Synthesis of composite latexes of polyhedral oligomeric silsesquioxane and fluorine containing poly(styrene-acrylate) by emulsion copolymerization

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ABSTRACT: A novel octavinyl polyhedral oligomeric silsesquioxane/fluorine containing poly (styrene-acrylate) (OvPOSS/FPSA) composite latexes with star-type structure was synthesized by emulsion copolymerization. The structures of OvPOSS/FPSA composite materials were characterized by Fourier Transform Infrared, which indicated that OvPOSS could be grafted onto FPSA latexes by emulsion copolymerization. Transmission electron microscopy images disclosed that FPSA latexes possessed obvious core–shell structure and OvPOSS/FPSA composite latexes probably present star-shape structure. Dynamic light scattering data indicated that the average diameter of OvPOSS/FPSA was slightly larger than that of FPSA, which was probably attributed to the encapsulation of POSS cages. Atomic force microscopy photos illustrated that the grafting reaction had increased the roughness of the composite surface. The water contact angle of composite films was found increasing as the percentage of OvPOSS increasing. Thermogravimetric analysis curves demonstrated that the OvPOSS/FPSA composite films displayed much better thermal stability than that of FPSA. © 2016 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 43455.

INTRODUCTION

Organic–inorganic hybrid nanocomposite materials have been regarded as a new generation of high performance material, they combine the advantages of both inorganic materials (rigidity, high thermal stability) and organic polymers (flexibility, electric insulation properties, ductility, and processability), and result in enhancing the coating properties such as hardness, strength, and thermal stability.[1–5] Polyhedral oligomeric silsesquioxanes (POSS) is a new type of organic–inorganic hybrid material which has a cage-like structure with 1–3 nm particle diameter size. The molecular structure of POSS is expressed shown with an empirical formula $R_n(SiO_{1.5})_n$, where R represents as a range of organic functional groups such as hydrogen, alkyl, alkene, aryl arylene groups, etc. POSS can be easily introduced into polymer system via blending, grafting, or copolymerization.[6–10]

Many POSS-based hybrid polymers with different architecture, such as dumbbell-type, pendent-type, bead-type, star-type, or network-type, have been prepared and exhibit a number of desirable properties, especially the high thermal stability, good mechanical properties, oxidation resistance, high glass transition temperatures, hydrophobicity, and flammability resistance.[11,12] POSS-based polymer and copolymer have being extensively

applied to prepare of different kinds of hybrid polymeric materials.

To embed POSS into various polymer matrices, a lot of novel approaches have been developed, such as atom transfer radical polymerization (ATRP), reversible addition-fragmentation chain transfer polymerization (RAFT), *in situ* solution polymerization, melt blending, radiation crosslink, and reactive blending.[13] However, there are few works to fabricate the POSS-contain polymers by using emulsion polymerization which is safe, convenient, and environment-friendly.[14]

Octavinyl polyhedral oligomeric silsesquioxane (OvPOSS) with eight vinyl groups is widely applied as polymerizable monomer and successfully incorporated into polystyrene (PS) matrix and poly(vinyl acetate) (PVAC) by means of emulsion copolymerization.[14–17] However, to the best of our knowledge, there has been no related report on surface treatment of fluorine containing acrylate resin with POSS. Therefore, the objective of the study is to graft OvPOSS onto the surface of fluorine containing acrylate resin to enhance the interfacial properties. In the present study, a novel octavinyl polyhedral oligomeric silsesquioxane/fluorine containing poly (styrene-acrylate) (OvPOSS/FPSA) composite latexes were synthesized by emulsion copolymerization
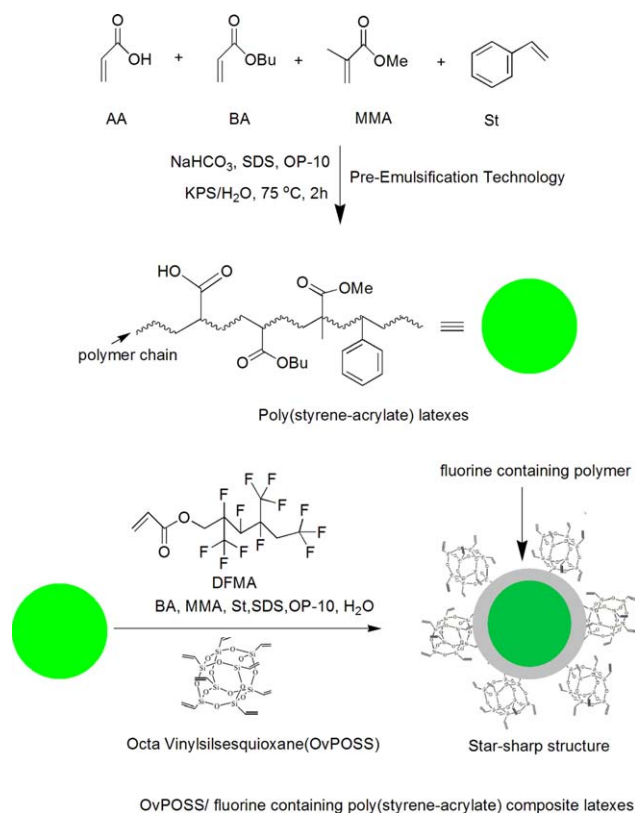
Scheme 1. The synthetic route of OvPOSS/fluorine containing poly (styrene-acrylate) composite latexes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

(Scheme 1), the micro-morphology, chemical structure, diameter size, hydrophobicity, and thermal stability have been investigated.

EXPERIMENTAL

Materials
Octavinyl polyhedral oligomeric silsesquioxane (OvPOSS), was purchased from Baxi Equipment Co. (Changsha, China). Dodecafluoroheptyl methacrylate (DFMA) was purchased from Harbin Xuejia fluorin silicon Chemical Co. (Harbin, China). Methyl methacrylate (MMA) was supplied by Shanghai Lingfeng Chemical Co. (Shanhai, China). Butyl acrylate (BA), acrylic acid (AA), and styrene (St) were supplied by Tianjin Fuchen Co. (Tianjin, China) and used without further purification. Nonyl phenyl polyoxyethylene ether-10 (OP-10), sodium dodecyl sulphonate (SDS), sodium bicarbonate (NaHCO$_3$) and potassium persulfate (KPS) were used as received without further purification. Deionized water was used for the polymerization process.

Preparation of OvPOSS/FPSA Composite Materials
OvPOSS/FPSA composite materials were synthesized by pre-emulsification technology and semi-continuous seed emulsion polymerization. The mixture of BA (24.5 g), MMA (25.5 g), St (17.5 g), and AA (2 g) was added to the SDS, and OP-10 aqueous solution (0.6 g SDS and 0.3 g OP-10 dissolved in 30 g deionized water) under a magnetic stirrer and pre-emulsified for 0.5 h to prepare core pre-emulsification monomer. In a

typical synthesis formulation: deionized water (40 g), SDS (1.0 g), OP-10 (0.5 g), KPS (0.17 g), and NaHCO$_3$ (0.30 g) were charged into a 500 mL four-neck flask with a machine stirring, and heated to 80 °C–82 °C under nitrogen atmosphere. Then 25 g of core pre-emulsification monomer was dropped into the mixture and processed for 20 minutes to prepare the seed latex, the rest and initiator solution (0.17 g KPS dissolved in 20 g deionized water) were added in 2 h with continuous stirring. The system was kept temperature at 80 °C–82 °C for 0.5 h after finishing dropping core pre-emulsification monomer, and then the shell pre-emulsification monomer with DFMA and OvPOSS (prepared by the same process, the ratio of monomers: 10 g BA, 10 g MMA, 8.5 g St, 10 g DFMA, 0.1–1 g OvPOSS) was added to system in 1 h. The initiator solution (0.17 g KPS dissolved in 10 g deionized water) was added throughout the process at a rate of 10–15 droplet/min. The reactor temperature was maintained at 80 °C–82 °C until 30 min after the addition was complete. The latex was filtered through a 200-mesh sieve. The FPSA latex was prepared from the same method without addition of OvPOSS. FPSA emulsion was prepared by the same processes without addition of OvPOSS.

The FPSA films and OvPOSS/FPSA composite films with thickness 5 μm on glass were prepared by spin coating process; the spin speed and time are 300 rpm and 18 s, respectively. The composite films were dried at 60 °C for 1 h.

Characterization
Transmission Electron Microscopy (TEM). The morphologies were directly observed by using a JEM-2100F transmission electron microscope (TEM) (JEOL Ltd., Japan) with an acceleration voltage of 200 kV. The samples were diluted with deionized water into 0.1 wt %, then blotted gently on the surface of carbon-coated copper grid, and dried at room temperature under atmospheric pressure.

Fourier Transform Infrared (FTIR). FTIR spectra of samples dispersed in dry KBr pellets were obtained by an Nicolet Avata360 FTIR spectrometer in a spectral range 400–4000 cm^{-1}.

Dynamic Light Scattering (DLS). The latex particle size and its distribution were determined with a granularity analyzer (ZS Nano S) from Malvern Co. (England).

Water Contact Angle (WAC). Static contact angle measurements using ultrapure water was performed with an OCA15 contact angle goniometer (Dataphysics Co., Germany) according to the sessile drop technique. At least five independent measurements were carried out and the mean value was determined.

Atomic Force Microscopy (AFM). The surface morphology of OvPOSS/FPSA composite films were studied by a scanning probe microscopy (cspm-3000, Benyuan Nano Co.) using a taping mode.

Thermogravimetric Analysis (TGA). The thermal stability of dried composite films were determined by the Thermogravimetric analyzer (TG/DSC, STA449C) (Netzsch Co. Germany) by heating the sample (8–10 mg) from room temperature to
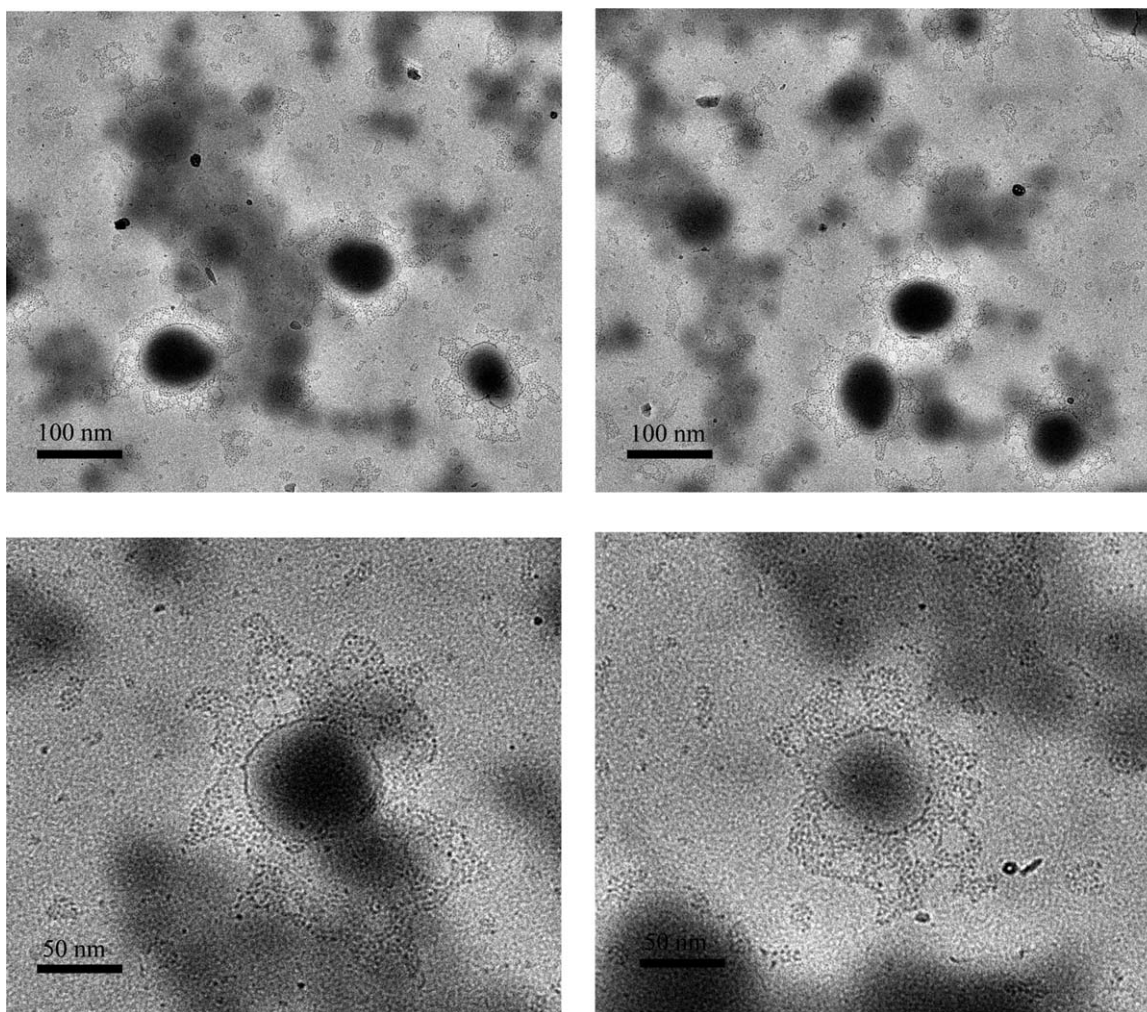
Figure 1. TEM photographs of composite latexes.

600 °C at 10 °C/min and at an air flow rate of 30 mL/min. In order to remove the water inside the films, the temperature would keep at 100 °C for 3 min. The TGA samples were prepared by the method described in the film preparation.

RESULTS AND DISCUSSION

The Preparation of the OvPOSS/FPSA Composite Materials

OvPOSS with eight vinyl groups is easily grafted onto the surface of polymer latexes via one-step free radical polymerization technique. However, the synthesized composite materials are mainly star-type rather than network structure due to the steric effect of cage-like structure of POSS, and those composite materials are soluble in most of the common organic solvents, such as THF, CHCl$_3$, dioxane, and toluene.[11–17] Figure 1 shows the TEM micrographs of the composite latexes. It can be observed that the FPSA latexes possessed obvious core–shell structure; the shell of the particles in gray color was referred to the copolymerization of DFMA. The POSS cages were grafted onto the surface of FPSA latexes. Furthermore, the composite structure was confirmed by dissolution experiment, the composite films were extracted with dioxane in soxhlet's extracter for 24 h, and it was found that the composite films were soluble, which dis-

closed that the network structure was not obtained. Those results disclosed that composite materials with star-type structure were probably obtained.
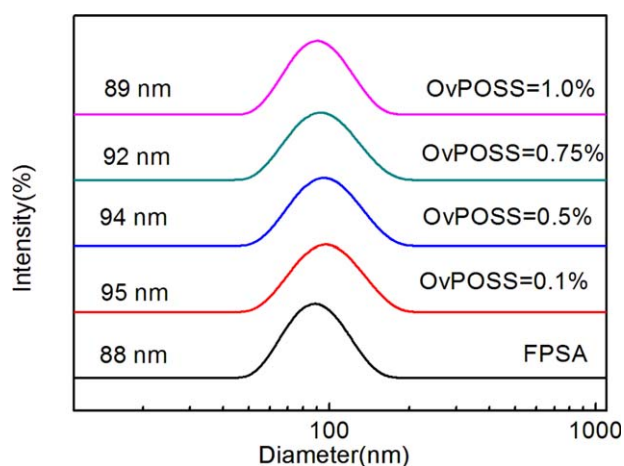

Figure 2. Particle size and distribution of FPSA particles and OvPOSS/FPSA composite particles with 0.1, 0.5, 0.75, and 1.0 wt % OvPOSS. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
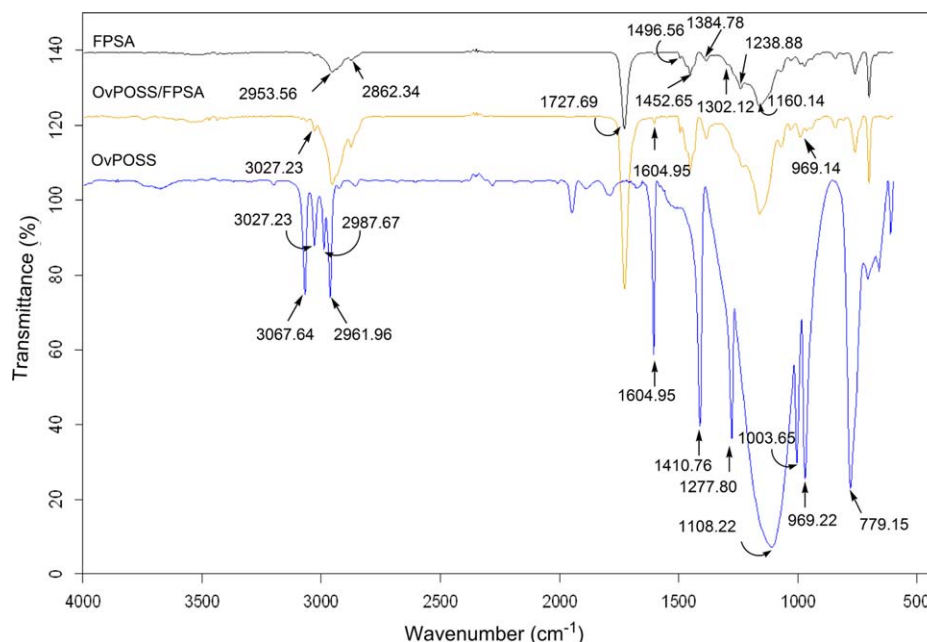
Figure 3. FTIR spectra of OvPOSS, FPSA, and OvPOSS/FPSA composite films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 2 illustrates the particle size distributions of the FPSA, OvPOSS/FPSA composite latexes. The average diameter of FPSA latexes is about 88 nm, while the diameter of OvPOSS/FPSA composite latexes is 95 nm, which is slightly bigger than that of the FPAS, it was probability attribute to the encapsulation of POSS cages, which shown in Scheme 1. It was reported that POSS cage can promote the crosslinking of the chains to form much denser particles.[12] Therefore, when the OvPOSS content increasing to 1.0%, the average diameter of the composite latex is decreased to 89 nm. The results were almost consistent with the results observed by the TEM, and provides further evidence that composite latexes with star-shape structure were prepared.

The Chemical Structure

Figure 3 shows the FTIR spectra of OvPOSS, FPSA, and OvPOSS/FPSA composite materials. In FTIR spectrum of FPSA, The characteristic stretching peaks of $-CH_3$ and $-CH_2$ groups are at 2953 and 2862 cm^{-1}, respectively. The stretching vibration of $C=O$ group at 1727 cm^{-1} is attributed to the carboxy of poly(styrene-acrylate) while the absorption peak at 1496 cm^{-1} is related to phenyl group. The typical absorption at 1302 and 1238 cm^{-1} are assigned to the $-CF$ and $-CF_3$ stretching vibration peaks, which provided evidence that DFMA is copolymerized with poly(styrene-acrylate).[18] There is a strong absorption peak at 1108 cm^{-1} belongs to the Si$-$O$-$Si stretching vibration band of POSS cage in the spectrum of OvPOSS,
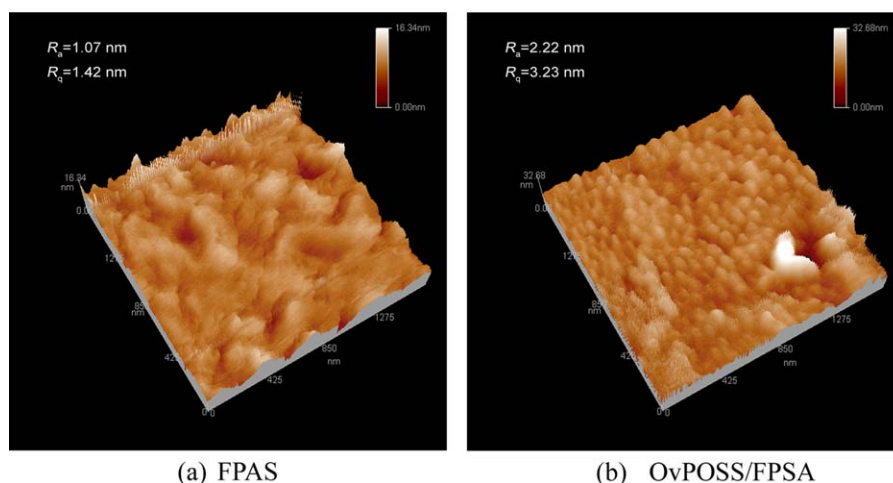

Figure 4. AFM images of FPSA and OvPOSS/FPSA composites films with sizes of 17 μm $\times$ 17 μm. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
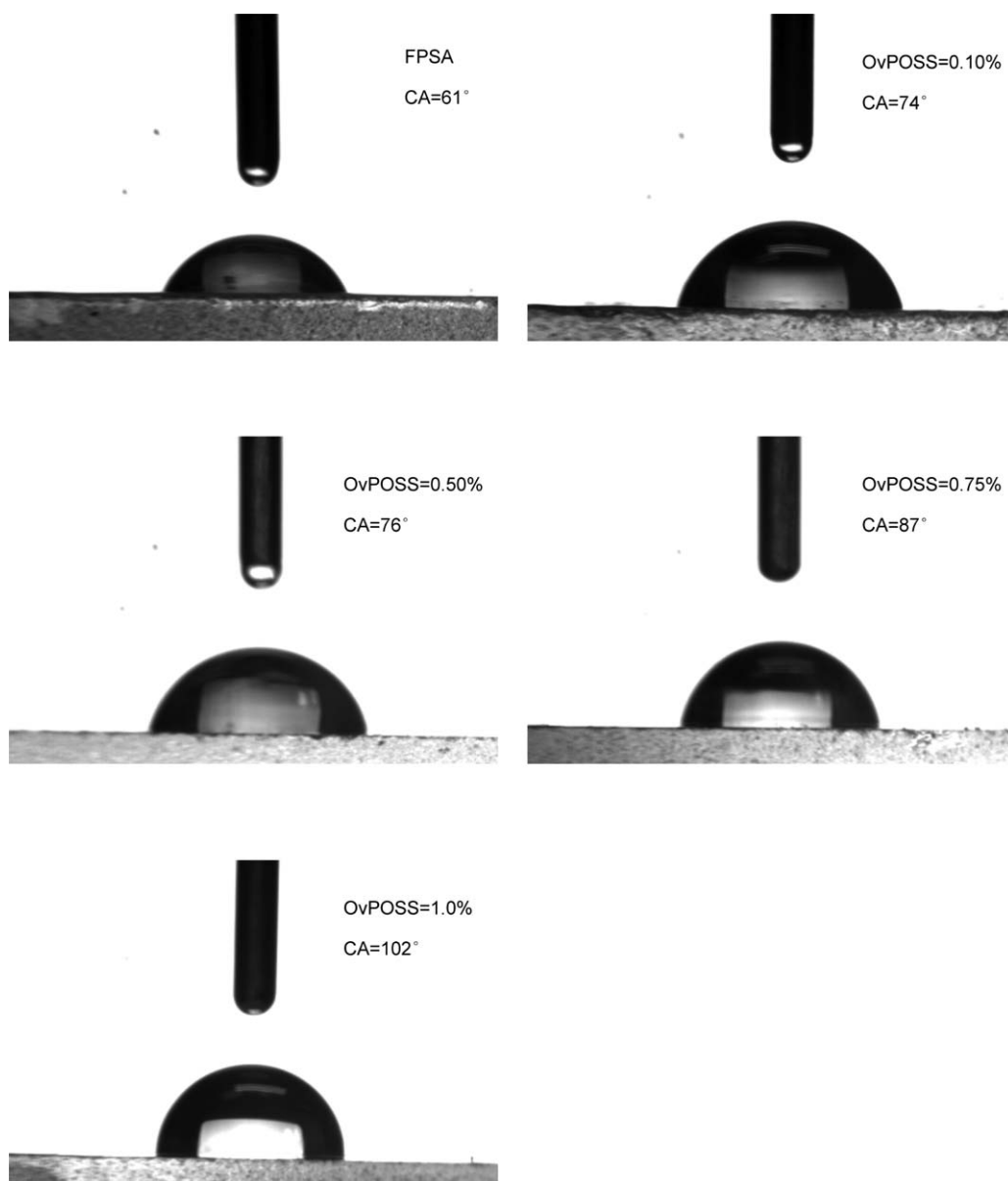
Figure 5. WCA of P FPSA and OvPOSS/FPSA composites films.

and 3027, 3067, 1604, and 969 cm^{-1} are due to the characteristic peaks of C=C groups. However, compared with the spectrum of FPSA, the absorption peak at 1160 cm^{-1} attributable to the stretching vibrations of —C—O group from poly(styrene-acrylate) became sharp and strong in the FTIR spectrum of OvPOSS/FPSA, resulted *from* the introduction of Si—O—Si groups into FPSA. At the same time, new absorption peak at 3027, 1604, and 969 cm^{-1} belong to C=C groups appeared. It can reasonably be assumed that OvPOSS had already successfully grafted onto the surface of FPSA particle, although only part of eight reactive C=C groups had carried out copolymerization.

The Surface Morphology

Surface topography and surface average roughness (R_a), root mean square roughness (R_q) of FPSA, and OvPOSS/FPSA composite films in an area of 1.7 μm $\times$1.7 μm were examined by AFM, as illustrated in Figure 4. It can be found that the surface of FPSA seems to be smooth and neat. After grafting reaction, the OvPOSS/FPSA composite surface was rougher than that of FPSA, the composite surface was enveloped by a layer of OvPOSS particles and many prominence were formed which though to be the aggregates of OvPOSS particles. In addition, the R_a and R_q of FPSA surface were 1.07 and 1.42 nm, respectively, while responding value was 2.22 and 3.23 nm in OvPOSS/FPSA surface, which confirmed that the grafting reaction had increased the roughness of composite surface.

The surface wettability of composite film surface is controlled by chemical composition and topography of composite surface, and higher hydrophobicity of a film can be reflected by higher contact angle of water on the film.[11,19] To examine the
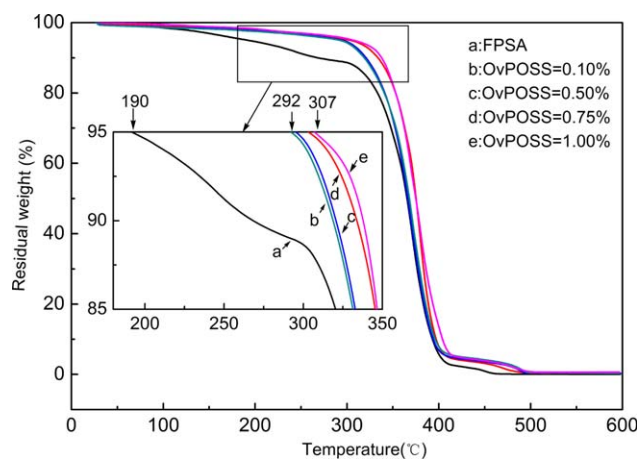
Figure 6. TGA curves of FPAS and OvPOSS/FPAS composite films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

hydrophobicity of the composite film surface, WCA measurements are carried out and shown in Figure 5. It can be found that obvious changes of WCA were observed from the FPSA and OvPOSS/FPSA composite films, the WCA increased from 74° to 102° with the increase of OvPOSS content from 0.1 to 1.0 wt %, which means that the addition of OvPOSS has strengthened the hydrophobicity of composite films. This could be explained that the introduction of DFMA had enhanced the surface free energy, while the grafting reaction of OvPOSS had increased the surface roughness, which is consistent with the AFM results.

The Thermal Stability

The thermal decomposition behavior of FPSA and OvPOSS/FPSA composite films was showed in Figure 6. The temperature corresponding to 5 wt % loss was defined as the initial degradation temperature (T_d).[1,20] The T_d of OvPOSS/FPSA composite films with 0.1 wt % OvPOSS is 292 °C, which is about 100 °C higher than that of the FPSA films, and also increases to 307 °C with 1.0 wt % OvPOSS. The results further confirms that the incorporation of OvPOSS groups on the surface of composite films enhances the thermal stability, and the increase of T_d was cause by the rigid nature of POSS cage which has the Si—O—Si framework and the steric effect of POSS may affect the movement of the local chain of the polymer.[17]

CONCLUSIONS

In present work, new OvPOSS/FPSA composite latexes were successfully synthesized by pre-emulsification and emulsion polymerization. The composite latexes possessed obvious core-shell structure and OvPOSS had successfully grafted onto the surface of FPSA latexes. The average diameter of OvPOSS/FPSA with 0.10 wt % OvPOSS (95 nm) was slightly larger than that of FPSA (89 nm), and decreased with increasing the content of OvPOSS. The grafting reaction had increased the roughness of the composite surface. The surface wettability of composite film surface was improved, and the WCA reached to 102° when increasing of OvPOSS content to 1.0 wt %. The thermal

stability of OvPOSS/FPSA composite films was evidently enhanced relative to that of the rigid nature of POSS cage.

REFERENCES

1. Liao, W. B.; Teng, H. P.; Qu, J. Q.; Masuda, T. *Prog. Org. Coat.* **2011**, *71*, 376.

2. Hou, G. X.; Gao, J. G.; Tian, C.; Wu, X. J. *Mater. Chem. Phys.* **2014**, *148*, 236.

3. Wohl, C. J.; Belcher, M. A.; Ghose, S.; Connell, J. W. *Appl. Surf. Sci.* **2009**, *255*, 8135.

4. Zhou, Q.; Wang, Z. Q.; Shi, Y. L.; Fang, J. H.; Gao, H. Q.; Loo, L. S. *Appl. Surf. Sci.* **2013**, *284*, 118.

5. Huang, D. Y.; Zhang, C. L.; Yu, K. F.; Wang, T. T.; Ma, J. X. *Polym. Bull.* **2014**, *71*, 1877.

6. Godnjaveca, J.; Znoja, B.; Veronovski, N.; Venturinia, P. *Prog. Org. Coat.* **2012**, *74*, 654.

7. Xu, H. Y.; Kuo, S. W.; Huang, C. F.; Chang, F. C. *J. Polym. Res.* **2002**, *9*, 239.

8. Liang, K. W.; Toghiani, H. Jr; Pittman, C. U. *J. Inorg. Organomet. Polym. Mater.* **2011**, *21*, 128.

9. Monticelli, O.; Fina, A.; Ullah, A.; Waghmare, P. *Macromolecule* **2009**, *42*, 6614.

10. Markovic, E.; Clarke, S.; Matisons, J.; Simon, G. P. *Macromolecule* **2008**, *41*, 1685.

11. Song, B.; Meng, L. H.; Huang, Y. D. *Appl. Surf. Sci.* **2012**, *258*, 10154.

12. Ke, F. Y.; Zhang, C.; Guang, S. Y.; Xu, H. Y. *J. Appl. Polym. Sci.* **2013**, *127*, 2628.

13. Ma, Y. L.; He, L.; Pan, A. Z.; Zhao, C. B. *J. Mater. Sci.* **2015**, *50*, 2158.

14. Wang, W. P.; Jie, X. X.; Fei, M.; Jiang, H. *J. Polym. Res.* **2011**, *18*, 13.

15. Wang, X.; Hu, Y.; Song, L.; Xing, W. Y.; Lu, H. D.; Lv, P.; Jie, G. X. *J. Polym. Res.* **2011**, *18*, 721.

16. Wang, W. P.; Ding, W. L.; Yu, J.; Fei, M.; Tang, J. Y. *J. Polym. Res.* **2012**, *19*, 9948.

17. Wang, W. P.; Shen, Q.; Zha, W. B.; Zhu, G. J. *J. Polym. Res.* **2011**, *18*, 1119.

18. Li, K.; Zeng, X. R.; Li, H. Q.; Lai, X. *J. Appl. Surf. Sci.* **2014**, *298*, 214.

19. Han, D. X.; Zhu, L. Q.; Chen, Y. C.; Li, W. P.; Feng, L. L. *J. Fluorine Chem.* **2013**, *156*, 38.

20. Liao, W. B.; Qu, J. Q.; Li, Z.; Chen, H. Q. *Chin. J. Chem. Eng.* **2010**, *18*, 156.