Photoeffects on Electrorheological Properties of TiO_2 Particle Suspensions

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The electrorheological (ER) effect of TiO_2/silicone oil fluids was investigated under illumination. Two types of commercial TiO_2 powders showed opposite photoeffects on the ER properties. While the photoinduced increase in the ER effect for the first type arises from the polarization of photogenerated charges, the decrease in the effect of the latter type appears to be due to photoelectrophoresis, which may be facilitated by effects associated with the large surface area and high water content.

Electrorheological (ER) fluids have gained much attention during the past decade, due to their promising applications in mechanical systems such as brakes, clutches and shock absorbers. ER fluids typically consist of electrically polarizable particles dispersed in low-dielectric oils. Application of an electric field induces polarization of the suspended particles, which, upon interaction, form chain-like structures between the electrodes, thus resulting in an increase in the apparent viscosity. The increase in fluid viscosity due to the application of the electric field is known as the electrorheological effect. Semiconductor materials are suitable for use in ER fluids because they develop large dipoles due to the polarization of electrons and holes in delocalized conduction bands.[1]

When semiconductor materials are used in ER fluids, their ER properties can change under illumination with photons of energy equal to or greater than the band gap energy. Only a limited number of reports are available[2,3] on such photoeffects. However, those reports do not involve detailed mechanistic studies of the photoeffects. We report here the photoresponse of TiO_2-based ER fluids. TiO_2 was felt to be the most suitable candidate for the present photoelectrorheological (PER) study as it is widely used in photoelectrochemistry and photocatalysis. Our results indicate that the photoeffects are dependent on the surface properties of the particles.

Two types of anatase TiO_2 were used: Degussa P-25 (Japan Aerosil Co., 29 nm dia., 50 m^2 g^{-1}), and ST-01 (Ishihara Sangyo Kaisha, Ltd., 20 nm dia., 320 m^2 g^{-1}). The powders were dried *in vacuo* at 150 °C. The dried ST-01 and P-25 powders contained 3.3 wt% and <0.5 wt% water, respectively.[4] ER fluids were prepared by dispersing TiO_2 particles (0.2 wt%) in silicone oil (20 cP viscosity, Toshiba Silicone Co., Ltd., Japan). The particles were dispersed by sonication for 60 min.

A schematic diagram of the experimental setup is shown in Figure 1. The PER cell (see inset) was constructed using single-sided SnO_2-coated conducting glass to enable simultaneous illumination and application of the electric field. The SnO_2 coating was removed from strips along both ends of the plate, leaving a central 1 cm × 1 cm area. Two such plates (SnO_2-coated sides facing each other) were separated using one thickness of insulating double-sided adhesive tape (0.25 mm thickness). A graduated glass tube was connected to the PER cell. In order to measure the changes in the viscosity due to application of the field, fluid was drawn up through the cell and into this tube and was then allowed to fall freely back through the cell under the influence of gravity. The level of the liquid was measured as a function of time, to determine the volume of fluid passing through the PER cell.

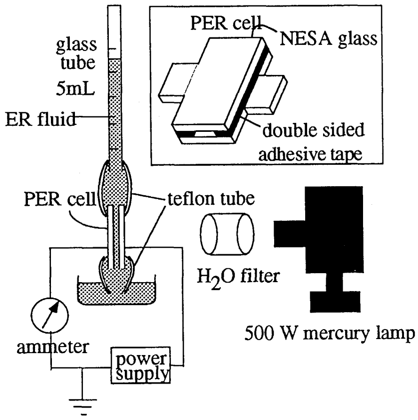

Figure 1. Schematic diagram of the viscometer. A blow-up of the cell is shown in the inset.

Changes in the viscosity of the fluid under various electric field and illumination conditions as a function of time are shown in Figure 2. The lines in the figure are curved due to the gradually decreasing hydrostatic pressure of the falling liquid. In comparison to field-free flow behavior (field-off-dark), the fluids stopped flowing much earlier under the application of the electric field (field-on-dark). This indicates an increase in the viscosity (ER effect) of the fluid due to applied field. However, under illumination, the two fluids showed different behavior. Illumination enhanced the ER effect of P-25-containing fluid (Figure 2a), while it reduced the ER effect of ST-01-containing fluid (Figure 2b). Thus the two types of fluids showed opposite photoeffects on the electrorheology.

The field-induced increase in the viscosity in the dark arises from interaction of polarized TiO_2 ($\varepsilon = 48$) particles in the fluid due to their dielectric mismatch with the silicone oil ($\varepsilon = 2$). The induced dipoles (dipole moment $d = \beta r_d^3 E$, where β is effective polarizability, r_d is particle radius and E is applied field), upon interaction form chain-like structures between the electrodes, causing an increase in the viscosity. Upon illumination, the polarization of photoinduced electrons and holes is expected to increase the dipolar field around the particle, leading to stronger, more numerous chains. Thus, the viscosity increases further, as observed in the case of P-25 fluid. However, surprisingly, the behavior of the ST-01 fluid under illumination was opposite.

Figure 3 shows the current recorded as a function of time under field-on-dark and field-on-light conditions during fluid flow. The current response corresponds to the flow-time plots in Figure 2. For both fluids, the observed dark currents were low,

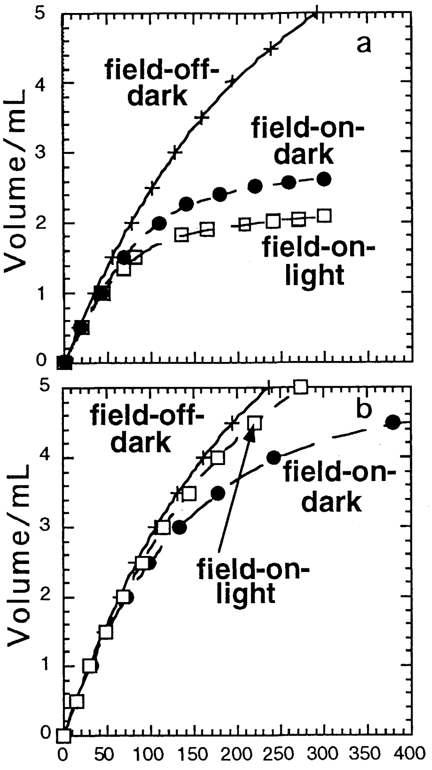

Figure 2. Behavior of the flowing TiO_2 suspensions containing (a) P-25 and (b) ST-01 as a function of time, under an applied field of 1.6 kV/mm.

indicating a small dielectric loss. Such losses are common even in electrorheological systems consisting of insulating particles. Upon illumination, photocurrents were observed in both fluids. The photocurrent observed for the P-25 fluid was very low in comparison to the values observed for the ST-01 fluid.

Low photocurrents for P-25 fluid are reasonable. The observed increase in the ER effect, together with a low photocurrent, indicates that the majority of the photoinduced electrons and holes is polarized under the influence of the strong electric field, and a small loss of carriers occurs through the chain-like structures, as in the dark. Additionally, the photocurrent can arise from the exchange of photogenerated charge with the electrodes, resulting in an accumulation of net charge on the particle, as observed by Aikawa et al.[5] The oscillation of such charged particles causes electrophoretic currents, which were higher in the case of ST-01, indicating the possibility of greater particle mobility (see below).

We also carried out microscopic observations of the particle suspensions using a modified experimental set-up in which the fluid was stationary. The observations were made under various field and illumination conditions using a CCD camera. The formation of chain-like structures between the electrodes was seen under field-on-dark conditions. In addition, some particle aggregates move between the electrodes. Such movement indicates the presence of charge on the particles, as discussed by Nagaya et al.[6] Upon illumination, we could see increased numbers of chain-like structures between the electrodes in the P-25 suspension. The oscillation of the aggregates also increased significantly. In the case of the ST-01 suspension, the chain-like structures in the dark were thick, but, upon illumination, they collapsed and formed thin chain-like structures. Furthermore, the increase in the frequency of oscillations of the clusters was greater than that observed for the P-25 suspension. This high frequency motion during illumination appears to be the cause of the decrease in the ER effect and of the high photocurrent.

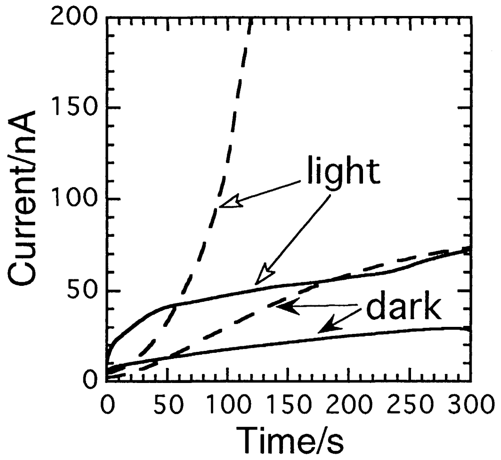

Figure 3. Current responses for P-25 (solid line) and ST-01 (dashed lines) suspensions under dark and illumination.

Although we are able to explain the increase in the ER effect for the P-25 fluid under illumination, the reasons for the decrease in the ER effect for the ST-01 fluid have not been elucidated yet. However, we feel that the higher surface area and the presence of residual water may be involved in this effect for ST-01. Both of these factors may be important in facilitating charge injection, so that the particles can be rapidly charged at the electrode surface, thus leading to high frequency electrophoretic oscillation. Such electrophoretic oscillations may dominate the interactions that give rise to the ER effect, thus decreasing it. Further studies are under way to elucidate the mechanisms.

References and Notes

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