Analysis of Surface Interaction between TiO_2 Fine Particles with Different Surface Modification in Isoparaffin by Using Colloid Probe AFM

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ABSTRACT

To control the dispersion stability of nanometer scaled fine inorganic particles in organic solvent, various kinds of surface modification of particles have been carried out. This paper focused on the surface modification of titanium oxide particles for the control of dispersion stability in isoparaffin. This combination of particles and solvent is aimed to be applied to electric rewritable paper using microcapsule included nanoparticles. The surface of titanium oxide was modified by multistage treatment, i.e., silane coupling treatment and random graft polymerization. Surface interaction between titanium oxide particles with various surface modifications was characterized by a colloidal probe atomic force microscope (AFM) method. The relationship between surface interaction force and dispersion stability of titanium oxide particles in isoparaffin solvent was discussed.

Keywords: electric rewritable paper, colloidal probe AFM, random graft polymerization, microcapsule, surface modification

1 INTRODUCTION

Electric rewritable paper [1] using microcapsule which involves titanium oxide and carbon black particles suspended in organic solvent is developing as a new application field of titanium oxide and carbon nanoparticles. Schematic drawings of the electric paper structure and fundamental operating principle are shown in Figure 1 [1]. Titanium oxide and carbon particles are dispersed in organic solvent, for example, isoparaffin, involved for microcapsules, and each particle charged inversely to move to the different electrodes. By the movement of each particle to different side of capsule, images are displayed on the surface of electric paper. To obtain particle dispersion stability in organic solvent, it is necessary to prevent aggregation of each particle and hetero coagulation of TiO_2 and carbon particles. The surface interaction control between dispersed particles and membrane of capsules is important to develop the image stability and the quick switching of the image and quality of images of electric paper. For this purpose various kinds of surface modification on both particles have been attempted [1, 2].

For the characterization of dispersion stability and surface interaction between particles, a colloid probe AFM method [3] has been developed to clarify the action mechanism analysis of particle surface treatment, for examples, polymer dispersant and/or surfactant adsorption [4], and modification by coupling agent [5] on particle surfaces. Furthermore, the adhesion behavior of drag particles in air was investigated by this AFM method [6]. This method is very useful to analyze and discuss the action mechanism of modified surface layers on particles.

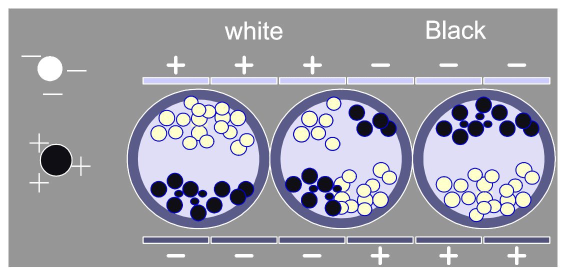

Figure 1: Schematic drawings of the electric paper structure and fundamental operating principle.

In this paper, by using colloid probe AFM method, surface interaction between TiO_2 particles with various surface treatments, i.e., silane coupling reaction and random graft polymerization was investigated in isoparaffin solvent. Based on the comparison with surface interaction and macroscopic suspension behavior, for examples, sedimentation behavior, the mechanism of surface treatment on the suspension stability of TiO_2 particles was discussed.

2 EXPERIMENTAL

2.1 Particle Surface Modification

Powder raw material used was fine TiO_2 powder (Dupont Co. Ltd., mean primary particle size was about 200 nm in diameter, Rutile type). In order to disperse TiO_2 powder in isoparaffin (Exxon Mobil Chemical, Isoper L), which is used for solvent oil in microcapsule, the surface of TiO_2 powder was treated by silane coupling agent and random graft polymerization. Schematic is shown in Figure 2. Silane coupling agent used was 3-(trimethoxysilyl)propyl methacrylate (Shin-Etsu Chemical Co. Ltd.) and was reacted on TiO_2 powder surface in aqueous solution with different reaction time. After silane coupling treatment (SC treatment), random graft polymerization, RGP, on particles was carried out by using lauryl methacrylate (LMA).

Each modified particle was characterized by FTIR after unreacted monomer was washed by toluene and the amount of carbons coupled and polymerized with particles was measured by a CHN analyzer.

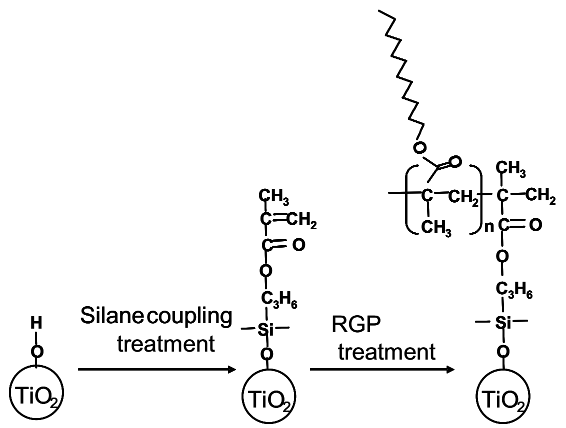

Figure 2: Schematic of surface treatment of TiO_2 particle.

2.2 Sedimentation Characterization

After surface treatment, each TiO_2 powder was dispersed in isoparaffin solvent at 2.7vol% and the dispersion stability and aggregation behavior was characterized by a laser scanning sedimentation tester (TURBISCAN, MA2000, Formulaction Co. Ltd., France). Time dependent sedimentation behavior of titanium oxide particles in isoparaffin was characterized by the volume of dense layer where the transmission of the laser light becomes zero.

2.3 Particle Interaction Measurement

To analyze the interaction between titanium oxide modified by silane coupling agent and random graft polymerization, the changes of repulsive and adhesion force on the surface of substrate in isoparaffin solvent were examined by AFM (PicoForce, Digital Instruments) with a colloid probe. Colloid probe was prepared by the following processes. Firstly, spray dried spherical granule of TiO_2 particles with about 10 μm in diameter was prepared from aqueous suspension. This granule was heated for 2 hours at the primary sintering temperature with slight neck growth at the contact point between primary particles. Single granule after heat treatment was adhered on an AFM commercial tip by using a micromanipulation system [4, 6]. An example of such obtained colloidal probe is shown in Figure 3.

Substrate was prepared by TiO_2 thin green compacts after heat treatment at same primary sintering temperature. The surface of both granule and substrate was modified by the same process of powders. After surface treatment, the force curve between particles in isoparaffin solvent was determined by an atomic force microscope.

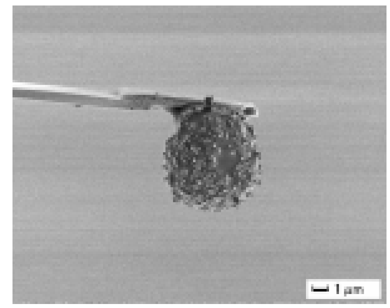

Figure 3: FE-SEM image of colloidal probe of titanium oxide.

3 RESULTS AND DISCUSSION

3.1 Surface Treatment Characterization

Figure 4 shows FTIR spectrums for particles before and after each surface treatment. For the case of RGP treated particles, C-H bending signal at 1400-1500cm^{-1}, C=O stretching signal at 1700cm^{-1}, and the signal at 2800-3000cm^{-1} was grown remarkably, which means the existence of LMA bonded with TiO_2 particles.

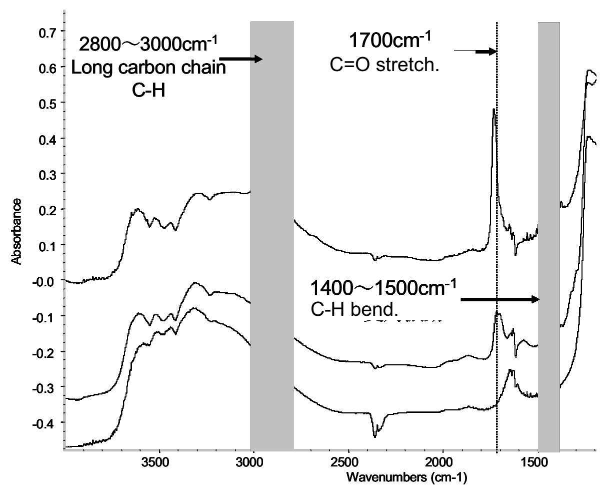

Figure 4: FT-IR analysis of surface treated TiO_2 (upper: RGP treated, middle: SC treated, and lower: without treatment).

Table 1 shows the amount of carbons bonded with TiO_2 particles measured by a CHN analyzer. The amount of reacted silane coupling agent and LMA per unit surface area on titanium oxide particle was calculated by the reacted carbon content. Based on this calculated result, about 3.9 LMA molecules were reacted with one coupling agent molecule on titanium oxide surface.

	Reacted carbon content (wt%)	Reacted monomer per unit surface area (μ mol/m^2)
SC treat	0.45	4.41
RGP treat	4.45	17.16

Table 1: Amount of reacted coupling agent.

3.2 Sedimentation Behavior

Sedimentation behavior of TiO_2 particles with different surface treatment in isoparaffin was shown in Figure 5. The rapid sedimentation of TiO_2 particles without surface modification was observed. This sedimentation behavior was promoted by silane coupling, SC, treatment without graft polymerization. It seems that the particle aggregation was promoted by silane coupling treatment. On the contrary, high dispersion stability without sedimentation was obtained by random graft polymerization, RGP. After several hours, no sedimentation occurred and kept high dispersion in isoparaffin. In order to analyze the change of sedimentation behavior by surface modification, the surface interaction between titanium oxide with different surface modification is evaluated by colloid probe AFM method.

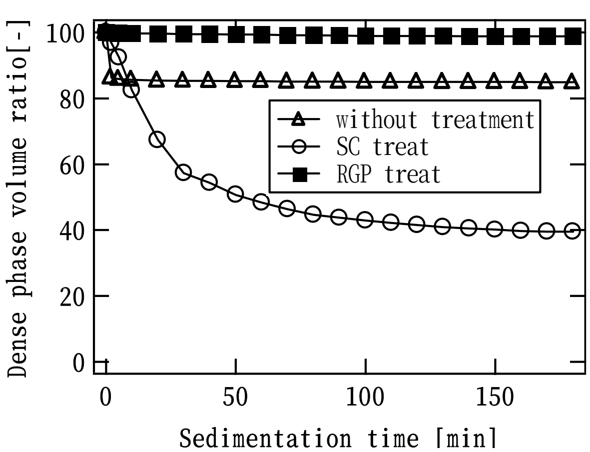

Figure 5: Sedimentation behavior of titanium oxide particle with different surface treatment in isoparaffin.

3.3 Particle Interaction between Titanium Oxide with Different Surface Modification

In order to analyze the change of dispersion stability in isoparaffin, surface interaction between TiO_2 particles with different surface modification was measured by a colloid probe atomic force microscope and results are shown in Figures 6 and 7. Figure 6 is the force curve of surface approaching process between colloid probe and substrate. Without surface modification, van der Waals-type attractive force appeared from a distance of about 5 nm. By the surface treatment of silane coupling and graft polymerization, the repulsive force appeared and increased by the multistage surface treatment. Since the amount of surface organic compound was grown by a graft polymerization of LMA, the large steric repulsive force was observed at the short surface distance less than 5 nm. Sedimentation was promoted by silane coupling (SC) treatment, however, the surface repulsive force was observed by a colloid probe AFM method. Since only attractive force was observed between the surfaces of original titanium oxide, it is estimated that the particle aggregation of non-treated particle is higher than that of SC treated particles based on the force curve during approaching process in Figure 6.

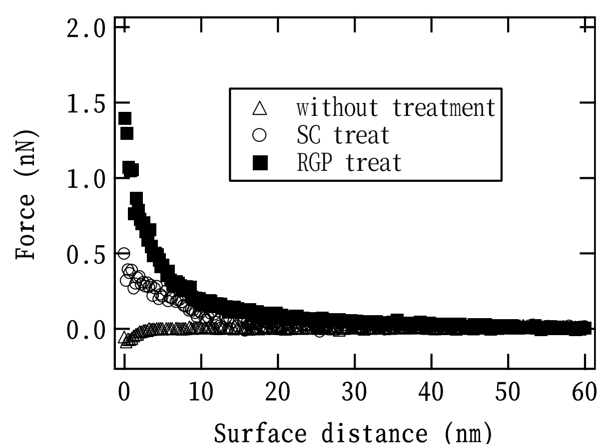

Figure 6: Force curve between titanium oxide colloid probe and substrate with different surface treatment in isoparaffin, trace process.

Figure 7 is the force curve during separation process of both surfaces. Since van der Waals force acted between particle surfaces, the adhesion force between untreated particles was observed. After only silane coupling (SC) treatment, the adhesion force increased in comparison with the untreated particles and long distance nonlinear attractive force was observed up to 30 nm in surface distance after the peak of attractive force appeared. This long distance attractive force seemed to arise by the entanglement of the hydrocarbon chains which was produced by the chain-like condensation of coupling agents on particle surface. Since this attractive force promoted aggregation of primary particles in suspension, the sedimentation of particles with silane coupling treatment was accelerated in comparison with that of untreated particles.

By random graft polymerization, adhesion force decreased and long distance attractive force was disappeared. It seems that the molecular structure of surface modified layer on particle was changed from chain like free structure to relatively rigid and packing structure by graft polymerization. The dispersion of primary particles was promoted by the strong steric repulsive force, the reduction of adhesion, and long distance attractive force between particles.

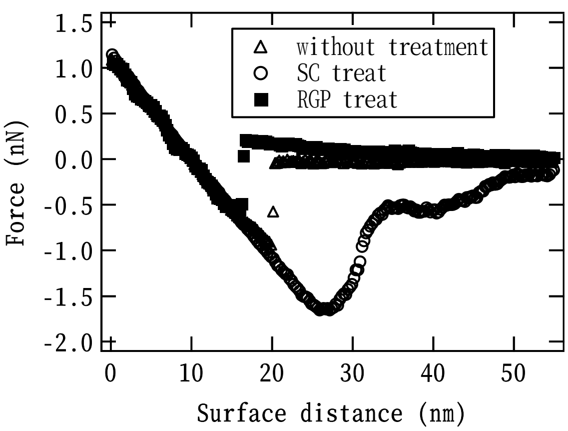

Figure 7: Force curve between titanium oxide colloid probe and substrate with different surface treatment in isoparaffin, retrace process.

4 CONCLUSION

For the development of rewritable electrical paper, TiO_2 particles were surface modified by silane coupling agent (SC treatment) and random graft polymerization (RGP treatment), and dispersied in isoparaffin solvent, and particle interaction was examined. The dispersion of primary particles was promoted by RGP treatment and sedimentation was well inhibited. Interaction between each TiO_2 particle was characterized by colloid probe AFM and higher repulsive force and lower adhesive force were observed for particles RGP treated. This coincides with the macroscopic sedimentation behavior of particle suspension.

ACKNOWLEDEMENT

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