

Preparation of Polymer-Coated TiO₂ Particles for Electronic Paper Based on Electrophoresis

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Abstract. The preparation and characterization of TiO₂ particles coated with an electrophoretic polymer using silane coupling agents and highly hydrophilic monomers (methyl methacrylate) are presented in this article. The organic layer was formed by radical polymerization and bonded to the surface of inorganic TiO₂ with a silane coupling agent. The polymer-coated particles were characterized by Fourier transform infrared spectrometry, field emission scanning electron microscopy, and thermogravimetric analysis. The size distribution and charge properties of the polymer-coated particles were measured, and the optical response of electrophoretic image display cells, containing the particles, was also investigated. It was found that coating materials having a branched alkyl side chain structure endowed the final polymer-coated particles with good stability and favorable electrophoretic properties in an electrophoretic medium. In addition, the charge polarity of the polymer-coated particles could be controlled using different silanizing reagents and polymers. Furthermore, electrophoretic image display cells, containing such particles, demonstrated good response and high reflectance in their white state. © 2010 Society for Imaging Science and Technology. [DOI: 10.2352/J.ImagingSci.Technol.2010.54.1.010506]

INTRODUCTION

Electrophoretic image displays (EPID) are paper-like nonemissive displays, which are also called electronic paper. Such displays have portability, flexibility, wide viewing angles, high contrast, low power consumption, and almost the same appearance as paper.¹ An EPID based on the electrophoresis of charged pigment in a hydrocarbon-based dielectric solvent under the influence of a driving electrical field is shown in Figure 1.^{2,3}

The charged particles in this system can be any light-reflecting material, which can undergo electrophoresis in electrophoretic media. In particular, titanium dioxide (TiO₂) has been most widely used for white EPID particles due to its extremely high reflectivity, excellent whiteness, covering power, chemical stability, and nontoxicity. However, it has the drawback of poor suspension stability in dielectric solvents due to its high specific gravity and high surface energy with metallic polar surfaces. Therefore, TiO₂ needs to be modified by either adsorbing various materials onto the surface of the particles or by chemically bonding cross-linking

polymers to improve its dispersion stability. For its use in an EPID, the materials used to modify TiO₂ should not only be strongly bonded to TiO₂ but also transparent and chargeable in an electrophoretic medium. Furthermore, polymers on the modified particles should not cause any reduction in the electrophoretic mobility of the particles.^{4,5} However, when the particles are coated with an organic material, such as a wax, it has been found that the interaction between the coating material and the TiO₂ surface is not strong enough and the coating material may separate from the surface of the pigment in some situations. Thus, it is commonly accepted that the coating layer must be chemically bonded to the particles.

Silane coupling agents are widely used in the preparation of organic/inorganic hybrids via -Si(OCH₃)₃ groups forming covalent bonds with inorganic materials. In the case of silane coupling agents, containing polymerizable groups, such as a vinyl group, it is possible to fabricate a polymer coating on the inorganic surface. In this study, the electrophoretic particles were fabricated in two steps. First, the silica coated pigments were surface bonded with silane coupling agents having polymerizable functional groups. Then, the polymerizable functional groups were reacted with monomers to form a polymer-coated layer on the inorganic pigment.

In recent years, there have been many reports focused on coating TiO₂ with polymethylmethacrylate (PMMA) or polystyrene (PS) to prepare TiO₂-polymer core-shell particles for use in electronic paper.^{6–8} According to these reports, PMMA coated TiO₂ does not have sufficient zeta potential and mobility for an electrophoretic display.⁹ PS-TiO₂ has been successfully used in an electrophoretic display and the response time has been improved to 2 s by applying 30 V to an EPID cell.¹⁰

However, we think that single or short polymer chains only improve particle stability to a certain degree, but poly-

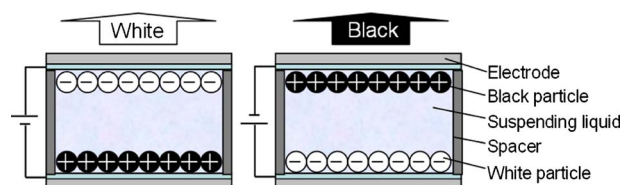


Figure 1. Schematic illustration of monochromatic electrophoretic image display.

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mer materials having side chains, branching from the main chain, could effectively improve the stability and electrophoretic mobility of particles in EPID medium.

On the other hand, the electric charging mechanism for EPID particles is not well understood. It has been found that the pigment can be initially charged before the polymer coating process. Reagent modifying processes can also endow the particles with charge insofar as they involve reagents that have chargeable groups. Furthermore, the polymer graft process can provide the particle charge when monomers that have chargeable groups are employed. Finally, a charge control agent (CCA) can also be added to the final suspension to charge the particles.

In this study, two kinds of silane reagents with polymerizable and chargeable groups were used to modify TiO₂. Lauryl methacrylate and 2-ethylhexyl methacrylate (2-EHMA), which both have branched alkyl side chains, were used as polymer coating materials. The characteristics of the polymer-coated TiO₂ as well as its electrophoretic performance in a dielectric solvent with a CCA were investigated.^{11,12}

EXPERIMENTAL

Materials

Alumina and silica coated nano TiO₂ pigment (Dupont R960, alumina and silica coated TiO₂, specific gravity = 3.9 g/cm³, and average diameter = 400 nm) was used for the core of the white EPID particles. Ethanol, toluene, and deionized water were used as solvent. 3-(trimethoxysilyl)propyl methacrylate (MSMA, 98%, Aldrich, Milwaukee, Wisconsin) and *N*-[3-(trimethoxysilyl)propyl]-*N'*-(4-vinylbenzyl)ethylenediamine monohydrochloride (TMSP, Aldrich) were used to modify the TiO₂ particles. Lauryl methacrylate (LMA, Aldrich) and 2-ethylhexyl methacrylate (2-EHMA, Aldrich) monomers were used to form the polymer layer on TiO₂. A nonionic surfactant sorbitan trioleate (Wako, Japan) was used as a suspension stabilizer. Hypersurfactant solspers 17000 (Avecia, Ltd.) was used as the CCA and IsoparG (Exxon Mobil Corp.) was used as the electrophoretic solvent.

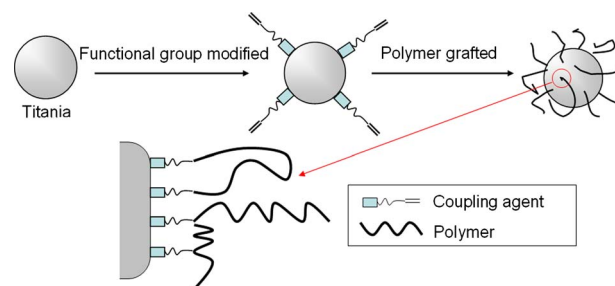


Figure 2. Schematic illustration of the polymer coated process for pigment.

Surface Modification and Preparation of Polymer Coated TiO₂ Particles

Figure 2 shows a schematic illustration of the surface modification process for the TiO₂ particles. There are two stages for the preparation of polymer-coated TiO₂. In the first step, ethanol, water, and the silane reagent were mixed and stirred rapidly for 10 min. Then TiO₂ was added and the mixture was stirred for 15 min. The resulting suspension was poured into plastic bottles and centrifuged at 5000 rpm for 30 min, and the liquid was decanted. This washing procedure was repeated two times and then the pigment was dried in a vacuum oven at 70°C for 5 h. In the polymer coating step, the silanized TiO₂ was added to a round-bottomed flask containing toluene and either lauryl methacrylate or 2-ethylhexyl methacrylate monomer. The resulting mixture was stirred rapidly under a nitrogen atmosphere for 20 min and then slowly heated to 50°C. Next, azo-bis-isobutyronitrile was added quickly. The suspension was then heated to 65°C and stirred for 18 h. The resulting suspension was washed with ethyl acetate or toluene and centrifuged at 5000 rpm for 30 min, and the liquid was decanted. This washing procedure was repeated two times, and the powder was dried in a vacuum oven at 65°C for 18 h. Table I shows some experimental information about the samples fabricated in this study.

Measurement

The chemical structures of the modified particles were determined by field emission scanning electron microscopy

Table I. Some experimental conditions and characteristics of polymer-coated TiO₂.

Sample No.	TiO ₂ (g)	Silianize (g)		pH	Monomer (g)		wt % ^a	Size (nm)
1	10	MSMA	1.6	4	LMA	2.5	2.0	380 ~ 400
2	10	MSMA	1.6	4	LMA	5	2.5	380 ~ 400
3	10	MSMA	1.6	4	LMA	7.5	3.0	380 ~ 400
4	10	MSMA	1.6	4	LMA	10	5.5	380 ~ 400
5	10	MSMA	1.6	4	LMA	20	6.9	380 ~ 400
6	10	TMSP	16	9	LMA	10	1.8	380 ~ 400
7	10	TMSP	16	9	2-EHMA	10	5.6	380 ~ 400
8	10	TMSP	16	7	2-EHMA	10	3.2	380 ~ 400

^aPolymer percent by weight of TiO₂.

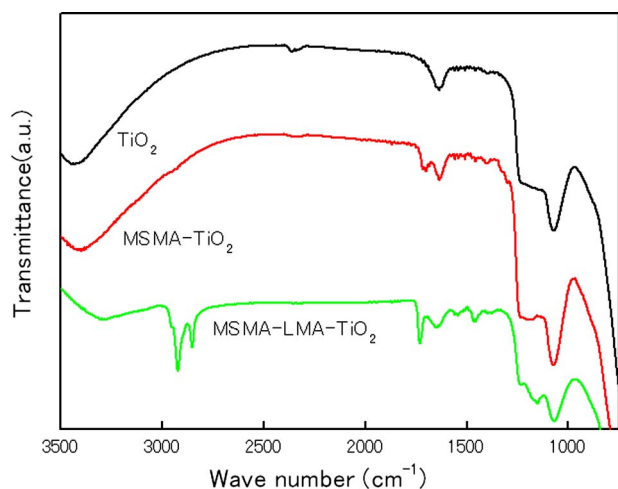


Figure 3. FTIR spectra of TiO₂, MSMA modified TiO₂ and LMA coated TiO₂.

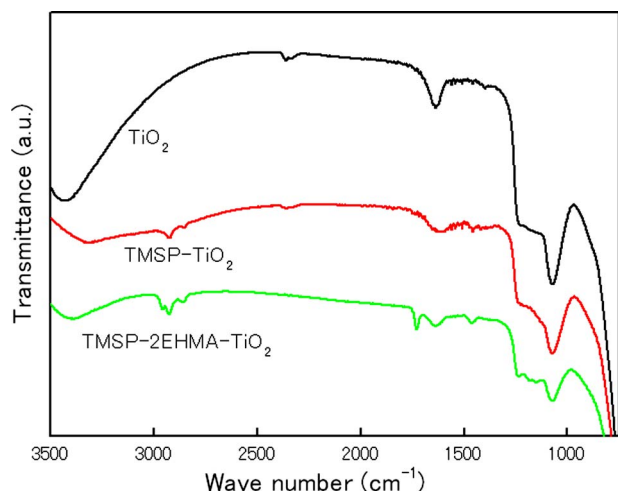


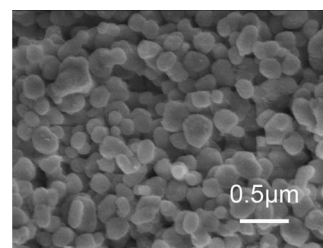
Figure 4. FTIR spectra of TiO₂, TMSP modified TiO₂ and 2-EHMA coated TiO₂.

(FTIR) (FTIR660Plus, JASCO). The thermal properties and contents of each material were examined via thermogravimetric analysis (TG/DTA 6300, Seiko Instruments, Japan). The size and zeta potential of the particles in dispersion medium were measured using an electrophoretic light scattering spectrophotometer (Zetasizer 3000HS, Malvern Instruments, USA). The surface appearance of the particles was observed by scanning electron microscope (SEM). Electrophoresis of the particles in the dispersion medium was investigated by a digital microscopy camera.

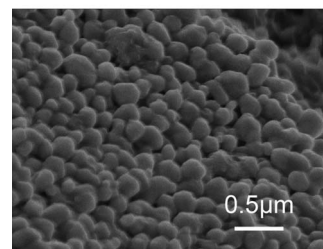
RESULTS AND DISCUSSION

Characteristics of Polymer Coated TiO₂

Figures 3 and 4 show the infrared spectra of unmodified TiO₂, TiO₂ modified by silane coupling, and polymer-coated TiO₂ particles as measured by FTIR. According to the spectra of the two polymer-coated particles, the C-H bands at 2853.17 cm⁻¹ and 2923.55 cm⁻¹ as well as the C=O



(a)



(b)

Figure 5. SEM photo of bare TiO₂ pigment (a) and LMA coated TiO₂ pigment (b).

Table II. Zeta potential of polymer-coated TiO₂ in IsoparG with Solsperse17000.

Sample	Reagent	Polymer	Polymer ratio (%)	Zeta (mV)
1	MSMA	LMA	2.0	-16
2	MSMA	LMA	2.5	-25
3	MSMA	LMA	3.0	-19
4	MSMA	LMA	5.5	-23
5	MSMA	LMA	6.9	-18

stretching peak at 1729.83 cm⁻¹ indicate that the polymer was successfully coated onto the TiO₂ particles.

Characterization of Particles

It was found from samples 6, 7, and 8 that the polymerizable group of TMSP reacted with 2-EHMA but reacted less readily with LMA. In addition, comparing sample 7 with 8, it can be concluded that the reaction condition of pH 9 is necessary when TMSP and 2-EHMA are used to modify TiO₂. The average size distribution of the polymer-coated particles was between 380 and 420 nm as measured by Zetasizer 3000; this range was also confirmed by SEM (Figure 5). It was thus demonstrated that the polymer layer formed on TiO₂ was very thin, having a thickness of only several nanometers.

Charge Properties of Polymer-Coated TiO₂

Solsperse 17,000, which has both negatively and positively charged groups, was examined as a CCA in this study. These results are presented in Table II. The LMA polymer-coated TiO₂ samples modified by MSMA had polymer ratios from 2 to 6.9% by weight of TiO₂ and a negative charge average of -30 mV. Furthermore, it was found that the original silica

Table III. Zeta potential of polymer-coated TiO₂ in IsoparG with CCA.

Sample	Reagent	Polymer	CCA	Charge polarity
4	MSMA	LMA	Solsperse 17000	Negative
7	TMSP	2-EHMA	Solsperse 17000	Positive
8	TMSP	2-EHMA	Solsperse 17000	Positive

Table IV. Concentration of compounds in electrophoretic dispersions.

	Compound	Conc. (wt %)
Pigment A	Polymer-coated TiO ₂	35
Pigment B	Black particle	2.5
Surfactant	Span85	0.5
CCA	Solsperse 17000	0.5
Solvent	IsoparG	61.5

coated R960 was negatively charged by Solsperse 17000. On the other hand, as shown in Table III, the 2-EHMA polymer-coated TiO₂ modified by the aminosilane TMSP was positively charged by Solsperse 17000. Thus, it was confirmed that the charge polarity of polymer-coated TiO₂ can be controlled by choice of either MSMA or TMSP. Considering that MSMA, LMA, and 2-EHMA are not chargeable materials, the positive charge can be explained as being caused by the amino group in the silanization reagent. By contrast, we believe that the hydroxyl groups on the silica/alumina layers of bare TiO₂ play an important role in imparting a negative charge to the polymer-coated TiO₂. At the same time, in our experiment, positive and negative charged particles did not aggregate when they were mixed in EPID solvent because of the steric hindrance due to polymer around the particles.

Electrophoretic Image Display Cell

Electrophoretic dispersions were prepared according to the formulations given in Table IV. The dispersions were injected into electrophoretic cells, which consisted of two pieces of transparent indium-tin oxide coated glass (3 × 3 cm², optical area 1 × 1 cm²) and separated by 100 μm spacers (Figure 6). Reflectance (λ = 550 nm) of the optical area was measured by a spectrophotometer system for determining the optical response of the electrophoretic dispersion. Figure 7 shows photographs of the white and black states of the electrophoretic cell. Figure 8 demonstrates the optical response of two electrophoretic cells, containing MSMA-LMA-TiO₂ and TMSP-2-EHMA-TiO₂, respectively. Black and white states could be indicated easily by applying 10 V to the electrodes. Reflectance of the white state was above 50% at the wavelength of 550 nm and the black to white response times of MSMA-LMA-TiO₂ and TMSP-2-EHMA-TiO₂ were 1 s and 2 s, respectively. The response time is greatly improved compared with the data for PS-coated TiO₂ and the reflectance of the white state is much higher. However, we observed that the switch from the

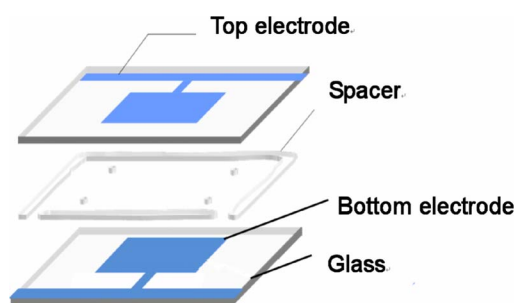


Figure 6. EPID cell structure.

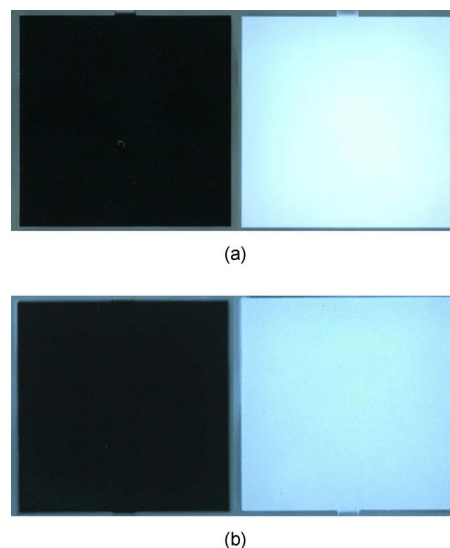


Figure 7. Black and white states of (a) EPID cell containing MSMA-LMA-TiO₂ and positively charged black pigment and (b) EPID cell containing TMSP-2-EHMA-TiO₂ and negatively charged pigment right; size 1 cm × 1 cm.

white to the black state took more than 5 s, as shown in Fig. 8(a), which we attribute to the electrode adsorption of TMSP-2-EHMA-TiO₂. This result could be the effect of the interaction between the polyelectrolyte layer of the electrodes and particles of the amino group of TMSP or of insufficient polymer coating. These effects were also observed on other samples, whose polymer ratio was less than 5 wt %. On the other hand, we believe that by adjusting the electrode adsorption intensity of particles, an appropriate threshold and bistable display can be achieved. We are performing further studies on this question. Figure 9 shows the reflectance of the electrophoretic cell containing MSMA-LMA-TiO₂ under applied voltages of 2.5, 5, and 10 V. To study the aging property of this cell, the voltage was switched on and off 50 times before this measurement was taken. Because of particle clustering and sedimentation, reflectance of the white state decreased to less than 50% after 50 switches. To solve this problem and improve display stability, the electrophoretic medium could be encapsulated, and indeed there are many reports regarding this technology.^{13,14}

Finally, we can state that by using polymer-coated TiO₂ fabricated as a part of this research, an electrophoretic cell

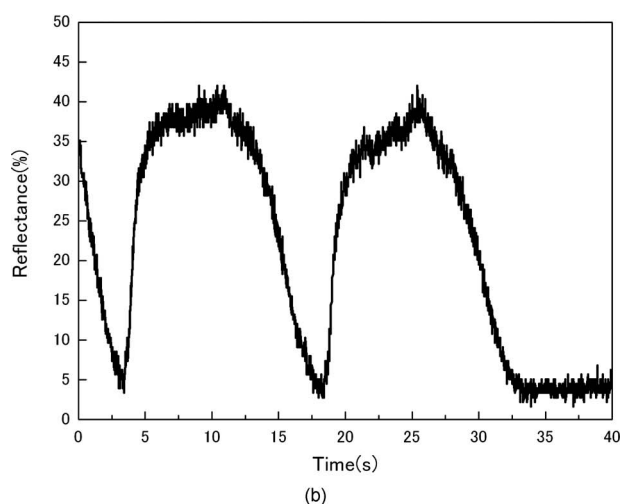
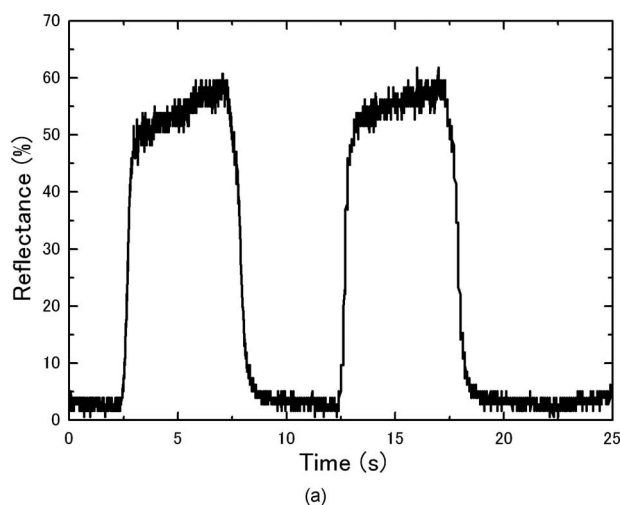


Figure 8. Optical response of two EPID cells: (a) contains MSMA-LMA-TiO₂ and positive charged black particle, applied voltage was ± 10 V, polarity was switched at 2.5, 7.5, 12.5, and 17.5 s. (b) contains TMSP-2EHMA-TiO₂ and negative charged black particle, applied voltage was ± 10 V, polarity was switched at 2.5, 12.5, 17.5, and 27.5 s.

with high reflectance in the white state, and fast response time from the black to white states, was successfully assembled.

CONCLUSION

LMA and 2-EHMA polymers having branched side chain structures were chemically bonded to SiO₂- and Al₂O₃-coated TiO₂ particles, using silane coupling agents.

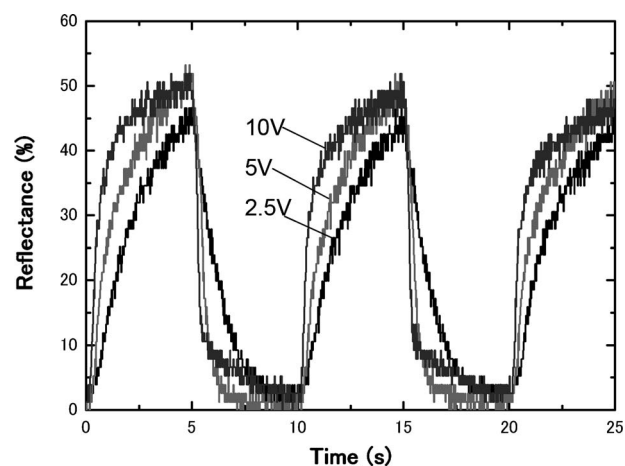


Figure 9. Optical response with different drive voltage.

These polymer-coated particles have good electrophoretic properties and stability in electrophoretic suspending solvent. In addition, the charge polarity of the polymer-coated particles in EPID medium can be controlled by changing the silane coupling agent and coating material. Furthermore, the optical response of EPID cells, containing the particles, shows good response and high reflectance in the white state.

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