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Characterization of Electrophoretic Particles for a Reflective Display Device

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Characterization of Electrophoretic Particles for a Reflective Display Device

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Titanium dioxide (TiO_2) nanoparticles were encapsulated with polystyrene (PS)-based copolymeric materials for an electrophoretic display application. This coating process was performed in order to improve the dispersion stability of electrophoretic pigment particles in a dielectric medium and to reduce the density mismatch between TiO_2 and the dielectric medium. The characteristics of polymer-coated TiO_2 nanoparticles of the density, chemical structure, particle size, shape, and morphology, were examined respectively by FT-IR, thermogravimetric analysis, particle size analysis, and SEM. Additionally, the electrophoretic mobility of the fabricated nanoparticles with a charge control agent was determined by measurements of the zeta potential.

Keywords: dispersion polymerization; electrophorectic display; electrophorectic particles; inorganic/organic composite particle; optical particles

1. INTRODUCTION

An electronic paper display technology known as an electrophoretic display is a non-emissive device based on the electrophoresis phenomenon of charged pigment particles suspended in a dyed solvent. It was initially proposed by Ota *et al.* in 1969 [1]. Electrophoretic display devices typically consist of a closed packed microcapsule monolayer filled with white/color charged particles, a suspension fluid, a charge control agent, and dispersion agents. When the system is exposed to an electric field, these charged particles move either up or down within the microcapsules, creating text or images [2,3]. Therefore,

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the electrophoretic colloidal suspension is the most essential part of an electrophoretic display device. With this component, it is necessary to enhance the dispersive properties of particles for rapid movement in a solvent. A major consideration related to colloidal stability in the electrophoretic suspension is the contribution of high electrophoretic mobility. The mobility of electrophoretic suspensions is connected to the zeta potential [4]. The zeta potential can measure the stability of pigment particles in a suspension and control the electrophoretic mobility. It has been reported that functional groups on a polymeric surface might play a key role in the charging manifestation on polymeric particles [5]. The concentration dependence of nonionic surfactants on the zeta potential in a non-aqueous dispersion has been examined [6]. The absorbed nonionic surfactant molecules develop resistance in the dispersed pigment particles to agglomeration in a low dielectric medium. They can either impart an electrical charge onto the particle surface and stabilize the suspension through an electrostatic mechanism or physically prevent the two surfaces from coming into adhesive contact through steric hindrance. The aim of the present paper is to provide an electrophoretic image description of functionalized pigment particles in a low permittivity suspension medium. To do this, polymer-coated TiO₂ nanoparticles were synthesized in a two-step dispersion polymerization process. The effectiveness of two-step dispersion polymerization in producing the composite particles is able to provide the estimated functional group on the composite particle, in this work we chose a carboxylic acid as the functional group. The electrophoretic display cell was then fabricated using the electrophoretic particle suspension showing the highest zeta potential.

2. EXPERIMENTAL

2.1. Synthesis of Pigment Particles

As the white pigment particle, polymer-coated TiO₂ composite particles were synthesized using the two-step dispersion polymerization method [7]. All chemicals used in this study were reagent grade without further purification steps. During the second stage of the preparation of the polymer-coated TiO₂ composite particle used in this study, five different amounts of methyl methacrylic acid (MAA) (5, 10, 20, 30, and 40 wt% of styrene monomer) that were used as the functionalized comonomer were slowly added to the reactor so that they would be incorporated onto the surface of the polymer-coated TiO₂ composite particles. This brought the functional group to the surface of the composite particle.

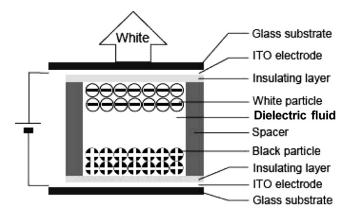


FIGURE 1 Electrophoretic testing cell: Sketch of black particle and white particle movements with an applied voltage in the electrophoretic testing cell.

Black particles (DMX-150YB-30-BK) were purchased from Soken Chemicals Co. (Japan) and were used as received.

2.2. Fabrication of an Electrophoretic Ink Panel

The electrophoretic suspensions were prepared by suspending the polymer-coated ${\rm TiO_2}$ composite particles as the charged white pigment together with the black pigment particles in a clear dielectric fluid [8]. From the results of the zeta potential measurements of the electrophoretic ink suspension with different types of oil soluble surfactants, a nonionic oil soluble surfactant, Span 85, induced the highest zeta potential [8]. Span 85 was chosen as the charge control agent in the creation of the electrophoretic ink suspensions.

Routine testing of the suspensions was done in simple test cells, and measurements of the contrast, response time, and conductivity were performed. The structure of the testing cell using the black and white particle suspensions is shown in Figure 1.

3. RESULTS AND DISCUSSION

Figure 2 shows the surface morphology of pristine TiO_2 and the polymer-coated TiO_2 composite particles. The pristine particles exhibit an irregular plate-like shape that is heterogeneously distributed, which is a characteristic that is usually associated with conventional nano-sized TiO_2 particles. When bare TiO_2 particles were introduced in the polymerization medium, investigation of the morphology of

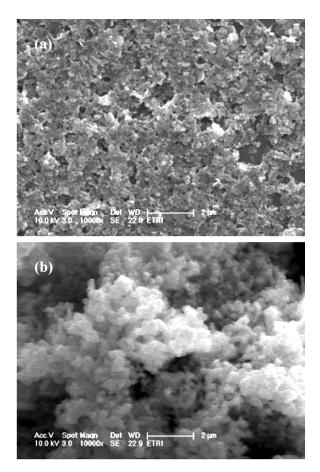


FIGURE 2 SEM images of (a) bare TiO₂ and, (b) PS-coated composite particles.

the resulting composite particles by FE-SEM revealed that small pure TiO_2 particles were covered with the polymer. The surface of the composite particles was smooth with a less irregular spherical shape. Bare TiO_2 particles were not detected over the entire surface of the sample.

The FT-IR spectra of the composite particles revealed characteristic peaks in the middle: C-H stretching at 3000 cm⁻¹, tertiary C-H stretching and aromatic C-C stretching at 1470 cm⁻¹, CH_2 bending at 1454 cm⁻¹, and CH_2 and CH_3 groups of a polymer backbone at 2800–3000 cm⁻¹. Within the increase in the MAA concentration in the polystyrene shell, the ratio of the peak intensity at 1690 cm⁻¹ to that at 1490 cm⁻¹ noticeably increased. This shows that more MAA

was copolymerized with crosslinked styrene. This result indicates the formation of composite particles.

TGA thermograms of polymer-coated TiO_2 composite particles and TiO_2 particles confirmed the encapsulation effect of the polymeric material on the TiO_2 particle. The density of the composite samples was found to range from 1.69 to $1.91\,\mathrm{g/cm^3}$ with various MAA contents according to a pycnometer. The encapsulation efficiency depended on the ratio of the core materials of TiO_2 to the polymer shell. For a 20% MAA functionalized polymer-coated TiO_2 composite particle, the thermogram reveals that composite particles are composed of 86% of TiO_2 and 14% of poly(styrene-co-methyl methacrylic acid).

The particle size and the particle size distributions were determined as shown in Figure 3. The average diameter of the TiO_2 was 316 nm, while that of the 20% MAA composite particles was 715 nm. The particle size distribution of the composite was observed to be relatively narrow compared to bare TiO_2 .

In order to determine the surface charge of the composite particles, the zeta potentials of electrophoretic white polymer-coated ${\rm TiO_2}$ composite particle suspensions that were composed of the white pigment and dielectric fluid were measured using a Zetasizer 2000 device (Malvern Instruments). Figure 4 represents the surface charge characteristics of the polymer-coated ${\rm TiO_2}$ composite particles depending on the functionality of the particles. The particles were dispersed

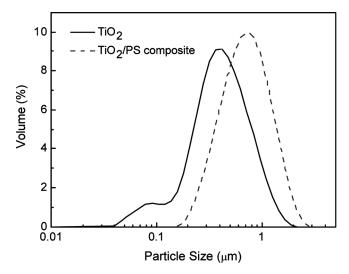


FIGURE 3 Particle size distribution of bare ${\rm TiO_2}$ and PS-coated ${\rm TiO_2}$ composite particles.

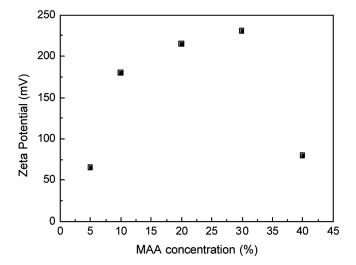


FIGURE 4 Zeta potential of the TiO₂/PS electrophoretic particle suspension with different MAA contents with 0.5 vol% Span 85 surfactant.

in isoparaffin oil with 0.5 vol% of Span 85. The zeta potentials of the particle suspension were affected by the surface functionality. The zeta potentials increased as the acidic group content increased in the low functional group concentration range. However, it reached its maximum value and then decreased.

Based on the result of the measurement of the zeta potential, 20 vol% white particles (10% MAA content) dispersed in 0.5 vol% of Span 85 concentrated isoparaffin oil was blended with 5 vol% of the black

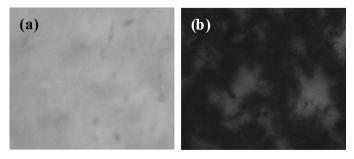


FIGURE 5 Photomicrographs of a black/white electrophoretic ink suspension cell in the power-on state: (a) $+10\,\mathrm{V}$ applied via the front electrode, (b) $-10\,\mathrm{V}$ applied via the front electrode.

particle suspension. This was then sonicated for 1 hr. The contrast ratio of the electrophoretic ink suspension was calculated via reflectivity at +10 V vs. that at -10 V using a test cell with a thickness of $150\,\mu m$. Figure 5 shows the performance of the black/white electrophoretic ink suspension in the cell after the application of $10\,V$. The reflectivity values of the black/white electrophoretic suspension cell were measured using a chromater (CS-100, Minolta Co.). The white state was measured at $211\ cd/m^2$ and the black state was measured at $11\ cd/m^2$. The contrast ratio (CR) of the black/white electrophoretic suspension in the cell was found to be 19:1 with a particle migration speed of approximately $60\,\mu m/sec$ in the 150- μm -thick testing cell.

4. CONCLUSIONS

The polymer-coated ${\rm TiO_2}$ composite particles were successfully prepared in a two-step dispersion polymerization process. The presence of carboxylic acid groups on the composite particles was confirmed by FT-IR. SEM results and particle size determinations of the composite particles showed a narrow size distribution and shape change, and no bare ${\rm TiO_2}$ particles were detected on the surfaces of samples. The density of the composite particles is equivalent to 1.7 g/cm³ due to density matching with the suspension media ($\rho_{\rm fluid} = 1.5 \,$ 1.5 g/cm³). The zeta potential of the composite particles in hydrophobic oil confirmed that the surface modification using the carboxylic acid group was proper in the adaption to an electrophoretic particle. In conclusion, the production of inorganic/polymer composite particles is expected to be very useful in the production of electrophoretic displays.

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