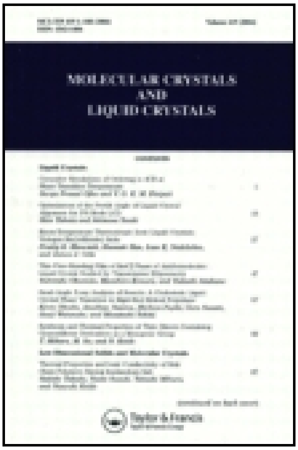

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Encapsulation of Inorganic Pigment and its Electromigration Phenomenon in Dielectric Medium

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Encapsulation of Inorganic Pigment and its Electromigration Phenomenon in Dielectric Medium

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Encapsulation of inorganic pigments can be useful to protect the pigments from the environment or to prevent particular clustering and aggregation, thereby extending the lifetime of the electrophoretic display when the pigments are used as electrophoretic particles. In this study, inorganic pigments were encapsulated by two step polymerization of methyl methacrylate, ethylene glycol dimethylate, and methacrylic acid. Chemical structure, the morphology and the thermal stability of the encapsulated pigments were investigated by FT-IR, optical and electron microscopies and TGA, respectively. Dispersion characteristics and the electrophoretic response of the encapsulated pigments in dielectric medium were investigated. In comparison with the neat pigments, the modified pigments showed much lower densities and their surface was totally changed.

Keywords: charge control agent; dispersion; electromigration; electrophoresis; encapsulation; inorganic pigment

INTRODUCTION

Inorganic pigments have been widely used in paint, printing inks and plastics [1–4]. Generally, inorganic pigments show better color properties

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than dyes. However, their strong aggregation tendency and high density causes poor dispersability in organic media. Recently, many research groups attempted to enhance the dispersion of inorganic particles by using several different methods [5–9]. Especially, the surface modification of inorganic particles by polymeric materials provides not only high electrostatic repulsion between particles but also repulsion of adsorbed polymer layers, known as steric repulsion. Moreover, the density of the inorganic particles is decreased, because the polymer layer has a lower density than that of the particles. Poly(methyl methacrylate) (PMMA) is known to be suitable as a shell material to encapsulate inorganic particles, thereby enhancing dispersion of the particles [10].

To utilize inorganic pigments as electrophoretic particles, the surface of inorganic pigments were modified to form a core-shell structure by the dispersion polymerization of acrylic monomers. In addition, poly(methacrylic acid) was polymerized on the surface of PMMA coated inorganic pigments to impart a charge moieties.

EXPERIMENTAL

Materials

Inorganic pigments ($PbCrO_4$, yellow color) with the average particle size of 0.3 μm were provided by DPI Co., and they were used without further purification. Methyl methacrylate (MMA, Sigma-Aldrich), methacrylic acid (MAA, Aldrich) and ethylene glycol dimethylate (EGDMA, Aldrich) were washed with a 10% aqueous sodium hydroxide solution, then distilled under reduced pressure to remove inhibitors and stored in a refrigerator. 2, 2′-azobisisobutyronitrile (AIBN, Aldrich) was purified by recrystallization from ethanol. And, poly (vinyl pyrrolidone) (PVP, $Mw = 55{,}000\,g/mol$) (Sigma-Aldrich) was used as received.

Surface Modification of Inorganic Pigments

The surface of $PbCrO_4$ particles was modified by a two-step dispersion polymerization. First, 1.5 g of $PbCrO_4$ was dispersed in PVP solution in methanol by sonication for 2 h at room temperature. A mixture of methyl methacrylate (5 g) and ethylene glycol dimethylate (0.4 g) were prepared, and it was added to the pigment dispersion with stirring for 30 min under the nitrogen gas. Polymerization was carried out at 60°C for 6 h in the presence of 0.8 g of 2, 2′-azobisisobutyronitrile as an initiator. To introduce charge moieties on the surface of poly(MMA-*co*-EGDMA) coated $PbCrO_4$ surface, 4.41 g of methacrylic acid was slowly added to the reactor and the reaction continued for 12 h at 60°C. After the reaction, deionized water was added to the reactor and poly (MMA-*co*-EGDMA)-MAA coated $PbCrO_4$ was isolated by centrifugation. The supernatant was decanted and the precipitant was washed with deionized water before drying.

RESULTS AND DISCUSSION

The chemical structure of the poly(MMA-*co*-EDGMA)-MAA coated $PbCrO_4$ pigments was investigated by FT-IR spectroscopy (Perkin Elmer System 2000). As shown in Figure 1, FT-IR spectrum of the modified pigment has the characteristic absorption peaks around $2950\,cm^{-1}$ and $1730\,cm^{-1}$, which are due to the C–H stretching and C=O stretching, respectively, of acrylic polymer [11], as well as strong absorption peaks of pigment itself in the range of $550–950\,cm^{-1}$ [12].

Thermogravimetric analysis (TGA) was carried out to determine the content of core pigments. Raw $PbCrO_4$, poly(MMA-*co*-EGDMA)-MAA, and the surface modified $PbCrO_4$ were heated to 650°C with the heating rate of 10°C/min in the nitrogen. In case of raw $PbCrO_4$ particles, there was no weight loss up to 650°C. Meanwhile, the copolymer started to degrade at around 170°C and decomposed at 470°C completely. For the modified pigment in Figure 2(c) about 26% of

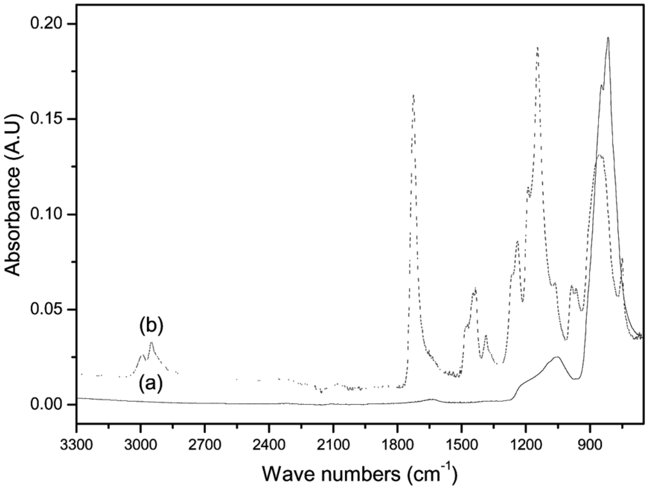

FIGURE 1 FT-IR spectra of (a) neat $PbCrO_4$, (b) $PbCrO_4$/poly(MMA-*co*-EGDMA)-MAA composite.

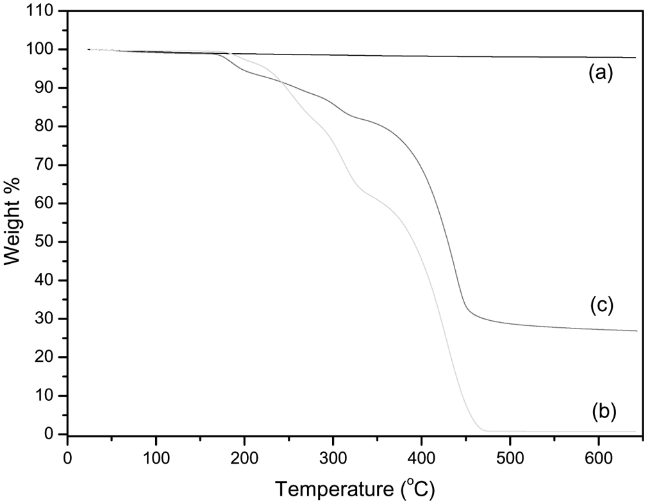

FIGURE 2 TGA thermograms of (a) neat $PbCrO_4$, (b) poly(MMA-*co*-EGDMA)-MAA, and (c) $PbCrO_4$/poly(MMA-*co*-EGDMA)-MAA hybrid composite particle.

the residue remained above 400°C, which is due to the inorganic pigment.

The densities of the pigments before and after modification were measured by a pycnometer. The density of the poly(MMA-*co*-EDGMA)-MAA coated $PbCrO_4$ was dramatically decreased to 1.47 g/cm^3, which was much smaller than that of the raw $PbCrO_4$ (5.68 g/cm^3). The surface of the pigment was covered by poly(MMA-*co*-EGDMA)-MAA with a lower density than $PbCrO_4$.

More direct evidences of the core-shell structure of poly(MMA-*co*-EDGMA)-MAA coated $PbCrO_4$ are shown in Figures 3 and 4. The modified $PbCrO_4$ was made of a core with a diameter of 700~800 nm and a polymeric shell with a thickness of 400~600 nm. Electrical properties including zeta potential values of the neat $PbCrO_4$ and the modified pigments in dielectric medium are summarized in Table 1. It is very interesting to note that the surface charge of the pigments changed from negative to positive upon surface modification. The electrophoretic migration of inorganic pigment particles was monitored in a simple electrophoretic display cell, which consisted of two ITO coated, transparent electrodes with a gap space of 350 μm. As shown in Figure 5, as a negative DC electric field ($E = 500$ V/mm) was applied to the upper electrode, the modified pigments moved upward, while the neat

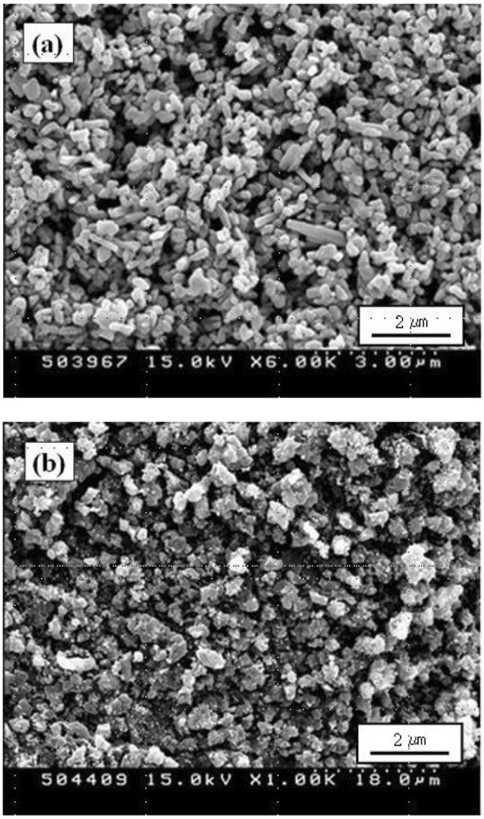

FIGURE 3 SEM micrographs of (a) neat $PbCrO_4$ pigment and (b) $PbCrO_4$/poly(MMA-*co*-EGDMA)-MAA composite particle.

TABLE 1 Zeta Potential of Neat $PbCrO_4$ Pigment and $PbCrO_4$/Poly(MMA-*co*-EGDMA)-MAA Particle

	Zeta potential (mV)	Mobility ($cm^2/V{\cdot}s$)	Electric field (V/cm)
Neat $PbCrO_4$ pigment	-19.49	-4.44×10^{-6}	161.63
$PbCrO_4$/Poly(MMA-*co*-EGDMA)MAA particle	25.62	5.84×10^{-6}	161.59

(medium = Halocarbon: Isopar-G, w/w 4:3).

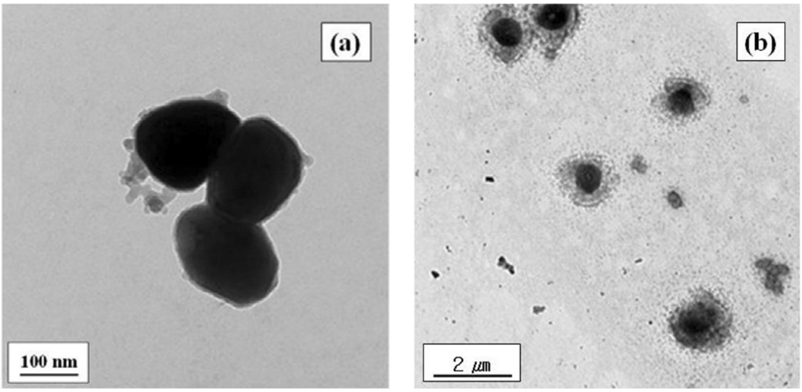

FIGURE 4 TEM micrographs of (a) neat $PbCrO_4$ pigment and (b) $PbCrO_4$/poly(MMA-*co*-EGDMA)-MAA composite particle.

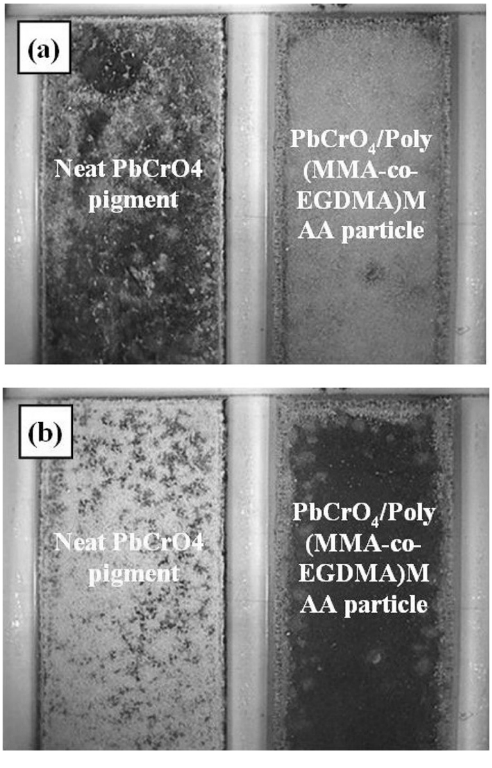

FIGURE 5 Electromigration of $PbCrO_4$/poly(MMA-*co*-EGDMA)-MAA composite particle in an electric field : (a) negative field is applied to the upper electrode, and (b) positive field is applied to the upper electrode (E = 500V/mm, Dielectric medium:Halocarbon:Isopar-G, w/w 4:3).

pigments migrated downward. In this experiment an inert blue dye was added to show the particle movement more clearly.

CONCLUSION

The surface of inorganic pigments ($PbCrO_4$) was modified by acrylic copolymer to suppress both the particle aggregation and the density mismatch between the pigments and low dielectric media as well as to impart positive charge on the surface of the pigments. Core-shell structure of poly(MMA-*co*-EDGMA)-MAA coated $PbCrO_4$ was successfully prepared by a two-step dispersion polymerization. The presence of carboxylic acid groups on the surface of the modified pigments was confirmed by FT-IR spectroscopy. The density of the pigment was dramatically decreased from $5.68\,g/cm^3$ to $1.47\,g/cm^3$ after surface modification. The surface modified pigments showed positive charges and their electrophoretic response was much better than the neat pigments.

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