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RESEARCH ARTICLE

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Preparation of raspberry-like PMMA/SiO_2 nanocomposite particles

Abstract Water-borne raspberry-like PMMA/SiO_2 nanocom-posite particles were prepared via free radical copolymerization of methyl methacrylate (MMA) with 1-vinylimidazole (1-VID) in the presence of ultrafine aqueous silica sols. The acid-base interaction between hydroxyl groups (acidic) of silica surfaces and amino groups (basic) of 1-VID was strong enough for promoting the formation of long-standing stable PMMA/SiO_2 nanocomposite particles when 10 mol% or more 1-VID as auxiliary monomer was used. The average particle sizes and the silica contents of the nanocomposite particles were in the ranges from 120–330 nm and 15%–20%, respectively. TEM and SEM observations indicated a raspberry-like morphology of the obtained nanocomposite particles.

Keywords raspberry-like structure, nanocomposite particles, nano-SiO_2

1 Introduction

In the past few years organic-inorganic nanocomposite particles have attracted rapidly growing interest for their superior properties. Those composite particles are composed of two kinds of ultrafine particles. They could be widely used as high abrasion-resist coating, new electric materials, magnetic materials or luminescent materials for the nano-effect of the composite materials[1–5].

However, since the surfaces of inorganic particles are usually hydrophilic, while polymers are usually hydrophobic, the surfaces of inorganic particles usually need to be modified or pretreated using some so-called coupling agents in order to promote the compatibility between the polymeric phase and the inorganic phase for obtaining a core-shell morphology. For instances, Luna-Xavier [6] synthesized silica coated PMMA composite particles via emulsion polymerization by using cationic initiator; Reculusa et al. [7] prepared the composite particles with core-shell morphology and raspberry-like morphology, respectively via microemulsion polymerization by using cationic and anionic surfactants. Bourgeat-Lami and Lang [9] reported the synthesis of polystyrene/silica nanocomposite particles with core-shell structure by dispersion polymerization of styrene in aqueous ethanol medium in the presence of surface-modified silica particles and poly (*N*-vinylpyrrolidone) as stabilizer. Obviously, the treatment of the surfaces of inorganic particles is very tedious and energy-consuming. To work out this problem, Barthet et al. [10] and Azioune et al [11] proposed a novel method to synthesize a series of raspberry-like core-shell nanocomposite particles with vinyl polymer as core and nano-silica as shell. In their method, 4-vinylpyridine (4-VP) was used as an auxiliary monomer. Thus the basic amino groups from 4-VP could interact with the acidic hydroxyl groups from nano-silica surfaces to enhance the compatibility between the organic phase and the inorganic phase, and the surface hydrophilic silica particles could act as Perking emulsifier [12] to stabilize the organic particles. This synthetic route probably has several advantages: (1) It is a simple, one-pot protocol based on readily available starting materials; (2) No surface pretreatment or modification of inorganic particles is necessary; (3) No addition of surfactant or co-surfactant is required. However, the auxiliary monomer they involved was only 4-VP, no other auxiliary monomers were successfully tried. Additionally, the formation mechanism of raspberry-like core-shell nanocomposite particles by this method is not clearly so far. Therefore, further work is very necessary in this area.

In the present work, we used 1-vinylimidazolw (1-VID) as the auxiliary monomer and successfully synthesized a series of long-standing stable raspberry-like PMMA/SiO_2 nanocomposite particles via a ‘soap-free’ heterophase polymerization in the presence of an ultrafine aqueous silica sol and water as the continuous phase. Since the surface

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hydroxyl groups of silica particle are acidic, the amino groups (basic) of 1-VID should promote the compatibility between the polymeric phase and the nanosilica phase. TEM and SEM observations indicated the formation of raspberry-like organic-inorganic nanocomposite particles.

2 Experimental

2.1 Materials

Methyl methacrylate (MMA) was purchased from the Shanghai Chemical Reagent Company (China) and purified by treating with 5% aqueous NaOH to remove the inhibitor and dried over by anhydrous calcium chloride for three days then stored at low temperature prior to use. 1-Vinylimidazole (1-VID, ＞98%) was purchased from the Yancheng Medical Chemical Company (China) and used as received. NS-30, (20 nm silica sol, pH 9.5, supplied as 30 wt% aqueous dispersion by the Yuda Chemical Company, China). Ammonium persulfate (APS) was purchased from the Shanghai Gaoqiao Petrochemical Company (China) and purified by recrystalization from water.

2.2 Synthesis of nanocomposite particles

Typical synthetic process is described as follows: the known amounts of 1-VID and aqueous silica sol were put into a 250 mL round-bottom flask equipped with a mechanical stirrer, a thermometer with temperature controller, an N_2 inlet, a Graham condenser and a heating mantle. The mixture was stirred at room temperature for 1h, and the pH of the mixture was adjusted to a required value using 0.1 mol/L aqueous NaOH or HCl solutions. MMA was then slowly added to the reaction mixture. The mixture was heated to 60℃, followed by addition of 1.0 wt% APS aqueous solution based on the MMA mass. The reaction was carried out at 60℃ for 24 h under a slow stream of N_2. The resulted milky-like dispersions were purified by centrifugation-redispersion cycles for several times until no free silica particles were found by TEM. Each time the supernatant was removed and then replaced with deionized water. Typical formulation for the preparation of raspberry-like nanocomposite particles was as follows: MMA 10 g; 1-VID 1.659 g; SiO_2 18 g; APS 0.1 g and H_2O 90 g.

2.3 Characterization of PMMA/SiO_2 nanocomposite particles

Particle Size Analysis: Dynamic light scattering (DLS, Beckman Coulter Company, USA) measurements were carried out on the diluted reaction solutions to obtain the average diameters of the particles. Each sample was repeated for three times to give the average particle size.

Chemical Composition Analysis: NS-30 silica sol was dried under vacuum oven at 60℃ for several days to obtain a constant weight, then a thermogravimetric analysis was conducted using a Perkin-Elmer (TGA-7 USA) instrument to determine the loss of surface moisture. Assuming that the incombustible residues were pure silica, it was found that the loss of surface moisture was around 15 wt%. About 5 mg dried nanocomposite particles were used to examine the SiO_2 content. All these experiments were conducted in air and heated from room temperature to 800℃ at a scan rate of 20℃/min. The SiO_2 contents of the nanocomposite particles were calculated after subtracting the loss of surface moisture.

Morphology of Nanocomposite Particles: A transmission electron microscope (TEM Hitachi H-600, Hitachi Corporation, Japan) was used to observe the morphology of the obtained nanocomposite particles. The nanocomposite particle dispersions were diluted and ultrasonized at 25℃ for 10 min and then dried on carbon-coated copper grids before examination. SEM images were obtained using a scanning electron microscope (SEM Philips XL30 apparatus). The nanocomposite particle dispersions were diluted and dried on cover glass and sputter-coated with gold prior to examination.

3 Results and discussion

3.1 Diameter of the nanocomposite particles

A series of nanocomposite particles were synthesized via a 'soap-free' heterophase polymerization under different reaction conditions, as summarized in Table 1. One could see that the conversion of MMA was above 90%, and the diameter of the composite particles was between 120~330 nm, which tended to decrease with the increase of the final silica content in the nanocomposite particles. Fig. 1 shows that the average particle size is in the range of 120–270 nm and tends to decrease with increase of the initial silica content of the reaction mixture, which exhibits the same behavior as traditional emulsifiers. All the particles had rather narrow size distribution, suggesting that the silica particles as 'Pickering emulsifier' had high stabilization power. The effect of 1-VID charge on the diameter of the obtained nanocomposite particles was also investigated and is shown in Fig. 2. When 6 mol% 1-VID was added to the system, no stable nanocomposite particles were obtained. It is because the less amino groups in the polymer molecules are not enough to adsorb more nano silica particles to stabilize the PMMA particles. The diameter of the nanocomposite particles tended to decrease with increase of the 1-VID content in the formulation. That's easy to understand: more 1-VID in the formulation means more nano-silica particles can be adsorbed and act as surfactant, which decreases the average diameter of the nanocomposite particles.

Table 1 Summary of PMMA/SiO_2 nanocomposite particles obtained under different conditions

Run	MMA/1-VID mol/mol	SiO_2/ MMA mass/mass	T (℃)	Particle size (nm)	Conv. (%)	SiO_2% wt%
1	85/15	1:1	60	270	95	15.9
2	85/15	1.4:1	60	247	94	16.4
3	85/15	1.8:1	60	192	94	17.1
4	85/15	2.2:1	60	163	96	18.7
5	85/15	2.6:1	60	120	93	20.0
6[a]	94/6	1:1	60	--	--	--
7	90/10	1:1	60	322	90	15.9
8	85/15	1:1	60	286	89	17.8
9	80/20	1:1	60	277	92	18.2
10	75/25	1:1	60	260	93	18.9
11	70/30	1:1	60	249	92	19.1

[a] Polydisperse aggregates and large amounts of coagulum were obtained.
Nanocomposite particles obtained with the other formulations kept stable for at least six months.

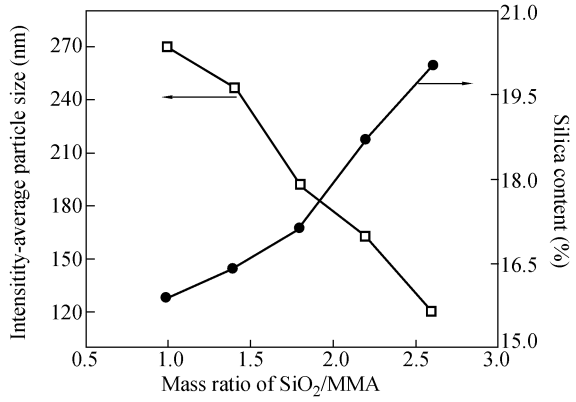

Fig. 1 Dependence of particle size and silica content on the mass ratio of SiO_2 in the reaction mixture

3.2 Final silica content in the nanocomposite particles

It was found that the final silica content tended to increase slightly (from 15.9% to 20%) with increase of the initial silica charge, which was probably because more silica particles could be adsorbed on the surface of PMMA via acid-base interaction at high silica concentrations. The effect of 1-VID charge on the final silica content was also listed in Table 1. What is unexpected is although silica particles were deposited on the surfaces of organic particles via acid–base interaction, the silica content hardly increased (15.9%~19.1%) with increasing the 1-VID charge from 15 mol% to 30 mol%, as shown in Fig. 2. It was probably because not all the 1-VID molecules participated in the free radical copolymerization process due to the low reactivity of 1-VID for its steric hindrance effect. In order to check this assumption, homopolymerization of 1-VID in the presence of silica sols was carried out at 60℃, but no composite particles were found after 48 h and only some low molecular weight polymer formed. It suggested that around 10 mol% 1-VID was enough to synthesize long-stable PMMA/SiO_2 nanocomposite particles with relatively high silica content.

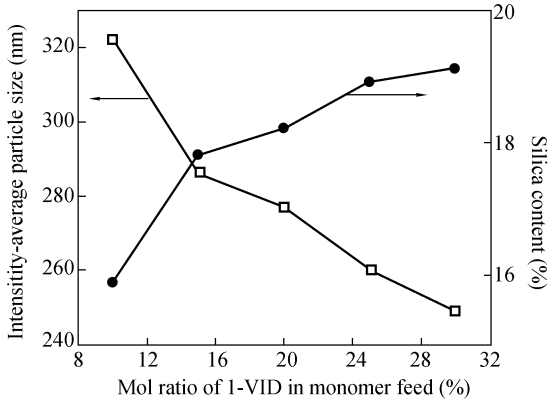

Fig. 2 Dependence of particle size and silica content on the mol ratio of 1-VID in monomer feed

3.3 Morphology of the nanocomposite particles

Figure 3a shows a representative scanning electron micrograph of the PMMA/SiO_2 nanocomposite particles. Although the magnification of SEM is relatively low, we can still observe approximately spherical particles with uniform size. In order to understand whether the silica beads were deposited on the surfaces of the organic phase, the obtained nanocomposite particles were observed by high-magnification TEM. Figures 3b and c present the typical TEM images of nanocomposite particles. It is found that the particle sizes are reasonably uniform, and the nanocomposite particles have raspberry-like morphology with silica beads adsorbed on the surface of the particles.

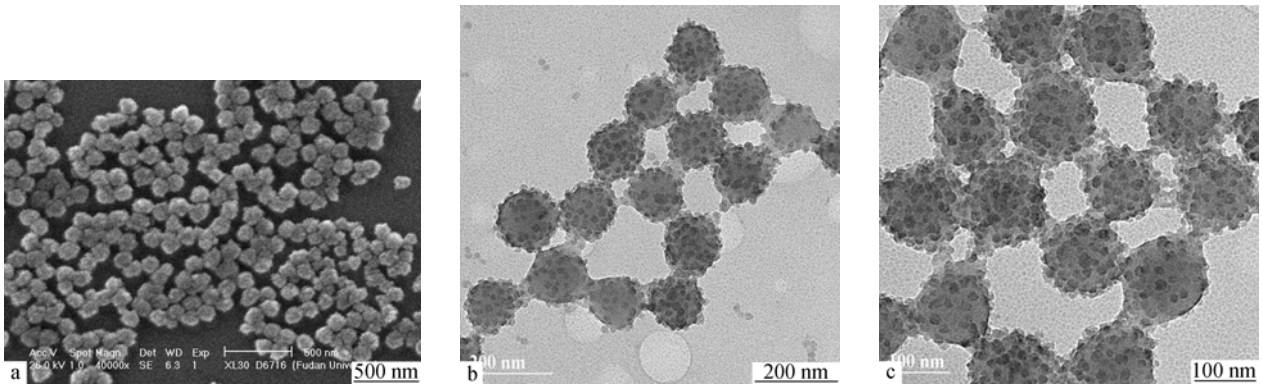

Fig. 3 Representative SEM (a) and TEM (b, c) images of the obtained nanocomposite particles
(a) sample 2; (b) sample 3; (c) sample 9

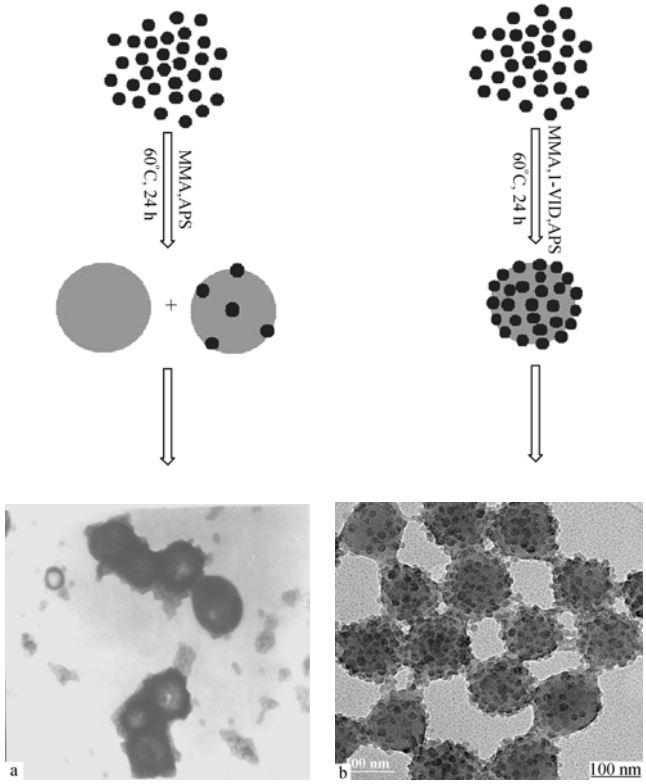

Fig. 4 The reaction scheme for the formation of PMMA/SiO_2 nanocomposite particles

3.4 Formation mechanism of PMMA/SiO_2 nanocomposite particles

In order to understand the formation mechanism of PMMA/SiO_2 nanocomposite particles, a control experiment without any silica sol was carried out, which only resulted in macroscopic precipitates, and no particles formed. In the meantime, another experiment was carried out in the absence of any 1-VID. The resulting milky-like dispersion was metastable and became coagulum after a few days. TEM image (Fig. 4a) of the metastable particles indicates some bare PMMA particles and free silica beads existed. TGA measurements showed that only 3% silica content was adsorbed on the particle surface due to the hydrogen bonding between silanol functions and carbonyl groups of PMMA. However, if 1-VID was introduced to the reaction system, raspberry-like PMMA/SiO_2 nanocomposite particles were obtained. Figure 4b shows the reaction scheme for the formation of PMMA/SiO_2 nanocomposite particles. Combined with the results of zeta potential measurements, it seemed that 1-VID acted as a 'binder' to connect the organic phase with inorganic silica particles. Since our nanocomposite par-

ticles were obtained in aqueous media without any surfactants or polymeric stabilizers, the hydrophilic ultrafine silica beads herein acted as emulsifiers to stabilize the nanocomposite particles. In the present work, the solubility of the organic phase is negligible in aqueous media; we suggested that the raspberry-like particle morphology was obtained directly from the polymeri-zation of silica-stabilized monomer droplets. According to this idea it can be supposed that dissolution of some oil-soluble initiators in monomers may lead to a 'bulk' polymerization in the monomer droplets and may also result in the formation of raspberry-like organic/inorganic nanocomposite particles. The related investigations are under way. Besides, by using this 'soap-free' heterophase polymerization method, some other nano inorganic particles, for instances, Fe_3O_4, Al_2O_3, TiO_2 and so on, are of great potential for preparing organic/inorganic nanocomposite particles.

4 Conclusions

A series of raspberry-like PMMA/SiO_2 nanocomposite particles were successfully synthesized in the presence of ultrafine silica aqueous sols with 1-VID as an auxiliary monomer via a 'soap-free' heterophase polymerization process. These particles had reasonable narrow size distribution, and the average particle sizes were in the range of 120–330 nm, and their silica contents were up to 20%. TEM and SEM observations confirmed the raspberry-like morphology of the obtained PMMA/SiO_2 nanocomposite particles. These composite particles are of potential interest as environmentally friend tough, abrasion-resistant and transparent coatings.

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