicated that the surface energy of film from this latex was as low as that of PTFE (*i.e.* 18.5 mN/m) by contact angle measurement. The water repellency of the film from polyurethane dispersion blended with the fluorinated core-shell latex was improved remarkably. When applied in leather finishing, a coat with excellent wet rub fastness was obtained. Therefore, it's very effective when the low surface energy fluorinated acrylate core-shell latex was applied as an additive in top coat to improve wet rub fastness performance.

Key words: surface free energy; fluorinated polymer; core-shell; leather; wet rub fastness

1 Introduction

Whole waterborne coating system for leather, as a part of clean leather-making processes, is one of the effective technologies for sustainable leather industry. However, there are some difficulties for meeting the high requirements, especially wet rub fastness and wear fastness, when it was applied to car seat leather. The use of cross linker such as aziridine, although it is harmful to human, is a common effective means for improving wet rub fastness of leather coats. But it was difficult to obtain balance of softness, good appearance and good rub fastness for cross linker was apt to bring about a hard coat. Therefore, easy to control and eco-friendly technologies were expected. A new acrylic polymer technology that can be used in top coat formulations for automotive upholstery, which displayed a unique balance of softness, good appearance, good appearance stability and good wear properties, was developed [1].

The fluorinated acrylate polymers, especially core-shell latex with fluorinated polyacrylate rich in shell, have special surface properties such as water resistance, oil resistance and self-clean character. Because of differences in surface tension and incompatibility, the fluorinated side chains might preferentially migrate to the surface during film formation and give low surface energy, even if only a minimum amount of fluorinated monomer was used. Marion *et al*[2, 3] and Chaocan Zhang *et al*[4] prepared and investigated core-shell latex particles containing a fluorinated polymer in the shell.

In our previous work [5, 6], a stable fluorinated acrylate copolymer emulsion with random structure (FPA-R) was prepared and hydrophobicity and surface free energy were investigated. The hydrophobicity of water-based PU binders was improved sharply with only 1% (wt) fluorine, and then the wet-rub resistance of leather coat was also enhanced remarkably. In this study, our aim is to design and prepare the core-shell latex with fluorinated polyacrylate rich in shell (FPA-CS), and confirm the core-shell structure by TEM and particle size analysis. Then contact angles and surface energy of films from FPA-CS were also measured. Finally, the application of FPA-CS as an additive in top coat formulation to improve wet rub fastness was investigated.

2 Experimental

2.1 Materials

*Corresponding author. Phone: +86-(0)28-85408868. E-mail: suli-zhangtymail@163.com

Dodecafluoroheptyl methacrylate (FMA) was obtained from XEOGIA Fluorine-Silicon Chemical Co., Ltd (Harbin, China). Butyl acrylate (BA) and methyl methacrylate (MMA) were supplied by Kelong Chemical Reagents Company (Chengdu, China). The initiator, ammonium persulfate (APS), was supplied by Beibei Fine Chemicals Company (Chongqing, China). The mixed emulsifier system was composed of sodium dodecyl sulfate (SDS) and polyoxyethylene alkyl ether (AEO), which were both supplied by Kelong Chemical Reagents Company (Chengdu, China), and an anionic fluorine-containing surfactant, which was obtained from XEOGIA Fluorine-Silicon Chemical Co., Ltd (Harbin, China). Hard polyurethane dispersion binder (PU) was supplied by Tingjiang Fine Chemicals Co., Ltd. (Sichuan, China). All these materials were used without further purification.

2.2 Preparation of FPA-CS Core-shell Latex

The FPA-CS core-shell latex containing fluorinated acrylate in shell was synthesized by two-stage semi-continuous emulsion polymerization. The fluorine-free polyacrylate core was polymerized by conventional emulsion polymerization (first stage), and then, the fluorinated shell was introduced to the seed particle by semicontinuous addition of monomers (second stage) in the same reactor under kinetically controlled conditions. Typically, the reaction was carried out in a 250 ml three-neck flask equipped with a mechanical stirrer, a condensation tube, a thermometer and a nitrogen inlet. For the synthesis of the core polymers, after purging N₂ for 30 min at first, the mixed emulsifier and deionized water were added to the flask in proportion, and this emulsion was heated by water bath with stirring. When the temperature inside the flask reached about 80°C, APS initiator and the mixed monomers of BA and MMA were simultaneously dropped, respectively. When a higher conversion reached, the core phase formed completely in the first stage. Then the second-stage monomer preemulsion, composed of FMA, the remaining BA, MMA, initiator, mixed emulsifiers, and deionized water, was slowly dropped into the reaction system for at least 4h to form the shell phase. After the dropping step was complete, the reaction was maintained for at least 2h at 80°C. Then the temperature was lowered to room temperature. Finally, the pH value of the stable FPA-CS latex was adjusted at the range of 6.5 to 7.0.

2.3 Characterization

2.3.1 Particle Size Analysis and Morphology Observation

The particle size and its distribution (polydispersity index) of the FPA-CS core-shell latex containing fluorinated acrylate in shell were measured by using a dynamic light scattering laser particle size analyzer (S90, Malvern Instruments, UK). The latex was diluted with deionized water before this measurement.

The morphology of the obtained FPA-CS core-shell latex particles were observed by a transmission electron microscope (H-600, HITACHI, Japan) with an acceleration voltage of 100 kV. The samples were stained with 1.5% phosphotungstic acid (PTA) solution and air-dried.

2.3.2 Contact Angle Measurement and Surface Free Energy Calculation

Water contact angles and n-dodecane contact angles of the polymer films, which were first prepared by casting the FPA-CS core-shell latex on a substrate such as a clean slide glass or a model polyurethane film and then dried at room temperature and further annealed at specific temperature, were measured by the sessile drop method with an optical contact angle measurement system (OCA 20, Dataphysics Company, German), respectively. Each contact angle presented here is the average values from 6 readings to get a reliable value for each sample.

Total surface free energies (γ), their polar (γ^P) and dispersion (γ^d) components were calculated by the extended Fowkes equation: $(1 + \cos \theta)\gamma_i = 2 (\gamma_i^d \gamma_s^d)^{1/2} + (\gamma_i^P \gamma_s^P)^{1/2}$ (1). Where γ_i is the surface tension of the wetting liquid, γ_i^d and γ_i^P are the dispersive and polar components, respectively. γ_s^d and γ_s^P for the latex films could be calculated by substituting values for water and n-dodecane into equation (1)

and solving the corresponding set of simultaneous equations. The summation of γ_s^d and γ_s^p gave the total surface energy $\gamma^{[7]}$. The n-dodecane contact angles can reflect oleophobicity of the film in some extent.

2.4 Finish Formulations and Leather Finishing

The effect of core-shell structure fluorinated polyacrylate FPA-CS latex on wet rub fastness of top coat was studied. The testing was made by a leather color rub fastness tester (GJ9E1, Yuyao Machinery Plant of Light Industry, Zhejiang, China). The basecoat formulation $m(\text{Black color paste}):m(\text{PU}):m(\text{water})$ is 1:3:2, and was applied by brushing, then the leather crust was dried at 60°C for 1 h. The top coat formulation $m(\text{FPA-CS}):m(\text{PU}):m(\text{water})$ is 3:47:50, and was applied using spraying, then the crust was dried in a 60°C oven for 2 h ad the topcoated leather was ironed at 90°C for 2 seconds. The top coat applied using PU only is the control test sample. Finally, the contact angle was measured using the above method and wet rub fastness of the finished leather were tested by standard QB/T 1327-1991.

3 Results and discussion

3.1 Morphology and Structure of FPA-CS Latex Particles

According to the polymer molecular design idea to prepare core-shell structure polymer latex particles with fluorine-free polyacrylate core and fluorinated polyacrylate shell, several stable FPA-CS fluorinated acrylate copolymer latices were prepared using seeded emulsion polymerization and starved-feed technology, which was highly favorable to form core-shell structure and prevent secondary nucleation of shell monomers. These latex films possessed low surface free energies, even if the lower fluorinated group contents were at their polymer chains, for their microphase separation characteristics as the previous study literature reported^[4,7]. The implications of some marks were illustrated as follows. For example, FPA-CS10(50) indicated that the ratio of $m(\text{FMA}):m(\text{BA/MMA})$ was 10:90, and $m(\text{FMA}):m(\text{BA/MMA in shell})$ was 50:50. FPA-CS20(60) indicated that the ratio of $m(\text{FMA}):m(\text{BA/MMA})$ was 20:80, and $m(\text{FMA}):m(\text{BA/MMA in shell})$ was 60:40. And FPA-CS20(100) indicated that the ratio of $m(\text{FMA}):m(\text{BA/MMA})$ was 20:80, and only FMA in shell.

In order to characterize the morphology and structure of the FPA-CS latex particles prepared, transmission electron microscope (TEM) and dynamic light scattering (DLS) measurements were employed in this study. Particle size analysis results of the seed particles and the final core-shell particles determined by DLS were listed in Table 1. It was shown from Table 1 that the Z-average diameter and polydispersity index of latex particles mentioned above were all less than 100nm and 0.200, respectively, indicating the monomodal distributions of nanometer latex particles were obtained. Furthermore, it was found that the polydispersity index of subsequent core-shell particles was hardly change, but only the Z-average diameter increased, when compared to the corresponding seed particles. These results suggested that no secondary nucleation occurred and the shell monomers polymerized onto the surface of fluorine-free polyacrylate seeds during the second stage polymerization. As a result, the core-shell composite particles with fluorine-free polyacrylate rich in core and fluorinated polyacrylate rich in shell were formed. Similar experimental results were reported elsewhere^[7,8].

Furthermore, it was also found that, on the one hand for FPA-CS latices with the same FMA dosage but different proportions of FMA to acrylate in shell, the larger proportion was employed, the increasing rate of Z-average diameter of corresponding core-shell latex decreased. For example, the increasing rate of Z-average diameter of FPA-CS10(50), FPA-CS10(80) and FPA-CS10(100) were 7.18%, 6.62% and 2.64%, respectively. Considering FPA-CS20(50), FPA-CS20(60), FPA-CS20(70) and FPA-CS20(100), the similar tendency also existed. On the other hand, for FPA-CS latices with the different FMA dosage but same proportions of FMA to acrylate in shell such as FPA-CS10(50) and FPA-CS20(50), FPA-CS10(100)

and FPA-CS20(100), the increasing rate of Z-average diameter of corresponding core-shell latex particles accreted with the increasing dosage of FMA. Therefore, it was shown that the thickness of the shell was in well agreement with the dosage of total shell monomers. According to the results from particle size analysis, it can be concluded that the core-shell particles with fluorine-free polyacrylate rich in core and fluorinated polyacrylate rich in shell have been successfully prepared.

Tab. 1 Particle size analysis of FPA-CS latices with core-shell structure

	Core-shell fluorinated polyacrylate latex	Z-average diameter (nm)	Polydispersity index	Increasing ratio of Z-average diameter (%)
FPA-CS10(50)	Seed particles	55.7	0.093	
	Core-shell particles	59.7	0.098	7.18
FPA-CS10(80)	Seed particles	71.0	0.075	
	Core-shell particles	75.7	0.076	6.62
FPA-CS10(100)	Seed particles	75.9	0.077	
	Core-shell particles	77.9	0.079	2.64
FPA-CS20(100)	Seed particles	64.6	0.093	
	Core-shell particles	69.0	0.092	6.81
FPA-CS20(70)	Seed particles	61.0	0.119	
	Core-shell particles	67.1	0.119	10.0
FPA-CS20(60)	Seed particles	63.2	0.105	
	Core-shell particles	71.3	0.111	12.8
FPA-CS20(50)	Seed particles	65.0	0.110	
	Core-shell particles	73.7	0.102	13.4

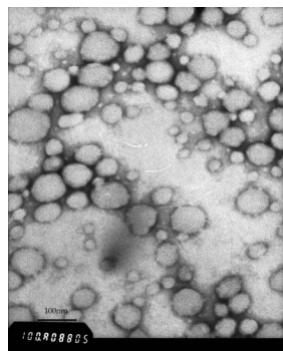


Fig.1 The TEM image of FPA-CS20(100) core-shell latex

Fig.1 illustrates the TEM image of the representative FPA-CS20(100) core-shell latex particles. As displayed in Fig.1, it can be observed clearly that the figure of FPA-CS latex particles is uniform spherical and two-phase structure. The light and dark regions in the particles correspond to fluorine-free polyacrylate core and fluorinated polyacrylate shell, respectively. As a result, the morphology observation by TEM is consistent with the results of DLS analysis collected in Table 1.

3.2 Contact Angle and Surface Free Energy of FPA-CS Latex Films

Table 2 shows the contact angles and surface energies of FPA-CS latex films formed on a slide glass substrate at 60 °C for 24 h. From Table 2, it was revealed that both water contact angles and n-dodecane contact angles increased and surface free energies decreased with the proportion of FMA to acrylate in shell components increased, for FPA-CS lateices with the same FMA dosage. The larger proportion of

FMA to acrylate in shell employed, the more prominent this phenomenon was. The imaginable reason is that core-shell structure with fluorine-containing polyacrylate rich in shell and an appropriate microphase separation between fluorinated components and fluorine-free components, and simultaneously the surface migration and aggregation of fluorine-containing side chains. For FPA-CS latices with different FMA dosages but the same proportion of FMA to acrylate in shell monomers, it was revealed the basic rules that the contact angle increased and the surface free energy decreased with the fluorine content increased. And from Table 2, it can also be found that the surface free energies of core-shell structure FPA-CS latex films were very low, and were at the same level as that of PTFE (*i.e.* 18.5 mN/m). It is well known that the contact angle of water can be used as a criterion for the evaluation of hydrophobicity of a surface. The bigger water contact angle and the lower surface free energy give the film higher hydrophobicity. Therefore, the core-shell FPA-CS latex film possessed excellent hydrophobic property.

Tab. 2 Contact angle and surface free energy of the core-shell latex films

	Contact angle (°)		Surface free energy (mN/m)		
	Water	n-Dodecane	γ	γ^d	γ^p
FPA-CS10(50)	96.5	47.6	20.95	17.58	3.37
FPA-CS10(80)	98.0	50.5	19.90	16.78	3.12
FPA-CS10(100)	98.2	51.0	19.74	16.64	3.10
FPA-CS20(100)	102.0	54.8	17.88	15.58	2.30
FPA-CS20(50)	103.7	45.8	19.46	18.06	1.40

3.3 Contact Angles of Polyurethane Films Blended with the core-shell FPA-CS Latex

Tab. 3 Influence of different substrates on water contact angles of PU films blended with core-shell structure fluorinated polymer latices

Substrate	FPA-CS dosage (wt%)	Contact angles of blended PU films (°)	
		FPA-CS10(100)/PU	FPA-CS20(100)/PU
Slide glass	2	99.9	103.2
	6	104.4	105.6
	10	104.9	105.4
Model PU	2	89.3	99.6
	6	102.3	101.9
	10	102.4	103.5

The hard polyurethane dispersion PU was blended with the core-shell latex FPA-CS10(100) and FPA-CS20(100), respectively, and then they were filmed on the slide glass substrate or the model PU substrate at 60°C for 24 h. Their contact angles were measured and listed in Table 3. It can be seen that the contact angles of PU films blended with the core-shell fluorinated acrylate FPA-CS latex were increased remarkably (the contact angle of PU film is 65.8°), and the more of FPA-CS dosage employed, the bigger contact angle was displayed. This demonstrated that the core-shell FPA-CS latex can be used potentially as an additive to improve the hydrophobicity of polyurethane dispersion leather coats. A reasonable explanation is self-stratification of the combination system of core-shell fluorinated FPA-CS latex/polyurethane dispersion, and the layer sequence and the degree of stratification are governed by their incompatibility and surface tensions. In general, the polymer (*e.g.* FPA-CS) with the lower surface tension migrates to the air interface during the stratification process, while the polymer (*e.g.* Polyurethane dispersion) with the higher surface tension is forming the primer layer [9]. Therefore, the preferable hydrophobicity can be obtained as a result of fluorine migration on the outer surface of coats. From Table

3, it was also found that the contact angle of film prepared on the model PU substrate was always smaller than that of film prepared on the slide glass substrate. It was considered that contact angles were related to polarities and surface energies of substrates.

3.4 Application of Core-shell FPA-CS latex in Leather Finishing

The contact angle and degree of wet rub fastness of the top finished leather were listed in Table 4. It was found that the contact angle was increased to over 100° and the wet rub fastness degree was increased to above 4.5, as a result of the addition of low surface energy fluorinated acrylate FPA-CS latex. And it is discovered that the wet rub fastness was positive correlation to the water repellency of the corresponding top coat. These results indicated that the application of low surface energy fluorinated acrylate FPA-CS latex as a additive in top coat was very effective to improve wet rub fastness property.

Tab. 4 Water contact angle and wet rub fastness of leather coats from PU dispersions

blended with core-shell fluorinated FPA-CS latices

Sample	Water contact angle (°)	Wet rub fastness (degree)
Control test sample	93.8	2.0
FPA-CS10(100)/PU	102.1	4.5
FPA-CS20(100)/PU	104.6	5.0

4 Conclusions

A lower fluorine-content core-shell latex copolymer with fluorinated polyacrylate rich in shell was manufactured by seeded emulsion polymerization and its morphology was confirmed by TEM observation and particle size analysis. The core-shell latices containing 10% to 20% fluorinated acrylate based on the weight of total monomers possessed very low surface free energy, which were as low as that of PTFE (*i.e.* 18.5 mN/m). Leather top coat with combination of the core-shell latex and polyurethane dispersion has excellent wet rub fastness. Therefore it can be concluded that the application of the low surface energy fluorinated acrylate FPA-CS latex as an additive in top coat to improve wet rub fastness performance is very effective.

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