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Polymer modified hematite nanoparticles for electrophoretic display

Mi Ah Lee · Bong Jun Park · In-Joo Chin · Hyoung Jin Choi

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Abstract Hematite nanoparticles (Fe_2O_3) as a red inorganic pigment were encapsulated with poly (methyl methacrylate-co-acrylamide) (PMMA-co-AAM) for application in the electronic paper display. Since the Fe_2O_3 nanoparticle has relatively high density (ρ=5.07 g/cm^3), it usually causes severe sedimentation problem in the suspending medium. In order to reduce density mismatch between inorganic pigment and dielectric medium, the Fe_2O_3 nanoparticles were modified by dispersion polymerization method. Zeta potential and electrophoretic property of the inorganic pigment coated with copolymers in a low dielectric medium were investigated by using electrophoretic light scattering. The surface morphology and molecular structure of the fabricated particles were measured via SEM and FT-IR, respectively. The amount of polymeric coating was also examined by using TGA.

Keywords Electrophoretic · Inorganic pigment · Zeta potential · Electronic paper

1 Introduction

Recently, electrophoretic techniques for the electronic paper display have been promoted by many academic and industrial researchers, in which the electronic paper has a lot of advantages over the conventional paper from static information and the re-writable characteristics from dynamic information [1–3]. Electronic paper display based on electrophoretic phenomenon has many advantages such as being easy to read, low cost, low power consumption, flexibility, portability, and high reflectivity [4]. Among the various approaches in the development of the electronic paper, electrophoretic display shows images and texts by migrating charged dispersed particles to the opposite electrode in the dielectric medium under an applied electric field. In order to be used for the electrophoretic application, physical properties of the electrophoretic particles such as dispersion stability, response time, and electrophoretic mobility should be fully considered [5]. The characterization of surface charge which takes an essential role in electrophoretic display is very important in explaining clearly surface physical properties and the behavior of suspension system. There have been many efforts to improve the physical properties, such as encapsulation of polymer on white pigment particles [6]. Electrophoretic color particles have recently attracted attentions of many researchers due to their potential applications in electronic paper display technology. Inorganic pigments can be good candidates due to their good optical properties and chemical stability. For the real application, the nanoparticles should have good dispersion stability and high electrophoretic mobility. For example, Yu et al. [7] investigated the colored particle using PMMA particles coated with dye. Kim et al. [8] also reported the electronic display application using colored particle and a white pigment. The colored pigment nanoparticles can also be used as colored ink particles because they posses enough resolution for display.

However, the inorganic pigment particles have some problems of dispersion stability and electrophoretic mobility due to their high density and weak surface charge [9]. For the pigment particles, therefore, dispersion stability in a low dielectric medium and sensitivity of surface charge for a charge control agent (CCA) [10, 11] should be developed.

M. A. Lee · B. J. Park · I.-J. Chin · H. J. Choi (✉)
Department of Polymer Science and Engineering, Inha University, Incheon 402-751, South Korea
e-mail: hjchoi@inha.ac.kr

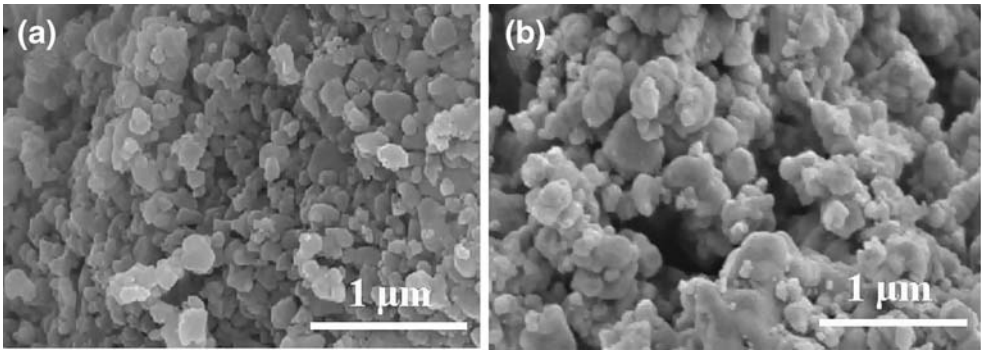

Fig. 1 SEM image (**a**) raw Fe_2O_3, (**b**) Fe_2O_3/poly (MMA-co-AAM) particles

In this study, in order to enhance surface charge of pigment particle and reduce the density mismatch between red pigment, Fe_2O_3, particle and suspending medium, the Fe_2O_3 nanoparticles were coated with poly (methyl methacrylate-co-acrylamide) (PMMA-co-AAM) by dispersion polymerization. The effect of polymer coating on the surface of Fe_2O_3 particles was measured. The zeta potential of the fabricated particles was further examined.

2 Experimental

2.1 Sample preparation

Monomers, acrylamide (AAM, Aldrich, USA), methyl methacrylate (MMA, Aldrich, USA) and stabilizer, polyvinylpyrrolidone (PVP, Mw=55,000, Aldrich, USA) were used as received without any further purification. The initiator, azoisobutyronitrile (AIBN, Junsei, Japan) was purified by recrystallization.

Both small amounts of AAM and AIBN were dissolved in MMA. PVP was dissolved in ethanol medium. The prepared medium was divided by two. In one part of the medium, the Fe_2O_3 nanoparticle was dispersed by using a homogenizer. Also, the prepared monomeric mixture was put into the rest of medium in a reactor. The polymerization was held for 1 h at 60 °C. During the polymerization, the Fe_2O_3 suspension was slowly dropped into the reactor using a dropping funnel. After being washed with ethanol, the sample was dried for 2 h at 60 °C. The Fe_2O_3 particles coated with poly (MMA-co-AAM) was obtained with powder form.

2.2 Characterization

Morphology and particle size were observed via scanning electron microscope (SEM, S-4300, Hitach). Molecular structure of the product particles was measured by using FT-IR (Perkin Elmer System 2000). In order to determine electrophoretic properties, the zeta potential was investigated by electrophoretic light scattering (ELS, Photal ELS-8000, Otsuka, Japan). A charge control agent was also added into the suspension of synthesized nanoparticles in the dielectric medium so as to improve their mobility. The density of the fabricated particles was

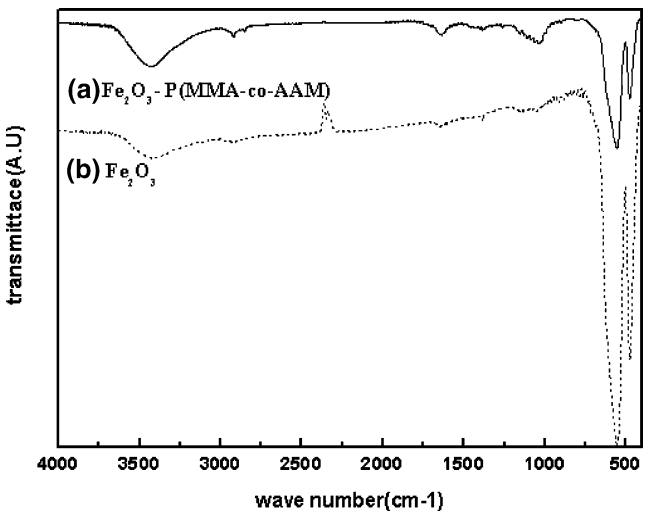

Fig. 2 FT-IR of spectra (*a*) Fe_2O_3/poly(MMA-co-AAM), (*b*) Fe_2O_3

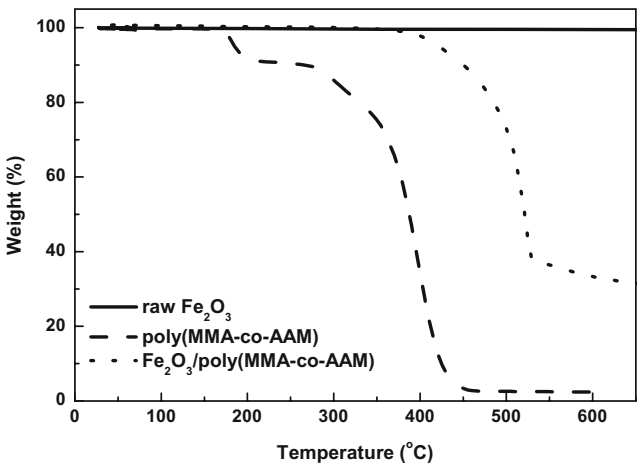

Fig. 3 The TGA diagram of raw Fe_2O_3, poly(MMA-co-AAM) and Fe_2O_3/poly(MMA-co-AAM)

measured by a gas pycnometer. The degree of polymer coating amount was measured by a thermal gravimetric analysis (TGA). The heating rate is 20 °C/min in a nitrogen gas. The recorded temperature range was from room temperature up to 700 °C.

3 Results and discussion

The Fe_2O_3 nanoparticles were encapsulated with poly (MMA-co-AAM) via dispersion polymerization of MMA in coexistence of AAM and Fe_2O_3. Fig. 1 shows SEM images of both raw Fe_2O_3 (a) and Fe_2O_3/poly(MMA-co-AAM) (b). In Fig. 1(a), the pristine Fe_2O_3 nanoparticles have an average particle size in about 50–300 nm with random shape. It was found that the particle shapes after processing were much changed from original shapes of the Fe_2O_3. However, there was an increase of particle size through the coating process.

The density of raw Fe_2O_3 and Fe_2O_3 coated with poly (MMA-co-AAM) was also defined via a pycnometer, respectively. The density of the Fe_2O_3 encapsulated with copolymer at 30 °C was measured, to be 2.0 g/cm^3, which is less than one-half of that of pristine Fe_2O_3 (ρ=5.2 g/cm^3). The value of the density is similar to that of the dielectric medium, hence the Fe_2O_3/poly(MMA-co-AAM) particles can improve the sedimentation in the suspending medium.

The molecular structure difference between Fe_2O_3 and Fe_2O_3 coated with poly(MMA-co-AAM) was also shown in FT-IR spectrum of Fig. 2. In the Fe_2O_3/poly(MMA-co-AAM) spectrum, the characteristic peaks at 1,636 and 1,039 cm^{-1} can be assigned to the C=O stretching and C–O stretching of polymeric unit, respectively. In addition, the peaks at 2,920 cm^{-1} originated from C–H stretching vibration of main chain. Also N–H stretching vibration of acrylamide unit was observed with 3,430 cm^{-1}. The characteristic peak of Fe_2O_3 was shown near 550 cm^{-1}.

Thermogravimetric analysis (TGA) measurement was also carried out to determine both thermal decomposition of the synthesized particles and contents of the polymer's layer in the final materials, as measured under nitrogen purged. Fig. 3 shows the TGA thermodiagram of raw Fe_2O_3, poly(MMA-co-AAM) and Fe_2O_3 coated with poly (MMA-co-AAM). Until it was heated up to 600 °C, the raw Fe_2O_3 particle remained in its initial state. The poly(MMA-co-AAM) reference particle starts to degrade sharply at around 300 °C and completely decomposes at 450 °C. The copolymer coated Fe_2O_3 demonstrates its weight loss in the range of 400–530 °C, which means to the degradation of polymer layer. The TGA diagram of the synthesized particles indicates that content of the polymer's layer was about 65%. Obviously, the onset temperature of thermal decomposition was shifted towards to the high temperature after the encapsulation process. This result demonstrates that the thermal stability was enhanced due to the strong interaction between polymer and Fe_2O_3 nanoparticles [12, 13].

The electrophoretic characteristics of the fabricated particles were analyzed by measuring zeta potential of the product suspended in a low dielectric medium oil. It is well known that the shear plane (slipping plane) is an imaginary surface separating the thin layer of liquid bound to the solid surface. The electrical potential at the shear plane is called zeta potential. The value of the zeta potential means charge on the particle surface and the state of the dispersion stability. When the fabricated particles were dispersed in the zeta potential of them was shown as −4.02 mV. The value is not much different from the zeta potential of raw Fe_2O_3 particles. In order to improve electrophoretic mobility and stability, the charge control agent (CCA) was added into the low dielectric medium oil. The zeta potential of the produced particles was indicated as positive value, 5.93 mV when the particles were dispersed with CCA, which zeta potential of Fe_2O_3 particle was affected by CCA. However, the encapsulated particles represent low density and enhanced dispersion stability which is indispensable properties for the electrophoretic paper display application.

4 Conclusion

Fe_2O_3 particles were coated with polymer by dispersion polymerization for potential applications in electronic display. It was found that the density of pigment particle was reduced through the coating process. Moreover, the zeta potential of the product particles showed positive value in the dielectric medium affected by charge control agent. From this result, it was recognized that the poly(MMA-co-AAM) lowers the density and acrylamide offers positive charge onto the surface of pigment particle.

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