

Study on Charge Mechanism of EPID Particles

Ming Wang, Taku Nakamura, Sakiko Nakamura, Nobukazu Miyagawa, and Takashi Kitamura

Graduate School of Advanced Integration Science, Chiba University, chiba-city, Japan

Abstract

Electrophoretic polymer coated inorganic pigment were synthesized by using silane coupling agent and highly hydrophilic monomers. Silane coupling agents which have charge and polymerable functional group were used to modify particles and monomers which have more than eight carbon atoms were used to form polymer coating layer on particles by radical reaction. Silane coupling agent serve pigment with charge, and polymer layer reduces the specific density of pigment and prevent the pigment from flocculating in electrophoretic solvent. By choosing proper silane coupling agent and coating monomer, the charge polarity of particles can be control and the final polymer coated pigment show good stability, quick response and high reflectance in electrophoretic image display.

1. Introduction

An Electrophoresis Image Display (EPID) is a kind of reflective-type display based on the electrophoresis of charged pigment in hydrocarbon-based dielectric solvent under the influence of driving electrical field as shown in Fig.1. The mixture of charged white and black particles is placed between two transparent electrodes which are separated by spacer and the image forms or changes when the charged particles move towards electrode to the observer by applying different voltage between two electrodes. [1]

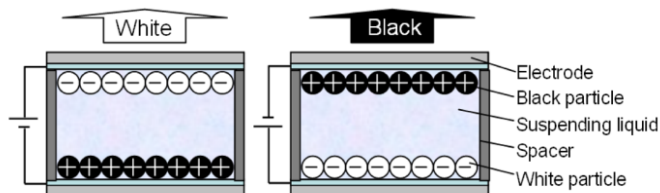


Figure 1. Schematic illustration of monochromatic Electrophoretic Image Display

TiO₂ nanoparticle is used as EPID white pigment due to its excellent whiteness, high covering power, chemical stability and non-toxicity. However, bear TiO₂ particle is not fit for EPID because it has two drawbacks. First, it cannot disperse well in dielectric solvent because of its high specific density and metallic surface. Second, adsorption of TiO₂ to electrode is easily happen during electrophoresis due to its metallic surface. To solve these problem, researchers use polymer materials to modify TiO₂ particle to provide it good solubility in organic EPID solvent. Recently, many reports introduced some methods of coating or grafting organic materials like polystyrene (PS), polymethyl methacrylate (PMMA), 2-ethylhexyl methacrylate (2EHMA), lauryl methacrylate (LMA) onto surface of TiO₂ to low its specific

density and improve stability of particle suspension of organic solvent. [2] [3] [4]

However, as EPID particles, one should not only stably disperse in organic solvent but also has polarity on its surface when it is dispersed in dielectric solvent. In the past, charging of particle has been achieved by adding charge control agents (CCA) into EPID medium or by coating particle with special polymer include charged group. CCA is a kind of surfactant which has charge group and it would adsorb on particle surface to provide it charge. There are many thereon to explain the charging process of CCA to particle, but we know little about how it works practically. [5] Because CCA just physically adsorb on to the particle's surface, it may drop away from particle's surface and dissolve into EPID medium. In this situation, conductivity of EPID suspension will be increased due to CCA dissolve and it is undesirable for EPID because the current would occur when voltage is applied on this EPID medium. At the same time, the use of CCA in EPID medium which contains two opposite charge particle is very complex. CCA may adsorb on both particle and take them same charge. Moreover the adsorption of CCA on electrode will also cause other problem. In the case of charged polymer coated particle, it is found that, opposite charge particle will attract each other and finally cause sedimentation or loss their mobility in opposite charge particles EPID medium. It could be explained by the static attraction between particles because charge groups on particles surface were exposed to each other. We believe that if charge group is chemically bonded on to TiO₂ and hided into polymer layer at the same time, these problems could be all solved.

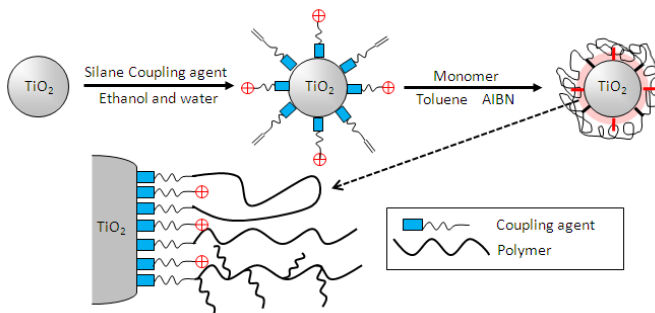


Figure 2. Schematic illustration of monochromatic Electrophoretic Image Display

Silane coupling agent is widely used in the preparation of organic/inorganic hybrids via -Si(OCH₃)₃ groups can effect a covalent bond between organic and inorganic materials. By using silane coupling agent which contains polymerizable group such as vinyl, it is possible to fabricate polymer coating layer on inorganic surface by radical polymerization.

3 kinds of silane coupling agent: SiCp A, which has polymerable group; SiCp B, which has positive charge group and SiCp C, which has negative charge group were used in this study.

EPID polymer coated TiO_2 was fabricated by two steps as shown in Fig.2. First, TiO_2 particles were surface bonded with two kinds of silane reagents, one had polymerizable functional groups and the other had charge group. Next, the polymerizable functional groups on reagent would react with monomers to form polymer coated layer at the surface of TiO_2 particles. The surface structure of polymer coated TiO_2 is also shown in Fig.2. Charge group is chemically bonded on TiO_2 surface so it would not desorb from TiO_2 surface as easily as CCA does. In this structure, these charge groups is at a distance of several atom scale from TiO_2 surface so they could extend to EPID solvent and show polarity. At the same time, the polymer outside could protect these charge groups from exposing into solvent and cause static attraction between two opposite charge particles.

In this study, positive charged and negative charged core-shell structure polymer coated TiO_2 were prepared, Charge group was directly chemically bonded on to TiO_2 surface and polymer formed outside of the charge group to protect them and improve solubility of TiO_2 in dielectric solvent.

2. Experimental

2-1 Materials

TiO_2 (Dupont R960, Alumina and silica coated TiO_2 , specific gravity=3.9g/cm³, Avg. dia. =400nm) was used for the core of white EPID particles. Ethanol and deionized water were used as solvent and Silane reagents SiCp A (3-(trimethoxysilyl)-propylmethacrylate, 98%, Aldrich), SiCp B (within positive charge group) and SiCp C (within negative charge group) were used as reagents to modify the TiO_2 particles. 2-ethylhexyl methacrylate (2-EHMA, Aldrich), Lauryl methacrylate (LMA, Aldrich), Octadecyl methacrylate (OCTD, Aldrich) monomers were used to form polymer layer on TiO_2 . Suspending fluid IsoparG (Exxon Mobil Corp.) was used as electrophoretic solvent and non-ionic surfactant, Sorbitan Trioleate (Wako chemi.) was used as suspension stabilizer.

2-2 Surface modification and preparation of polymer-coated TiO_2 particles

There are two stages for preparing polymer coated TiO_2 in this study. In the first step, ethanol, water and silane agents were mixed and stirred rapidly for 7 minutes and TiO_2 was added, the mixture was stirred for 5 minutes. The resultant suspension was poured into plastic bottles and centrifuged at 5000 rpm for 30 minutes, and transparent liquid was decanted. The washing was repeated for 2 times by ethanol and pigment finally dried in vacuum oven at 70°C for 5 hours. Silanized TiO_2 was added into a round-bottomed flask with toluene and lauryl methacrylate or 2-ethylhexyl methacrylate monomer. In the polymer coating step, resulting mixture was stirred rapidly under a nitrogen atmosphere for 20 minutes, then slowly heated to 50°C. After AIBN was quickly added, the suspension was heated to 70°C and stirred for 18 hours. The resultant suspension was wash by ethyl acetate or toluene and centrifuged at 5000 rpm for 30 minutes, and the liquid decanted.

The washing was repeated twice, and the powder was dried in vacuum oven at 65°C for 18 hours. Toluene was added in to flask and the suspension was centrifuged at 6000rpm for 20 minutes. Transparent toluene was decanted and washing was repeated for 3 times by toluene. Finally, the particle was dried for 7 hours in a vacuum dryer at 70°C.

3. Measurement

3-1 Polymer weight ratio to TiO_2 particles

Thermal properties and polymer weight ratio to TiO_2 particles were investigated via thermo gravimetric analysis (TG/DTA 6300, Seiko Instruments.)

3-2 Size and Zeta potential

Size and zeta potential of particles in dielectric solvent IsoparG with or without surfactant sorbitan trioleate (particle is 0.01wt %, IsoparG is 0.005wt %) were measured by using Zetasizer. (3000HS, Malvern Instruments).

3-3 Electrophoresis

Electrophoresis mediums were prepared by dispersing 1wt% polymer coated TiO_2 and 0.5% surfactant sorbitan trioleate into IsoparG. The Electrophoresis medium was injected in to an electrophoretic cell, composed of two pieces of glasses separated by 25 μm spacers as shown in Fig.3. Top glass has two ITO electrodes and the distance between two ITO electrodes is 1mm. When the voltage was applied onto these two electrodes, EPID particles would move from one electrode to the other electrode. Electrophoresis of particles was investigated on top view of the cell by Digital Microscope Camera.

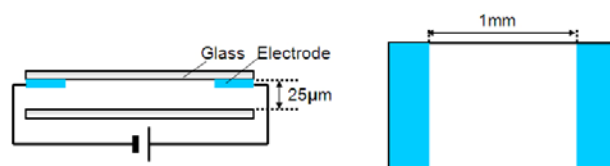


Figure 3. Schematic of parallel type electrodes cell

4. Result and discussion

4-1 polymer weight ratio to TiO_2 particles

Thermo gravimetric analysis dates of several samples were summarized in table 1. Silanize coupling agents modified particle lost 1% of its weight when it was heated from 150°C to 450°C. This lost weight is supposed to be the silanize coupling agents which is chemically bonded onto TiO_2 surface. Polymer coated particle lost 5% of its weight when it was heated from 150°C to 450°C. The lost weight is silanize coupling agent and polymer which were coated onto TiO_2 surface.

Table 1 Weight Ratio of Polymer coated on TiO₂ particle

No.	SiCp		wt%	monomer	wt%
1	SiCpA	SiCpB	1.3	2EH	5.1
2	SiCpA	SiCpB	1.3	OCTD	5.2
3	SiCpA	SiCpC	1	2EH	4.4
4	SiCpA	SiCpC	1	LMA	4.8

4-2 Size and Zeta potential

It has been confirmed that all the polymer coated samples could well disperse in organic solvent IsoparG without any surfactant. According to the zeta potential data of polymer coated particles, without nonionic surfactant sorbitan trioleate, particles show little polarity in dielectric solvent IsoparG. When nonionic surfactant sorbitan trioleate was added in to this suspension, both two kinds of polymer coated particles, positive or negative charge silanize coupling agents modified particles, showed intense polarity respectively. Zeta potential of particle within positive silanize coupling agent (SiCpB) was more than +70mV and negative on was less than -44mV. The reason for why particles could get charge with the addition of nonionic surfactant has not been understood and we are now doing further study on it.

Table2 Zeta potential of polymer coated TiO₂ in IsoparG

No.	Dispersibility		Zeta potential (mV)	
	IsoparG	IsoparG Surfactant	IsoparG	IsoparG surfactant
1	○	○	7.9	91
2	○	○	9.2	70
3	○	○	-3.6	-56
4	○	○	-4.5	-44.6

4-2 Observation of electrophoresis of polymer coated particles

Fig4 shows us the electrophoresis of polymer coated TiO₂ within positive charge silanize coupling agents. In first photo, these white particles were dispersed in EPID medium homogeneously. When the voltage was applied on two electrode at left and right of the photo, particles were moving to negative electrode on the left. Finally, all the particles were adhered to the left negative electrode. Reverse the applied voltage, all the particles could come back to EPID medium and move to opposite electrode. Particle do not adsorbed onto electrode because the organic polymer acts as insulating barrier by steric hinder.

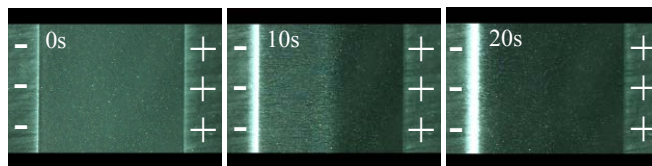


Figure 4. Electrophoresis of Positive Charged Particle Moving to Negative Electrode (left is negative electrode)

The same phenomenon was also investigated with EPID medium containing polymer coated TiO₂ within positive charge silanize coupling agents.



Figure 5. Electrophoresis of Negative Charged Particle Moving to Positive Electrode (left is negative electrode)

Dual particles EPID suspension were prepared by dispersing 0.5wt% positive charged polymer coated particle and 0.5wt% negative charged polymer coated particle into IsoparG within 0.5wt% sorbitan trioleate. The electrophoresis of two opposite charge particles in EPID medium is shown in Fig.6.

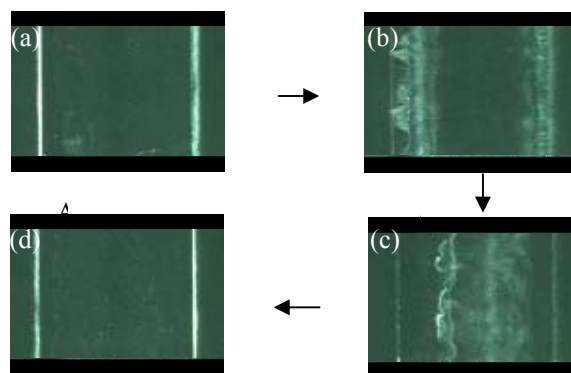


Figure 6. Electrophoresis of Negative and Positive Charge Particle in One Cell

Two kinds of opposite charged particles were adsorbed onto electrodes separately in Fig.6 (a). When applied voltage was reversed, both two particles left electrodes and moved to opposite electrodes in Fig.6 (b). Two kinds of opposite stroke each other in the middle of EPID cell in Fig.6(c) and finally reach opposite charged electrode without agglomeration.

5. Conclusions

1. Polymer coated TiO₂ EPID particles, charged by directly chemically bonding silanize coupling agent which has charge group on to TiO₂ surface and then coated with hydrocarbon polymers, were prepared in this study. It has been confirmed that the polarity of final EPID particles could be control by choosing charged silanize coupling agents.
2. The polymer layer outside particle could protect two opposite charge particles from static attraction and improve its dispersibility in dielectric solvent.
3. By adding nonionic surfactant sorbitan trioleate into EPID medium, both positive and negative particles could be intensely charged. We are doing further study for explaining this phenomenon

References

[1] B. Comiskey, J.D. Albert, H. Yoshizawa, J. Jacobson, Nature 394, 253, 1998

- [2] Lee Soon Park, Jin Woo Park, Hae Yun Choi, Yoon Soo Han, Younghwan Kwon, Hyung Suk Choi, Current Applied Physics 6, pp. 644–648, (2006)
- [3] Seong-Tae Hwang, Yoon-Bong Hahn, Kee-Suk Nahm, Yoon-Sik Lee, Colloids and Surfaces A: Physicochem. Eng. Aspects, pp. 259, 63–69, (2005)
- [4] Yu Rong, Hong-Zheng Chen, Han-Ying Li, Mang Wang, Colloids and Surfaces A: Physicochem. Eng. Aspects 253, pp.193–197, 2005
- [5] Ming Wang, Sakiko Nakamura, Nobukazu Miyagawa, and Takashi Kitamura, Pan-Pacific Imaging Conference'08, pp.452-455, (2008)

Author Biography

Ming Wang received his BS in Material Physics and Chemistry from Beijing Institute of Graphic Communication. (2007.4). Since then he has continued his study for PhD in Kitamura Lab., Chiba University. His work has focused on electronic paper technology, especially Electrophoretic Images Display and microcapsules.