

Synthesis and Friction Properties of Copper/PMMA Composites by Soapless Emulsion Polymerization

Xiaokun Ma,^{1,2} Xiaodan Su,¹ Bing Zhou,¹ Xu Zhao,¹ Yumei Tian,¹ Zichen Wang¹

¹Institute of Chemistry, Jilin University, Changchun 130023, People's Republic of China

²PetroChina Research Institute of Jilin Petrochemical Company, Jilin 132021, People's Republic of China

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ABSTRACT: Copper (Cu)-doped polymethylmethacrylate (PMMA) composites were prepared by soapless emulsion polymerization. In this process, copper nanoparticles were modified by sodium oleate (SOA) and the surface property of Cu nanoparticles changed from hydrophilic to hydrophobic. The hydrophobic Cu nanoparticles could not only avoid the oxidation of Cu in air but also improve the compatibility between Cu nanoparticles and PMMA. The TEM micrographs revealed that Cu nanoparticles were encapsulated in PMMA polymer microspheres. In addition,

the uniform Cu/PMMA composite microspheres could be synthesized in such a soapless emulsion polymerization process. It was worth mentioning that the friction property in oil was well improved when little nanocomposites were added into the base oil, which indicated that the composites can be widely used in lubricating oil. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 2837–2842, 2011

Key words: soapless emulsion polymerization; composites; copper; PMMA; compatibility

INTRODUCTION

Nanocomposites materials have emerged as an area of intense current interest motivated by potential applications in optics, electronics, ionics, magnetics, catalysis, sensors, biology, and others.^{1–5} Many literatures about metal nanoparticles doped polymers composites had reviewed and discussed the electronic and optical properties of these materials. Zois et al.⁶ had dispersed micron spherical iron (Fe) particles into thermoplastic polymer (polyamide (PA), polyethylene (PE), polyoxymethylene (POM), or blend PE/POM) matrix to prepare various metal-polymer composites. In PE-Fe, PA-Fe, and POM-Fe composites the Fe particles were randomly dispersed in the polymer matrix. However, in the PE/POM-Fe composite, the polymer matrix is two-phase and the Fe particles were localized only in POM phase. The concentration and frequency dependence of dielectric properties were discussed and a feasible schematic model was proposed to explain the morphologies of various composite materials.

Feng et al.⁷ successfully synthesized PANI/gold (Au) composite hollow spheres by PS/sulfonated PS core/shell gel particle templates. The Au nanoparticles were synthesized by boiling H₂AuCl₄ aqueous solution with trisodium citrate and the size was

about 30 nm. When the PANI hollow spheres were added to the Au colloid for 12 h, the Au nanoparticles could be adsorbed on the surface of PANI, leading to the formation of PANI/Au composites. The thickness of the PANI shell and the number of Au nanoparticles decorating the PANI could be controlled effectively by adjusting the concentration of PANI and Au colloid. By incorporating Au nanoparticles onto the PANI surface, the electrical conductivity of the composites was increased with the shell thickness increasing. On the other hand, the conductivity of PANI/Au composite hollow spheres with a shell thickness of 30 nm is $8.74 \times 10^{-3} \text{ S cm}^{-1}$; it is 3.88 times higher than that of pure PANI. Especially, this method could be extended to prepare other composite hollow spheres with different compositions.

Porel et al.⁸ provided a simple *in situ* method to achieve free-standing metal nanoparticle-embedded polymer film. The small sizes and narrow distributions achieved under the mild conditions and short processing time are very significant. The silver (Ag) nanoparticles in polymers had a broad size distribution (10–60 nm) and the size of Ag nanoparticles could be controlled with heating time. The Ag-PVA composite system illustrates the simple *in situ* process for the fabrication of free-standing metal nanoparticles-embedded polymer film. The films with immobilized and size-tuned metal nanoparticles appear to be attractive candidates for optical limiting application.

Metal nanoparticles exhibit properties differing from bulk metal due to quantum size effects, including novel electronic, optical, and chemical behavior.

Correspondence to: B. Zhou (zhoubing@mail.jlu.edu.cn).

The properties may be tuned via control of shape, size, interparticle spacing, and dielectric environment, and methods to vary these have been developed.^{9–13} However, we have to face a serious problem about the stabilization of the metal nanoparticles during the application in all the fields. When exposed to an ambient environment, metal nanoparticles corrode through charge transfer reactions, which may cause deterioration occurring at the metal surface. Among those modification methods, encapsulation by polymers has become an attractive method recently. During this modification process, the thickness of the outer layers and the metal content can be controlled.

Soapless emulsion polymerization has received more attention in recent decades because it provides advantages for the synthesis of monodisperse latex. Furthermore, few surfactants or no surfactants have been used in such systems that could avoid the some disadvantage in the polymer postprocessing. In this type of system, polymer particles are stabilized by ionized initiators. Homogeneous nucleation mechanisms have been proposed for emulsifier-free systems and many polymer monomers were adapted to the soapless emulsion polymerization process. Especially, the studies on PMMA polymer microspheres by soapless emulsion polymerization have been widely discussed.^{14,15}

In this work, Cu/PMMA composites were prepared by soapless emulsion polymerization process due to the better compatibility between hydrophobic Cu nanoparticles and MMA monomer. The Cu/PMMA composite microspheres could prevent the oxidation of Cu nanoparticles. On the other hand, the friction coefficient of base oil could be reduced when little Cu/PMMA composites were added into the base oil. Such special property should have an attracted increasing interest for lubricating oil industry.

EXPERIMENTAL

Materials

The methyl methacrylate (MMA) was chemical reagent with a density of 0.943 g cm^{-3} , and was obtained from Tianjin Chemicals Factory (China). Ammonium persulfate (APS) were purchased from Shantou Xilong Chemicals factory as an initiator. Bluestone (CuSO_4) and sodium hydroxide (NaOH) were provided by Beijing Chemicals factory. Hydrazine ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$) was commercially obtained from Tianjin Fengchuan Chemicals factory. Sodium oleate (SOA) was analytical reagent and was obtained from Shanghai Chemicals Reagent Factory (China). All of the reagents were analytical reagent without further purification. Distilled and deionized water was used throughout the work.

Preparation of hydrophobic Cu nanoparticles

The precursor Cu nanoparticles were prepared by solution-phase reduction of Cu (II). Briefly, 0.02 mol Bluestone (CuSO_4) was mixed with 20 mL 50 vol % hydrazine ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$) in alkaline aqueous solution (NaOH) in the presence of 3 wt % sodium oleate, which was used as a kind of surfactant and stabilizer to make nanoparticles hydrophobic and prevent them from being oxidized as well. The reaction was carried out in water bath of 80°C , and 5 min later the resultant Cu nanoparticles with dark-purple color were got. After being centrifuged and washed thoroughly with copious amount of distilled water, the resulting precipitate was dried in vacuum at room temperature for use later.

Preparation of Cu/PMMA nanocomposites

In a 500-mL flask, the SOA-modified Cu nanoparticles were dispersed in the mixture of MMA (5 mL) and deionized water (100 mL) and the reactants were ultrasonically dispersed at room temperature for 10 min. During the ultrasonic process, the flask was deaerated with nitrogen gas and was sealed by the rubber corks to avoid the oxidation of Cu nanoparticles. Then, the mixture became into stable mauve emulsion. The hydrophobic Cu nanoparticles could well disperse into the MMA monomer. The emulsion polymerization was carried out in the flask equipped with mechanical stirrer, reflux condenser, and nitrogen gas inlet system. APS (0.100 g) was dissolved in 30 mL water and was added dropwise in 10 min to initiate the emulsion polymerization. After deaerating with nitrogen gas, the polymerization was carried out at 60°C for 12 h. The color of the emulsion turned to bice gradually at the beginning of polymerization (about 30 min) and never changed until the polymerization terminated. And the amount of Cu nanoparticles in the composites was changed from 4 to 6 wt %.

Characterizations

FT-IR was recorded by a Shimadzu FTIR-8400S that employs a KBr pellet method. X-ray diffraction (XRD) patterns of the products were performed on a model XRD-6000 using filter Cu $K\alpha$ radiation. Transmission electron microscopy (TEM) images of the Cu/PMMA nanocomposites were collected on a Hitachi H-800 electron microscope operated at 200 keV. Samples for TEM studies were prepared by dispersing the powders ultrasonically in water and retaining a drop of colloid on carbon holey grids. The friction coefficient in base oil was measured by the MMU-10 pin-on-disk tester. The friction tests with a rotating speed of 300 rpm and a constant

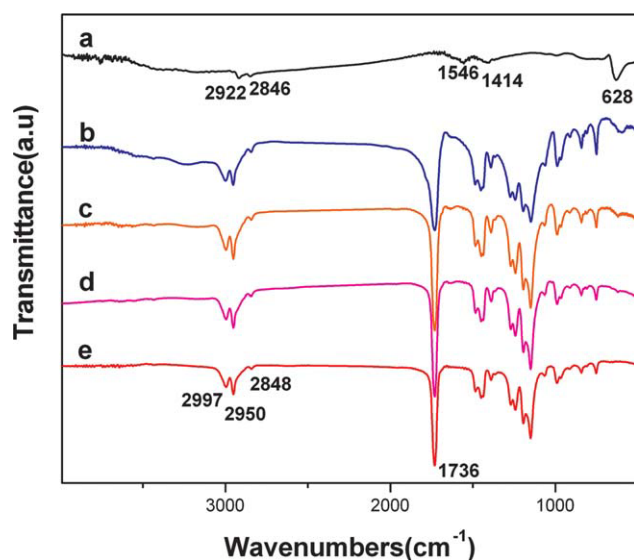


Figure 1 IR spectrum of (a) SOA-modified Cu nanoparticles; (b) Cu/PMMA composites with 6.5 wt % Cu; (c) Cu/PMMA composites with 5.4 wt % Cu; (d) Cu/PMMA composites with 4.2 wt % Cu; (e) pure PMMA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

load of 300N would last for 3000 s. The ultrasonication bath (KH-100B) operated at 220 V/50 Hz was purchased from Kunshan He Chuang Ultrasonic Instrument.

RESULTS AND DISCUSSION

FT-IR spectra of the Cu/PMMA nanocomposites

Figure 1 showed that the FT-IR spectra of (a) SOA-modified Cu nanoparticles, (b–d) the Cu/PMMA nanocomposite samples, and (e) pure PMMA. In Figure 1(a), the stretching vibration of the C–H at 2922, 2846 cm^{-1} came from the $-\text{CH}_2$ in the SOA and the typical bands of the COO^- at 1546, 1414 cm^{-1} could be found.¹⁶ And the typical adsorption band at 628 cm^{-1} was derived from the Cu–O bond.^{17,18} In Figure 1(b–d), the peak at 628 cm^{-1} weakened gradually when the content of Cu nanoparticles in the composites decreased. However, in the spectrum of pure PMMA there was no peak at 628 cm^{-1} at all, as shown in Figure 1(e). Therefore, these differences indicated that the Cu nanoparticles could be encapsulated in the PMMA polymer microspheres, and the PMMA layer would shield the characteristic vibration of Cu–O bond.

X-ray diffraction of the Cu/PMMA nanocomposites

The presence of Cu nanoparticles in the Cu/PMMA composites could be confirmed by XRD analysis, and the plots were shown in Figure 2. In the curve (a), there was an obvious peak at 43.3° and 50.4°,

which was corresponding to the diffraction peak of Cu (JCPDS, File No.04-0836), and a weak peak at 36.6° is of Cu_2O (JCPDS, File No.03-0892), as a result, it showed that a low amount of the Cu particles were oxidated after the surface modification process. The plots (b)–(d) in Figure 2 showed the X-ray diffraction peaks of the Cu/PMMA composites. The characteristic X-ray diffraction peaks at 43.3° was observed which indicated that the Cu nanoparticles were encapsulated in the PMMA matrix, and the intensity of the diffraction peak at 43.3° increased with the amount of Cu nanoparticles. The differences in the XRD intensity were consistent with the result of FT-IR spectra, which should be ascribed to the Cu nanoparticles were encapsulated in the PMMA matrix.

Morphology of the Cu/PMMA nanocomposites

The morphology of Cu/PMMA nanocomposite microspheres was characterized by TEM. The size of Cu nanoparticles was about 3 nm and they were easy to aggregate together as shown in Figure 3(a). In the Figure 3(b), the pure PMMA polymer microspheres were prepared under the same conditions through the soapless emulsion polymerization and the uniform diameter was about 70 nm. When the Cu nanoparticles participated in the system, the diameter of composite microspheres became bigger and the diameter of composite microspheres was about 80 and 110 nm, respectively, as shown in Figure 3(c,d). Especially, the diameter of composite microspheres was increased with the amount of Cu nanoparticles increasing. There was some brightness difference in the micrographs of Cu/PMMA

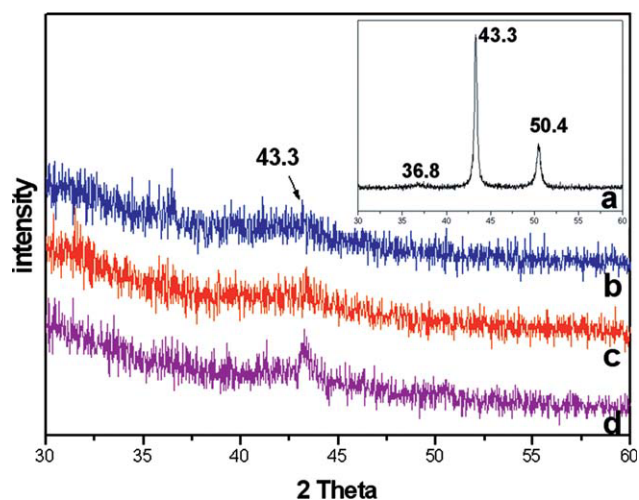


Figure 2 XRD plots of (a) Cu pretreated with SOA; (b) Cu/PMMA composites with 4.2 wt % Cu; (c) Cu/PMMA composites with 5.4 wt % Cu; (d) Cu/PMMA composites with 6.5 wt % Cu. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

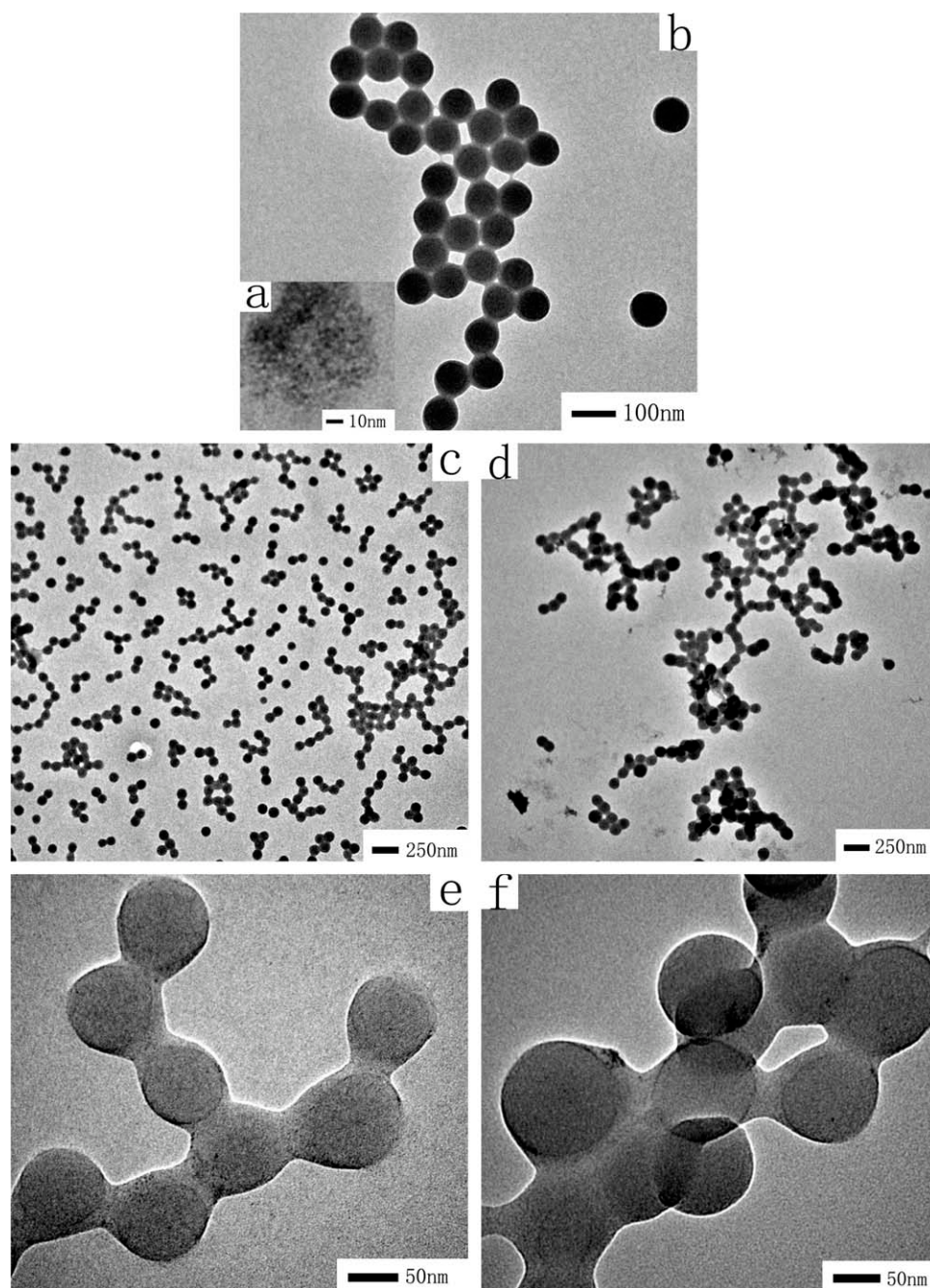


Figure 3 TEM photograph of (a) the photograph of Cu nanoparticles; (b) pure PMMA microspheres; (c), (e) Cu/PMMA nanocomposite microspheres with 4.2 wt % Cu; (d), (f) the photograph of Cu/PMMA nanocomposite microspheres with 5.4 wt % Cu.

composite microspheres because the distribution of Cu nanoparticles was uneven. Under the higher magnification, the Cu nanoparticles could be found in the PMMA microspheres and most of them were located at the edges of the spheres as shown in Figure 3(e,f). On the other hand, the aggregation state of Cu nanoparticles was improved after the polymerization process. The TEM micrographs indicated that the Cu nanoparticles were encapsulated in the PMMA microspheres. The mechanism of homogene-

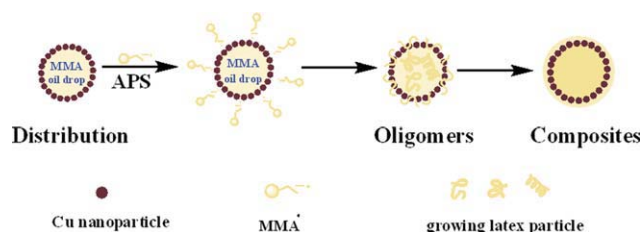
ous nucleation should be similar to that of the $\text{CaCO}_3/\text{PMMA}$ composite in a soapless emulsion polymerization process that had been reported.¹⁹

For the soapless emulsion polymerization of MMA, the generation of the latex particles was certified to follow the mechanism of homogeneous nucleation. At the beginning, SOA-modified Cu nanoparticles were dispersed in the mixture of MMA and deionized water by ultrasonic. Because of the hydrophobic surface property of SOA-modified Cu

nanoparticles, most of them could be infiltrated into the MMA organic monomer and arranged around MMA droplets. When the polymerization was initiated by APS, the low temperature (60°C) induces the polymerization reaction rate keep slow. With the radical groups transferring, MMA monomer droplet began to polymerize and growing to MMA oligomers. During this period, Cu nanoparticles still could be adsorbed around the oligomers. When the oligomers reached their critical chain length, the composites precipitated from the aqueous phase and then formed as primary particles, and the Cu nanoparticles can be encapsulated in the primary particles. Moreover, the Cu nanoparticles were located at the edge of the composite microspheres could be explained as shown in scheme 1. As a result, the Cu nanoparticles were encapsulated into PMMA polymer matrix, which should bring the more prominent properties of composites, such as the improvement of friction property in oil.

Friction property of the Cu/PMMA composites in oil

Figure 4 showed the friction coefficient of (a) pure base oil and (b), (c) Cu/PMMA composites mixed oil. In the all mixture the amount of Cu/PMMA composites to base oil was 1 wt %. The friction coefficient of pure base oil was changed from 0.11 to 0.06 and 0.03, when the amount of Cu nanoparticles in the composite increased from 5.4 to 6.5 wt %, as shown in Figure 4(b,c), respectively. In addition, the plots of the mixture became more regular than that of the pure base oil. The decrease of friction coefficient could be explained as follows: First, the spherical Cu/PMMA composites should smooth the surface of friction apparatus and get the lower friction coefficient.²⁰ Second, it is well known that the Cu nanoparticles own extremely good friction property. Once the composites were broken during the friction process, the Cu nanoparticles should be released from the microspheres and reduce the friction between the contact surface of the apparatus. In conclusion, as shown in Figure 4(b,c) the friction coefficient



Scheme 1 Schematic illustration of the formation process of Cu/PMMA nanocomposites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

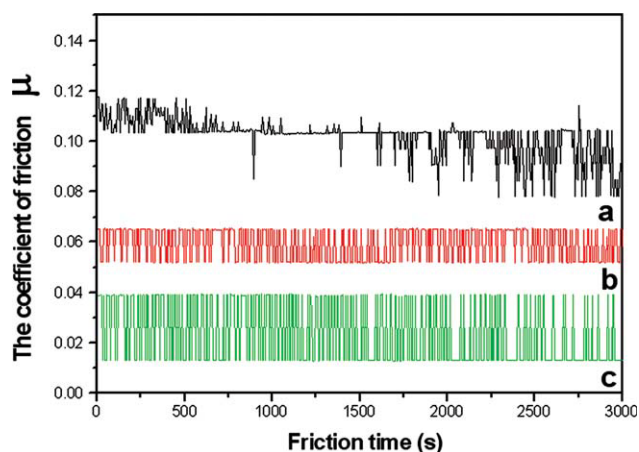


Figure 4 Variation of friction coefficient with time for (a) in pure base oil; (b) 1 wt % Cu/PMMA nanocomposite (including 5.4 wt % Cu) added into oil; (c) 1 wt % Cu/PMMA nanocomposite (including 6.5 wt % Cu) added into oil. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

went down with the amount of Cu nanoparticles increased. On the other hand, the broader distribution curve was found after the amount of Cu nanoparticles to PMMA was 6.5 wt %. The phenomenon should be associated with the diameter of composite microspheres. As mentioned above, the diameter of composite microsphere became bigger when the amount of Cu nanoparticles increased in the composites. Nevertheless, the broader distribution curve had not affected the friction coefficient in oil and became smaller. The Cu/PMMA composite microspheres could effectively improve the friction property of the base oil and the amount of composite was in such a low percent.

CONCLUSIONS

In this article, Cu/PMMA nanocomposites were synthesized by soapless emulsion polymerization. The hydrophobic SOA-modified Cu nanoparticles could be encapsulated in the PMMA matrix due to the good compatibility between the Cu nanoparticles and the PMMA polymer matrix. The method could prevent the oxidation of Cu nanoparticles in polymerization process and obtain the functional composite microspheres. Especially, the friction coefficient of base oil decreased when a little composite microspheres were added into the oil; the unusual property are promising in lubricating oil industry.

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