Sol–Gel Process of Alkoxysilane in Emulsifier-Involved Aqueous Emulsions: A One-Pot Synthetic Route to Emulsions of Core-Shell Composite Particles and Their Applications

Lin Niu, Zhengbin Xia, Liang Lei, Yanhong Zhang, Li Zhong
School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, China
Correspondence to: Z. Xia (E-mail: cezhbxia@scut.edu.cn)

ABSTRACT: In this work, a one-pot route to prepare emulsions of silica/polymer core-shell composite particles was developed through the direct sol–gel processing of alkoxysilane on the surface of newly synthesized template polymer particles in emulsifier-involved aqueous emulsions. It included two continuous steps: first, the polymer emulsions were synthesized through emulsion polymerization, and second, the template particles in the emulsions were directly coated with silica via sol–gel reaction of precursors without adding ethanol or removing emulsifiers. The size and morphology of the composite particles were characterized, and the results showed that the silica/polymer composite particles with core-shell structure could be prepared only on the basis of cationic template emulsions, and the *in situ*-coating reaction of sol–gel precursors carried on easier with the increasing of the positive charge density on the surface of template particles. The films formed from the composite emulsions were found to have superior optical and flame-retardant properties compared to polymer films, owing to the core-shell composite microstructure of the particles. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 128: 4237–4244, 2013

INTRODUCTION

The silica/polymer composite particles with tailored core-shell morphologies have long been the primary focus in fields of functional materials. These particles integrated two dissimilar compositions together in a microscale vessel and could act enhanced chemical and physical properties than the single-composition counterparts. The hierarchical structure of particles allows the resultant materials to have a structure of microphase separation or to be possessed into hollow morphologies, which makes the core-shell composite particles attractive for applications in many areas ranging from carrier microspheres to high-quality coatings.[1–9]

In the preparation of composite particles with inorganic shells, the method of sol–gel template synthesis is commonly used to introduce silicon compositions onto the surface of the polymer particles, which involves the polycondensation reaction of monomeric precursors such as tetraethoxysilane (TEOS). However, there exist two main disadvantages in the current sol–gel template processing, which hinder the use of silica-shell composite particles in practical applications.

First, in current techniques, the sol–gel modification of precursor on template polymer particles is generally proceeding in ethanol or other nonhydrolytic organic solvents, in order to weaken the hydrolysis and condensation of alkoxysilane and better control the particle morphology.[10–21] However, the template polymer particles are always synthesized through aqueous emulsion polymerization, and so the template particles should be centrifugal-separated, dried under vacuum, and shifted to ethanol before sol–gel processing. This manipulation is too complex to be applied in industry, while the film properties and cost efficiency of the final product are also lowered due to the use of ethanol.

Second, in the preparation of template particles, certain functional groups should be grafted onto the particle surface in advance, such as hydroxyl, carboxyl, and amino groups, to help attract the siloxane oligomers and ensure the effective assembly of silica on the particle surface.[22] But emulsifiers, which are commonly used in emulsion polymerization, also tend to assemble on particle surfaces and have an adverse effect on the function of surface groups. So, emulsifier-free emulsion polymerization is widely chosen to prepare the template polymer particles to exclude the interference of emulsifiers, especially in the aqueous sol–gel modifications.[13,23] However, emulsifier-free emulsion polymerization is not an ideal route to synthesize

Additional Supporting Information may be found in the online version of this article.

polymer particles with fine structures, which lowered the properties of the final composite emulsions and limited their practical applications.

To sum up, nowadays, the template methods for preparing silica/polymer core-shell composite particles are almost all involved in ethanol-phase modifications, which are not suitable for industrial applications. There are also aqueous-phase sol–gel processing reported, but most are based on emulsifier-free emulsion polymerization, and the properties of the composite emulsions would be influenced by this polymerization method.[24–29] Therefore, it is necessary to explore the sol–gel reaction process of alkoxysilane in emulsifier-involved aqueous emulsions, through which a one-pot synthetic route to emulsions of core-shell composite particles could be developed, and the properties could be enhanced.

In this work, the template polymer particles will be prepared through emulsifier-involved emulsion polymerization; afterward, the surface sol–gel processing is performed directly in the aqueous emulsions without adding ethanol or removing emulsifiers. Two series of template emulsions (anionic and cationic) will be prepared respectively to explore the influence of emulsifier and surface charge properties of template particles on the morphology of the composite particles, in terms of particle size, composition, and morphology of the particles before and after the sol–gel processing. Furthermore, the composite emulsions will be casted to form films and the relevant properties will be measured, thereby to prove its feasibility in applications.

EXPERIMENTAL

Materials
Sodium dodecyl sulfate (SDS, Guanghua, Guangzhou), TEOS (Guanghua, Guangzhou), potassium persulfate (KPS, Kermel, Tianjin), hexadecyl trimethyl ammonium bromide (CTAB, Bio, Shanghai), and 2,2′-azobis(isobutyramidine) dihydrochloride (AIBA, Runxing, Qingdao) were all purchased in AR grade, while 2-acrylamide-2-methylpropanesulfonic acid (AMPS, Zhenxing, Huixian) and 3-(methacryloxy) propyltrimethoxysilane (MPS, Union Silicon, Nanjing) were supplied in technical grade. Acryloyloxyethyl trimethyl ammonium chloride (MTC, Alfa) was an aqueous solution of 72.0 wt %. All the above reagents were used as accepted without further purification. Methyl methacrylate (Asahi Kasei), butyl acrylate (Asahi Kasei), and styrene (St, Asahi Kasei) were washed with sodium hydroxide solutions (5.0 wt %) for three times and distilled to remove the inhibitor before use. DI (deionized) water was used throughout.

Methods
The preparation of the emulsion of silica/polymer composite particles could be divided into two steps: the preparation of template polymer emulsions and the sol–gel processing afterward, as shown in Figure 1.

Preparation of Template Emulsions
The template polymer emulsions were synthesized through aqueous emulsion polymerization in which the emulsifiers were used. Two series of polymer template emulsion were synthesized in this experiment. One was anionic emulsion prepared with
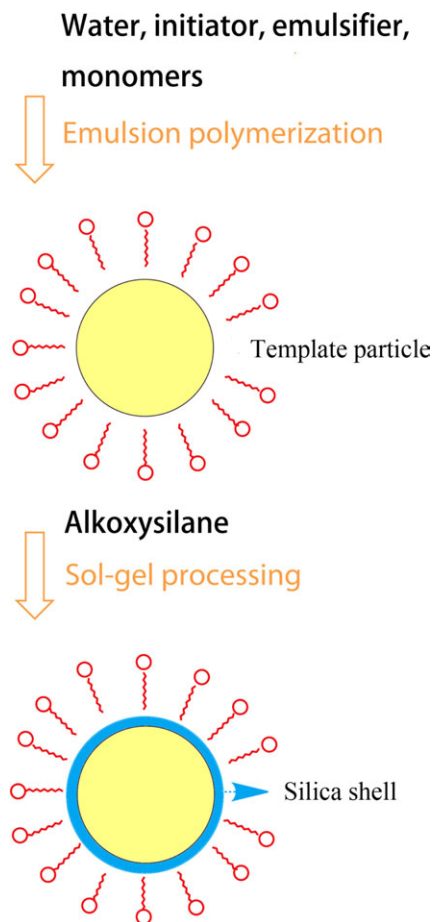

Figure 1. Illustration of the ideal preparation process of silica/polymer core-shell composite particles. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

SDS as emulsifier and KPS as initiator, while the other was cationic emulsion made from CTAB and AIBA. St was used as the template material all through the experiment if without special description, and MPS was used as comonomer to copolymerize with St to provide silanol reaction site on the template particle surface for the next sol–gel process. Although cationic emulsion could also be prepared with anionic initiator, we still chose cationic initiator AIBA to reduce the interference between different electric-charged reagents.

To clarify the influence of emulsifier on the next sol–gel modification, a series of template emulsions were synthesized with varied emulsifier amount and marked as S1–S4 for anionic samples and C1–C4 for cationic samples.

The typical procedure was as following: first, emulsifier (SDS/CTAB) and initiator (KPS/AIBA, 0.3 g) were dissolved in water (285.0 g), and the pH value of the solution was adjusted to 7.0 ± 0.1 with sodium bicarbonate solution. Then, St (15.0 g) and MPS (1.5 g) were mixed and pre-emulsified, after which the mixture was transferred into the reaction vessel, and the polymerization was carried on at 60°C under nitrogen atmosphere for 12 h. The solid content of the resultant emulsion was about 5.5 wt %.
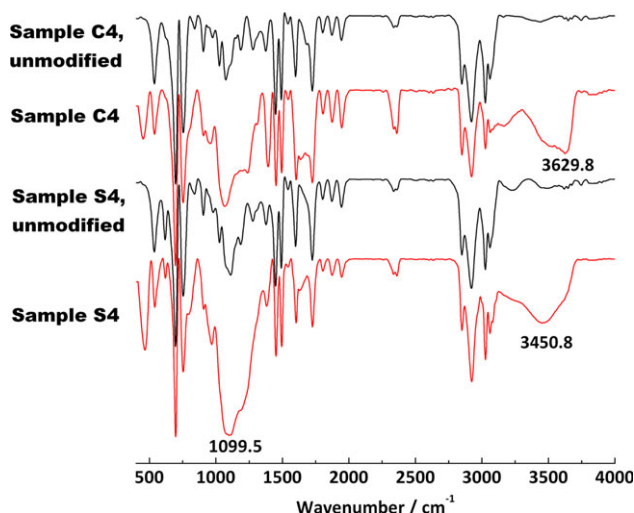
Figure 2. Typical FTIR spectra of the anionic emulsion (S4), cationic emulsion (C4) and the corresponding templates. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The influences of surface charge properties of template particles were also explored. Samples with graded surface charge densities were prepared with the addition of different amounts of ionizable monomer and marked as A1–A5 for anionic samples and M1–M5 for cationic samples.

For the recipes containing ionizable monomer (AMPS/MTC), the ionizable monomer was added into the reaction vessel dropwise after 6 h of the emulsion polymerization. The addition of AMPS or MTC was finished within 30 min and then the polymerization reaction continued for 6 h.

Sol–Gel Processing

In this step, TEOS (1.5 g) was directly added into the template emulsion (30.0 g) after the pH value of emulsion was adjusted. To keep the colloidal stability of emulsions during adjustment, the pH value was calibrated to 10.0 for anionic emulsions and 3.0 for cationic emulsions, respectively. The mixture was stirred for 12 h and aged for 36 h in sealed vessel under ambient temperature, and the emulsion of silica/polymer composite particles was finally prepared.

Characterization

The microstructure of the composite particles was observed by transmission electron microscopy (TEM, Hitachi, H-7650) without staining. To compare the morphology changes of the particles before and after sol–gel process, the diluted emulsions (1.0 wt %) were dip-coated onto glass plates, dried at 40°C under vacuum, and calcinated at 600°C in air; afterward, the morphology changes were observed by atomic force microscopy (AFM, Being, CSPM5000). Fourier transform infrared spectrophotometer (FTIR, Hitachi TENSOR-27) was used to measure the composition of the solid components in the emulsions, by dispersing the dried samples in KBr tablets. The particle size of the emulsions was measured with dynamic light scattering (DLS) using a Malvern Laser Particle Sizer (Malvern, 2S-Nano-S). The silica content of the composite materials was determined by a thermal analyzer

(TGA, Netzsch, STA-449C-Jupiter), with constant heating rate of 10°C/min from 30 to 800°C.

Moreover, films were prepared by casting composite emulsions into glass culture dish and annealed at 60°C. Then the film was ignited in air, and the remaining structure was observed by scanning electron microscopy (SEM, LEO, 1530VP).

RESULTS AND DISCUSSION

Effects of Emulsifier

The influence of emulsifier on the morphology of the final composite particles was studied at first. From the FTIR spectra, in Figure 2, we could see the composition change of the emulsion after sol–gel modification. The absorption peaks around 3400 cm^{-1} are attributed to the silanol groups remained after the sol–gel reaction, while the bands located at 1099 cm^{-1} are attributed to the stretching vibration of the network Si—O—Si bonds. Accordingly, we could find that the hydrolysis and polycondensation reaction occurred in the emulsions, and the composite samples were acquired.

From Figure 3, it could be seen that the particle diameter of two kinds of template emulsions all changed slightly after the sol–gel process, but the trends are different. In the anionic emulsion system, the particle diameters all became a little smaller after modification, while the particle size got a slight increase in the cationic emulsions. This should be attributed to the different electrostatic interaction effects between the template particles and the siloxane oligomers in two systems.

In the anionic emulsion system, electrostatic repulsive effect existed between the anionic template particles and the siloxane oligomers. As the siloxane oligomers generated from TEOS were
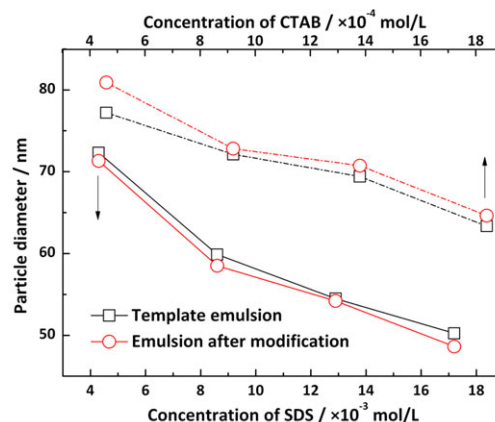
Sample	Emulsifier concentration (mol/L)	Sample	Emulsifier concentration (mol/L)
S1	4.30×10^{-3}	C1	4.60×10^{-4}
S2	* 8.60×10^{-3}	C2	* 9.20×10^{-4}
S3	12.90×10^{-3}	C3	13.80×10^{-4}
S4	17.20×10^{-3}	C4	18.40×10^{-4}

* The critical micelle concentration (CMC).

Figure 3. Comparison of particle size before and after the sol–gel process. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
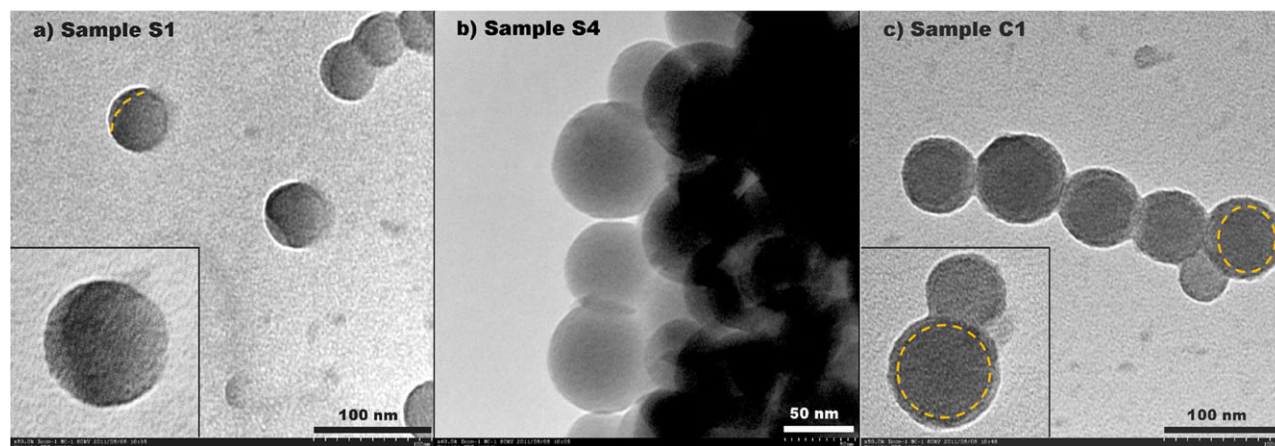
Figure 4. TEM images of the composite particles. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

also negative-charged, it was difficult for them to pass through the electric double layer around the anionic template particles and carry out the condensation reaction with the silanol groups on the particle surface. In this case, the template particle tended to keep its original size and morphology as shown in Figure 4(b). The siloxane oligomers were inclined to scatter in the aqueous phase and finally generated tiny silica particles, which would influence the DLS results and lower the average particle size consequently. The existence of excess anionic emulsifiers aggravated this process, as the adsorption of emulsifier molecules on the particle surface would enhance the electrostatic repulsion. For the template particles of sample S1 (C < CMC), which were not fully wrapped by emulsifiers, small amount of siloxane oligomers could reach their surface and perform condensation reaction there, forming composite particles with heterogeneous structure as shown in Figure 4(a).

Comparatively, there was electrostatic attraction effect between the template particles and the siloxane oligomers in cationic emulsions. This was because that the polymer particles were positive-charged due to the cationic initiator and emulsifiers used, and so the siloxane oligomers could be attracted onto the particle surface and react there to form regular core-shell structure as shown in Figure 4(c). And it could be found that the excess cationic emulsifiers did have an adverse effect on the formation of core-shell structure, as the particle diameter change was largest in sample C1 (C < CMC). This might result from the interference of excess micelles toward oligomers.

Effects of Surface Charge Density
The electric charge of the particles mainly originated from the adsorption of emulsifier molecules and the ionization of the functional groups on the surface of the particles. Therefore, the surface charge density of the template particles could be adjusted by adding a certain amount of ionizable monomers in polymerization process. For the anionic emulsion system (sample A1–A5 series), AMPS was used as comonomer to synthesize the template emulsions based on sample S3 (with SDS concentration of 12.90×10^{-3} mol/L), while MTC was used to synthesize the cationic emulsions system (sample M1–M5 series) based on sample C3 (with CTAB concentration of 13.80×10^{-4} mol/L).

Figure 5 showed the influence of the ionizable monomer content on the size and morphology of the composite particles, measured with DLS and TEM. It could be found that for the anionic emulsion system, the particles diameter were almost the same before and after modification, even with the increasing of AMPS content. This was because the enhancement of negative charge density on the template particle surface made it more and more difficult to carry out the *in situ*-coating reaction due to the electrostatic repulsion effect. So the siloxane oligomers in anionic emulsions tended to self-aggregate and finally formed tiny inorganic particles scattering in the aqueous phase, as demonstrated in Figure 5(b). As for the cationic emulsion system, the size of composite particles increased obviously with the increasing of MTC content [Figure 5(a)]. When MTC content was 3.0 wt %, the diameter differential between the template particles and the composite particles was about 1.0 nm [$d_2 - d_1 = 1.0$ nm, as shown in Figure 5(c)], and this value increased to 14.6 nm [$d_2 - d_1 = 14.6$ nm, as shown in Figure 5(d)] when MTC content was 15.0 wt %. This was because the positive charge density on the template particle surface was increased by the introduction of cationic monomer MTC, which enhanced the attractiveness between the template particle and the siloxane oligomers and lead to the formation of core-shell structure through the *in situ*-coating reaction [Figure 5(c,d)].

To better observe the microstructure of the nanocomposite particles, the diluted template and composite emulsions were dip-coated onto the glass plates, and the morphology of particles before and after calcination was observed through AFM and shown in Figure 6. For anionic composite emulsion (sample A5), comparing the surface morphology shown in Figure 6(a,b), it could be found that the film became smoother after calcinations. This suggested that there existed nearly no inorganic shell around the template particles, so that the film could not remain a granular surface after removing the polymer particles by heating. In contrast, the surface morphology of the film made from cationic composite emulsion (sample M5) was almost the same before and after calcinations [Figure 6(c,d)]. Meanwhile, the plates dip-coated with template emulsions were also calcined, and it was found that the films were close to disappear after calcination. So it could be proved that the particles of polymer/silica core-shell
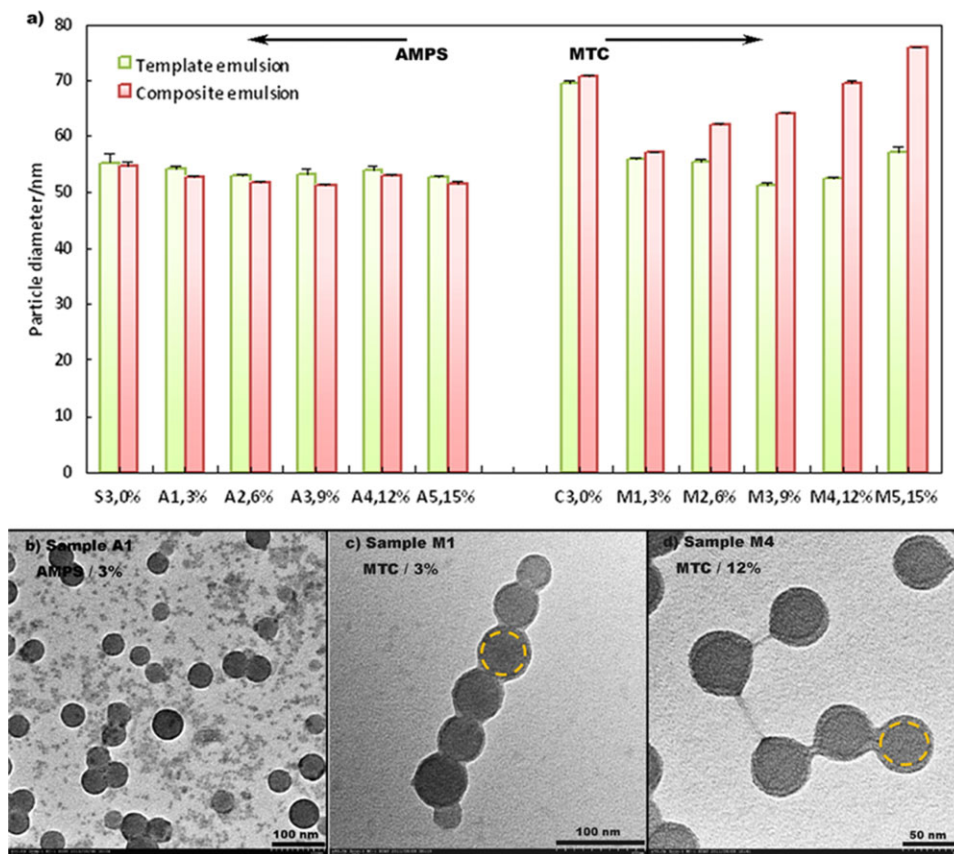
Figure 5. Influence of the ionizable monomer content on the size and morphology of the composite particles. (a) The particle size comparison (DLS results) of the template emulsion and its corresponding composite emulsion; (b) TEM image of anionic composite emulsion; (c, d) TEM image of cationic composite emulsion. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
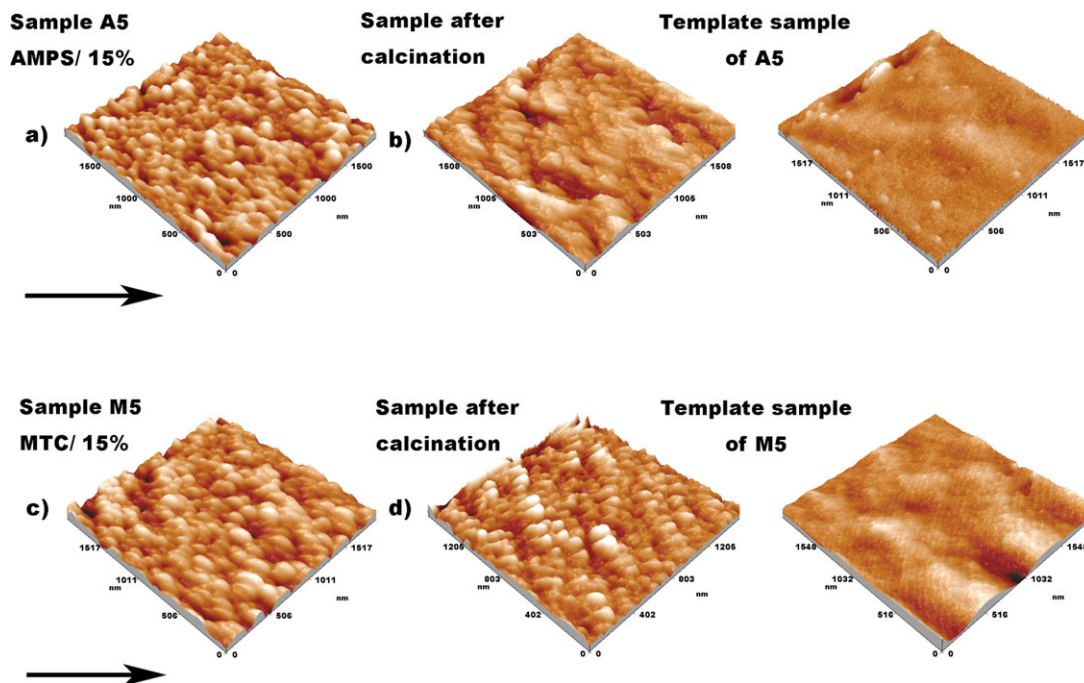

Figure 6. AFM images of the films made from anionic and cationic composite emulsions. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
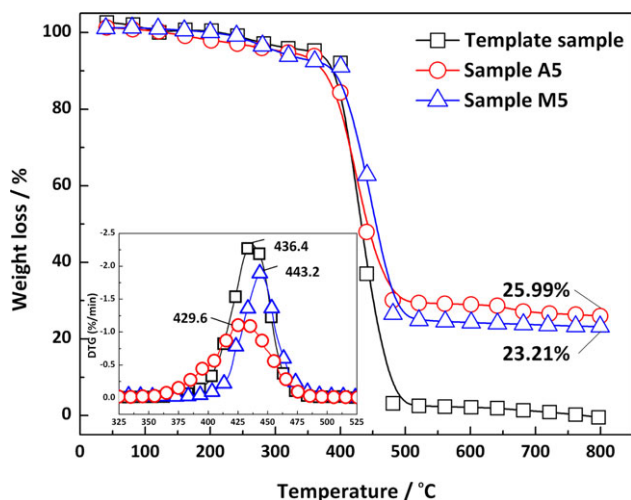
Figure 7. TGA and DTG curves of the solid composite materials made from A5, M5, and the template emulsion. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

structure were generated in cationic composite emulsion by the *in situ* sol–gel reaction on the surface of the template particles.

Accounting of the Alkoxysilane Conversion

The theoretical silica content in the final composite materials was 23.90 wt % for both anionic and cationic systems, which could be calculated according to the recipes in "Methods" section. The actual silica content was measured by using a thermal analyzer (TGA), and the values were found to be close to the theoretical one, just as illustrated in Figure 7. It should be noticed that TGA data measured here were the silica contents of the emulsions rather than the silica contents of the composite particles, for the free siloxane precipitates were difficult to separate in both anionic and cationic emulsions. From the TGA and DTG curves, we could find that, no matter for the anionic composite emulsion, cationic composite emulsion, or template emulsion samples, there existed only one degradation stage during heating, which corresponded to the decomposition of template polystyrene part. This suggested that most alkoxysilane molecules have transformed into silica (Si—O—Si structure) through condensation reaction, so that the inorganic components could remain in the ash after heating.

From the silica content, we could find that the utilization efficiency was ideal to prepare silicon-modified composite emulsions through sol–gel processing with alkoxysilane. Combined with the market price of the raw materials and the recipe, the materials' cost of the composite emulsion ($\sim$ 11.0 wt %) was about 1559.51 RMB/ton for anionic type and 2158.84 RMB/ton for cationic type. The price of common acrylic emulsions (40.0 wt %, Celvolit® acrylic emulsion) in market is about 80,000 RMB/ton. In view of the possible performance improvement of cationic composite emulsions, we believed that it was economically feasible to prepare the silica/polymer composite emulsions through the sol–gel processing with alkoxysilane.

Properties of the Composite Emulsions

To sum up, the silica/polymer core-shell composite particles could be directly prepared via the sol–gel processing of alkoxysi-

lane in aqueous cationic emulsions with acceptable financial cost. Through adjusting the composition of the polymer template, it is possible to prepare applicable materials with the composite emulsions with various special properties.

To prove this, we used one new template emulsion ($T_g = 10.63°C$), which could form film under 60°C to replace polystyrene as template, and so the coating properties of the composite emulsions could be checked. Then the template particles were coated with silica shell by the sol–gel process, forming composite particles with multilayer core-shell structure. The corresponding film was obtained by casting the composite emulsions into glass culture dish and dried at 60°C, and the relevant properties were tested as below.

The optical clarity of the films made from the template and composite emulsions was assessed by UV–vis spectrometry, and the results were shown in Figure 8. It could be found that the film transparency of the composite emulsion was better than that of the template emulsion. This was because that the silica shells were homogenously distributed in the bulk of films with the coalescence of the composite particles during the film-formation process. As the refractive index of silica (1.458) is less than the value of polymer of poly(methyl methacrylate) type (1.4893–1.4899), the light transmittance of the composite film was enhanced.[30]

The silica/polymer microscale composite materials have long been used to enhance the flame-retardant properties of coatings. Normally, sol of silica particles was used as the source of inorganic composition, which was incorporated into the coatings to improve its flame-retardant property, but this direct addition of inorganic particles might actually result in a decline in the film properties. This was because that the inorganic particles were easy to aggregate in coatings, unevenly distribute inside the film, and would finally result in an incomplete protective layer on base materials in the film-formation process. The vulnerable
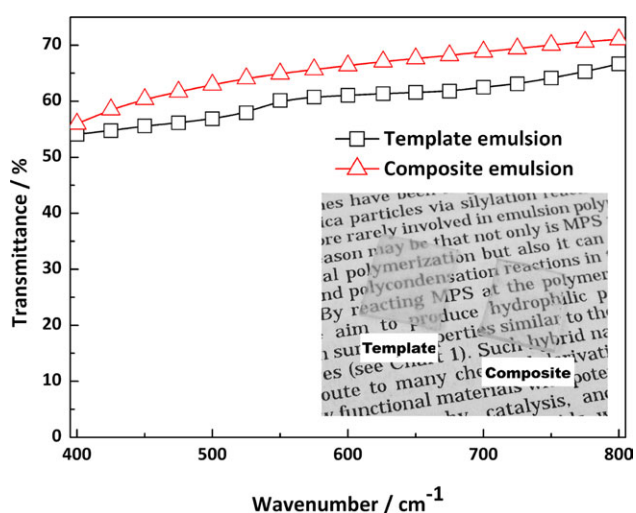

Figure 8. The transmittance spectra of the films made from template emulsion (film thickness: 800 gym) and composite emulsion (film thickness: 1080 gym). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
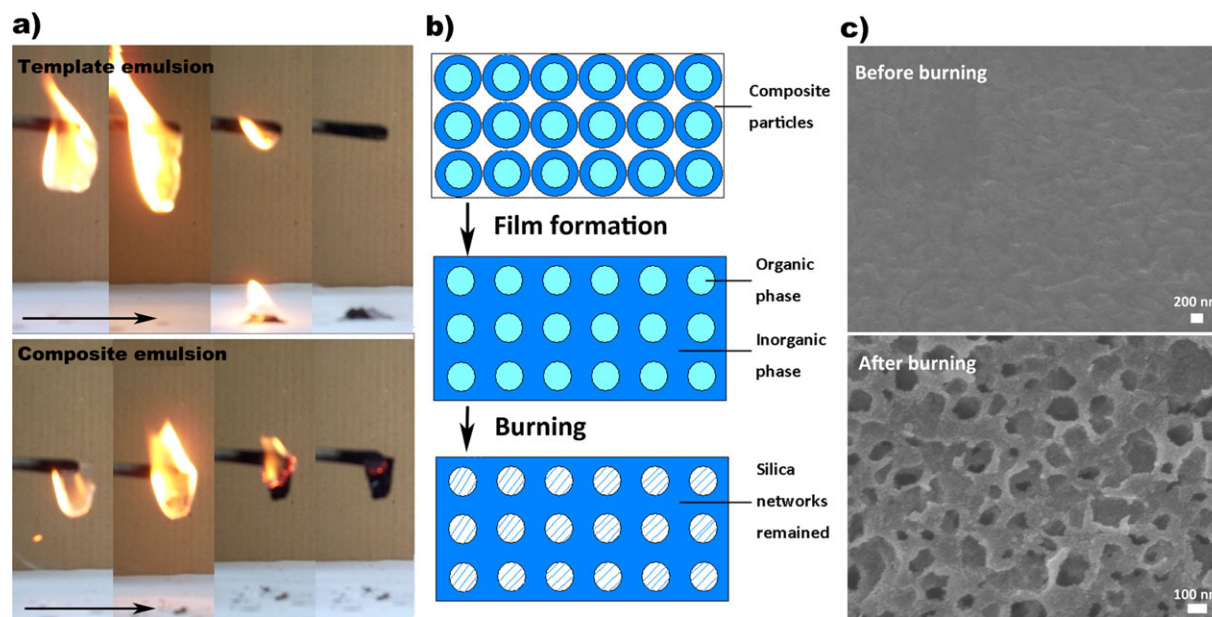
Figure 9. (a) The burning behavior of the template emulsion film and composite emulsion film; (b) the schematic representation of the structural change of the composite emulsion films after burning; and (c) the corresponding SEM images. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

parts would bring down the flame-retardant property of the whole material, and the effectiveness of coatings was reduced.[31]

Based on the cationic composite emulsion, an intact heat-insulating film could be formed. This was because that the silica shell would uniformly distribute in the film and form nanoscale interpenetrating networks with the coalescence of composite particles. The organic phase could be trapped as a whole by the silica networks during and after burning, so that the dripping of burning coatings could be avoided compared to the organic coatings, as illustrated in Figure 9. Meanwhile, the carbon remained after burning of polymer would deposit on the silica networks and form a porous silica/carbonaceous residue layer on substrate surface, which could insulate fire and heat afterward.[32,33]

CONCLUSIONS

In summary, a convenient, one-pot route for preparing emulsions of silica/polymer core-shell composite particles was developed based on the direct sol–gel processing of alkoxysilane in the emulsifier-involved cationic polymer emulsions. It included two continuous steps: first, the template particles were synthesized through the emulsifier-involved emulsion polymerization, and then the surface of the particles was coated with silica from sol–gel precursors such as TEOS in the aqueous phase without adding ethanol or removing emulsifiers.

Anionic and cationic template emulsions were prepared, respectively, and the influence of emulsifiers and the surface charge density of the template particles were studied. The results showed that the silica/polymer composite particles with core-shell structure were prepared only on the basis of cationic template emulsions. For anionic emulsion, the template particles bear the same negative charges as the siloxane oligomers generated from TEOS, and so there existed electrostatic repulsion between them. In this case, the oligomers were easier to form siloxane precipitates in the bulk phase rather than condensed on the template particle surface. Things were different for the cationic template emulsions, because the cationic particles could attract the negatively charged oligomers onto their surface. Silica shell could be produced on the surface of cationic template particles by sol–gel process, forming composite particles of silica/polymer core-shell structure. Moreover, with the increase in the positive charge density on the surface of cationic particles, the *in situ*-coating reaction of sol–gel precursors was easier, even under the obstruction of excess emulsifier molecules. The cast film formed by composite emulsions based on cationic template emulsion was found to have excellent optical and flame-retardant properties owing to the core-shell composite microstructure of particles.

REFERENCES

1. Tissot, I.; Novat, C.; Lefebvre, F.; Bourgeat-Lami, E. *Macromolecules* **2001**, *34*, 5737.

2. Yang, J.; Hu, D.; Fang, Y.; Bai, C.; Wang, H. *Chem. Mater.* **2006**, *18*, 4902.

3. Schmid, A.; Fujii, S.; Armes, S. P.; Leite, C. A. P.; Galembeck, F.; Minami, H.; Saito, N.; Okubo, M. *Chem. Mater.* **2007**, *19*, 2435.

4. Ji, H.; Wang, S.; Yang, X. *Polymer* **2009**, *50*, 133.

5. Ding, X.; Jiang, Y.; Yu, K.; Tao, N.; Zhao, J.; Wang, Z. *Mater. Lett.* **2004**, *58*, 1722.

6. Hong, J.; Han, H.; Hong, C. K.; Shim, S. E. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 2884.

7. Schottner, G. *Chem. Mater.* **2001**, *13*, 3422.

8. Watanabe, M.; Tamai, T. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 4736.

9. Yang, Z.; Niu, Z.; Lu, Y.; Hu, Z.; Han, C. C. *Angew. Chem. Int. Ed.* **2003**, *42*, 1943.

10. Ni, K.; Shan, G.; Weng, Z.; Sheibat-Othman, N.; Fevotte, G.; Lefebvre, F.; Bourgeat-Lami, E. *Macromolecules* **2005**, *38*, 7321.

11. Liu, B.; Yan, E.; Zhang, X.; Yang, X.; Bai, F. *J. Colloid. Interf. Sci.* **2012**, *369*, 144.

12. Tissot, I.; Reymond, J.; Lefebvre, F.; Bourgeat-Lami, E. *Chem. Mater.* **2002**, *14*, 1325.

13. Lu, Y.; McLellan, J.; Xia, Y. *Langmuir* **2004**, *20*, 3464.

14. Chen, Y.; Kang, E. T.; Neoh, K. G.; Greiner, A. *Adv. Funct. Mater.* **2005**, *15*, 113.

15. Liu, H.; Wang, D.; Yang, X. *Colloids Surf. A* **2012**, *397*, 48.

16. Guo, X.; Liu, X.; Xu, B.; Dou, T. *Colloids Surf. A* **2009**, *345*, 141.

17. Pi, M.; Yang, T.; Yuan, J.; Fujii, S.; Kakigi, Y.; Nakamura, Y.; Cheng, S. *Colloids Surf. A* **2010**, *78*, 193.

18. Du, X.; He, J. *Mater. Res. Bull.* **2009**, *44*, 1238.

19. Taniguchi, T.; Kashiwakura, T.; Inada, T.; Kunisada, Y.; Kasuya, M.; Kohri, M.; Nakahira, T. J. *Colloid Interf. Sci.* **2010**, *347*, 62.

20. Fan, H.; Lei, Z.; Pan, J. H.; Zhao, X. S. *Mater. Lett.* **2011**, *65*, 1811.

21. Liu, J.; Zhang, G.; Ao, W.; Yang, K.; Peng, S.; Muller-Goymann, C. *Appl. Surf. Sci.* **2012**, *258*, 8083.

22. Wang, L.; Asher, S. A. *Chem. Mater.* **2009**, *21*, 4608.

23. Wang, S., Zhang, M.; Wang, D.; Zhang, W.; Liu, S. *Micropor. Mesopor. Mater.* **2011**, *139*, 1.

24. Ge, C.; Zhang, D.; Wang, A.; Yin, H.; Ren, M.; Liu, Y.; Jiang, T.; Yu, L. J. *Phys. Chem. Solids.* **2009**, *70*, 1432.

25. Syoufian, A.; Inoue, Y.; Yada, M.; Nakashima, K. *Mater. Lett.* **2007**, *61*, 1572.

26. Qian, Z.; Zhang, Z.; Song, L.; Liu, H. *J. Mater. Chem.* **2009**, *19*, 1297.

27. Tamai, T.; Watanabe, M. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 273.

28. Graf, C.; Vossen, D. L. J.; Imhof, A.; Blaaderen, A. *Langmuir* **2003**, *19*, 6693.

29. Bourgeat-Lami, E.; Tissot, I.; Lefebvre, F. *Macromolecules* **2002**, *35*, 6185.

30. Zhang, J.; Liu, N.; Wang, M.; Ge, X.; Wu, M.; Yang, J.; Wu, Q.; Jin, Z. *J. Polym. Sci., Part A: Polym Chem.* **2012**, *48*, 3128.

31. Zou, H.; Wu, S.; Shen, J. *Chem. Rev.* **2008**, *108*, 3893.

32. Sahoo, P. K.; Samal, R.; Swain, S. K.; Rana, P. K. *Eur. Polym. J.* **2008**, *44*, 3522.

33. Gilman, J. W.; Jackson, C. L.; Morgan, A. B.; Harris, R.; Manias, E.; Giannelis, E. P.; Phillips, S. H. *Chem. Mater.* **2000**, *12*, 1866.