



Polysiloxane/poly(fluorinated acrylate) core–shell latexes and surface wettability of films



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ABSTRACT

The core–shell polysiloxane/fluoroacrylate copolymer latexes $p(D_4/D_4^V)/p(BA/MMA/FA)$ are prepared for coating materials. $P(D_4/D_4^V)$ core is synthesized by ring-opening polymerization of octamethylcyclotetrasiloxane ($Si_4O_4(CH_3)_8$, D_4) and tetravinyltetramethylcyclotetrasiloxane ($Si_4O_4(CH_2)_4(C_2H_5)_4$, D_4^V). $P(BA/MMA/FA)$ shell is obtained by semi-continuous seed emulsion copolymerization of methyl methacrylate (MMA), butyl acrylate (BA) and fluorinated acrylate (FA) via. Four different FA are used in this paper: hexafluorobutyl acrylate (6FA), trifluoroethyl methacrylate (3FMA), hexafluorobutyl methacrylate (6FMA) and dodecafluoroheptyl methacrylate (12FMA). The as-prepared latexes are characterized by Fourier transforms infrared (FT-IR) spectroscopy and 1H NMR measurement. The typical core–shell structure is proved by transmission electron microscopy (TEM) and differential scanning calorimetry (DSC). The effect of different shells on the core–shell particles and the surface properties of films are characterized by TEM, dynamic light scattering (DLS), scanning electron microscope coupled with the energy dispersive spectrometry (SEM-EDX), static contact angles (SCA) for surface free energy, and quartz crystal microbalance with dissipation (QCM-D) monitoring for surface water absorption. With the increase of fluorinated side chain in the shell, the individual core–shell particles as 70–90 nm are obtained. The surface free energy for $p(D_4/D_4^V)/p(BA/MMA/12FMA)$ film (19 mN/m) is much lower than other three films (28–29 mN/m). During the film formation, the self-aggregation of $-CF_3$ groups onto the film surface for lower surface free energy and the polysiloxane groups onto the substrate for better adhesion. Therefore, $p(D_4/D_4^V)/p(BA/MMA/12FMA)$ film is much more homogeneous, less wettability and less water absorption.

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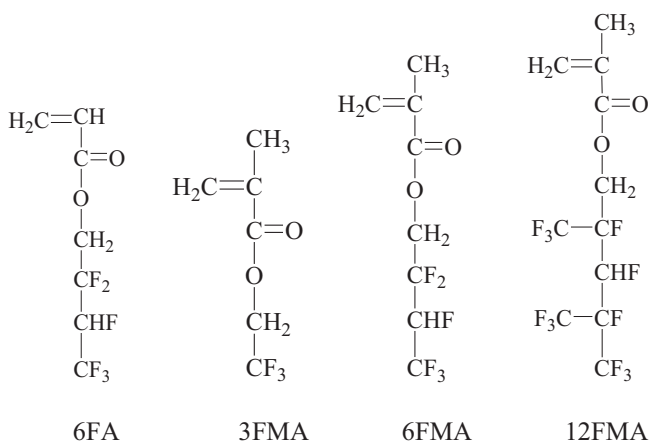
1. Introduction

The fluorosilicone copolymers are reported to have extraordinary surface properties [1–3], good thermal stability [4,5], and excellent film properties [6–8]. Therefore, they are extensively used as coating materials to take the advantages that the excellent water/oil repellency and the low surface free energies provided by the fluorinated polymers [9,10], and that the high thermal stability and adhesion to the substrate offered by the polysiloxane [11,12]. However, the key problem is the chemical structure of fluorosilicone copolymers for optimizing the synergism of each individual component. One of the most effective methods for obtaining fluorosilicone copolymers is to incorporate the polysiloxane into the fluoroacrylate polymer [13–15].

There are various synthesis strategies to incorporate the polysiloxane into the fluoroacrylate polymer, such as the polysiloxane-poly(fluorinated acrylate) interpenetrating polymer networks [11], the block fluorosilicone copolymer [16,17], the polysiloxane modified by fluorocarbon side chains [18] and the core–shell fluorosilicone latexes [19,20]. Among these methods, the heterogeneous polymerization, especially the semi-continuous seed emulsion polymerization for core–shell latex, is by far the most frequently used effective technique [21,22]. Actually, the architecture of core–shell fluorosilicone copolymers for the well-defined coating materials is still a challenge work because of the chemical composition of the core and the shell. On the one hand, the polysiloxane obtained normally through ring-opening polymerization of octamethylcyclotetrasiloxane ($(Me_2SiO)_4$ (D_4) and hexamethylcyclotrisiloxane ($(Me_2SiO)_3$ (D_3)) [23] is able to reduce the surface free energy of films, which is responsible for the hydrophobic character of Si–O segments and is commonly used in water repellency when it is designed as the shell [24–26]. On the other hand, the fluoroacrylate copolymer with trifluoromethyl ($-CF_3$) groups could produce a low surface free energy by densely covered on the surface of film [27–30], which is the reason that the

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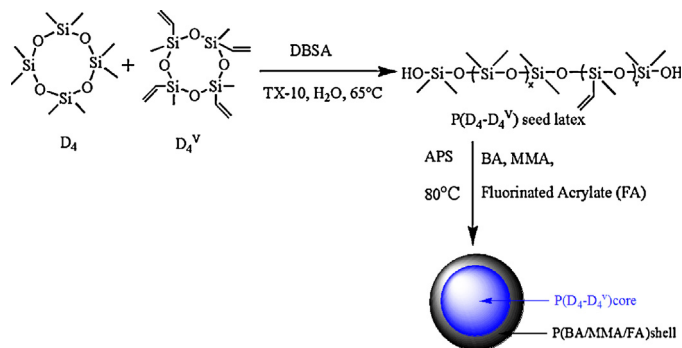
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Scheme 1. Chemical structure of 6FA, 3FMA, 6FMA and 12FMA.

current studies for a low surface free energy are mainly focused on increasing the length of fluorinated side chains in the case of low fluorine content [31–33,16]. Especially, the terminal fluorinated groups are proved to have extremely great effect on the lower surface free energy by the self-migration and self-organization of $-\text{CF}_3$ groups onto the film surface [34,35]. However, considering both of polysiloxane and fluoroacrylate copolymer, although the bulk surface free energy of polysiloxane is proved to be lower compared to most of other carbon chain polymers, its improvement is rather limited and less significant than that by incorporating fluorinated side groups into the polymer. Therefore, in order to develop the coating materials with low surface free energy, it is better to design the core-shell fluorosilicone copolymers using the polysiloxane as the core and the fluoroacrylate polymer as the shell.

This paper presents the synthesis and the film properties of core-shell polysiloxane/fluoroacrylate copolymer latexes for coating materials. The polysiloxane $p(\text{D}_4/\text{D}_4^{\text{V}})$ with $\text{C}=\text{C}$ and $\text{Si}-\text{OH}$ terminal groups, obtained from the cationic ring-opening polymerization of octamethylcyclotetrasiloxane ($\text{Si}_4\text{O}_4(\text{CH}_3)_8$, D_4) and tetravinyltetramethylcyclotetrasiloxane ($\text{Si}_4\text{O}_4(\text{CH}_3)_4(\text{C}_2\text{H}_3)_4$, D_4^{V}), is served as the core for improving the adhesion to the substrate, and the copolymer $p(\text{BA}/\text{MMA}/\text{FA})$, obtained by methyl methacrylate (MMA), butyl acrylate (BA) and fluoroacrylate (FA) monomer, is served as the shell for facilitating the surface self-segregation in the creation of low surface free energy. Four different fluoroacrylate monomers are used in this paper: hexafluorobutyl acrylate (6FA), trifluoroethyl methacrylate (3FMA), hexafluorobutyl methacrylate (6FMA) and dodecafluoroheptyl methacrylate (12FMA) in Scheme 1. The core-shell polysiloxane/fluoroacrylate copolymer latexes, $p(\text{D}_4/\text{D}_4^{\text{V}})/p(\text{BA}/\text{MMA}/\text{FA})$,



Scheme 2. Synthesis route and suggested chemical structure of $p(\text{D}_4/\text{D}_4^{\text{V}})/p(\text{BA}/\text{MMA}/\text{FA})$ latex.

$p(\text{BA}/\text{MMA}/\text{FA})$, are obtained by semi-continuous seed emulsion copolymerization. Their core-shell structures and morphologies are characterized by Fourier transforms infrared (FT-IR), hydrogen nuclear magnetic resonance (^1H NMR) measurement, transmission electron microscopy (TEM), dynamic light scattering (DLS), and differential scanning calorimetry (DSC) analysis. The surface properties of films is evaluated by the determination of static contact angles (SCA), scanning electron microscope coupled with the energy dispersive spectrometry (SEM-EDX), and the quartz crystal microbalance with dissipation monitoring (QCM-D).

2. Results and discussion

2.1. The synthesis of core-shell $p(\text{D}_4/\text{D}_4^{\text{V}})/p(\text{BA}/\text{MMA}/\text{FA})$ latex

The preparation process for latexes is given in Scheme 2. The polymerization condition and the detailed recipes of prepared latex samples are listed in Table 1. The observation of films formed by the synthesized latexes indicate that Sample 4 with 0.8 g D_4 , 0.2 g D_4^{V} , 6 g BA, 4 g MMA and 2 g FA performs better film surface with transparency and sufficient flexibility. Therefore, Sample 4 made by 6FA, 3FMA, 6FMA and 12FMA (Scheme 1), respectively, is discussed. The as-prepared latex of Sample 4 as Scheme 2 is characterized by FT-IR (Fig. 1) and ^1H NMR. The FT-IR spectra of D_4 , D_4^{V} , $p(\text{D}_4/\text{D}_4^{\text{V}})$ are used for comparison. In D_4 (Fig. 1a), the characteristic absorptions at 2964, 1261 and 809 cm^{-1} are produced by the stretching vibration, asymmetrical angular vibration and rocking vibration of $-\text{SiCH}_3$, but the peak at 1074 cm^{-1} is the typical dissymmetrical stretching vibration of $\text{Si}-\text{O}-\text{Si}$. In D_4^{V} (Fig. 1b), except the typical absorption of $-\text{SiCH}_3$ and $\text{Si}-\text{O}-\text{Si}$, the absorption at 3055, 1407, 1008, 960 and 1597 cm^{-1} are corresponding to the stretching vibration, scissor

Table 1
The polymerization condition and detailed recipes of prepared samples.

	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6
First step for $p(\text{D}_4/\text{D}_4^{\text{V}})$ core (65 °C, 2–4 h)						
Water (g)	30	30	30	30	30	30
DBSA (g)	0.13	0.13	0.13	0.13	0.13	0.13
TX-10 (g)	0.2	0.2	0.2	0.2	0.2	0.2
D_4 (g)	0.2	0.4	0.6	0.8	1.0	1.2
D_4^{V} (g)	0.2	0.2	0.2	0.2	0.2	0.2
Second step for $p(\text{D}_4/\text{D}_4^{\text{V}})/p(\text{BA}/\text{MMA}/\text{FA})$ latex (80 °C, 4.5 h)						
BA (g)	6	6	6	6	6	6
MMA (g)	4	4	4	4	4	4
FA (g)	2	2	2	2	2	2
APS (g)	0.06	0.06	0.06	0.06	0.06	0.06
Conversion (%)	92.15	94.54	95.78	95.82	88.71	98.3

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