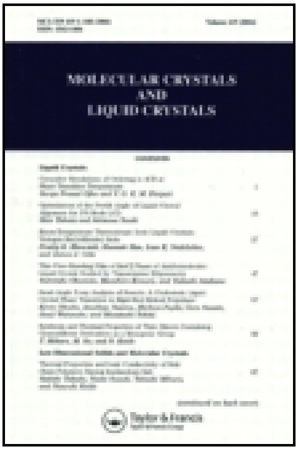

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Effects of Particle Modification on Properties of Particle/Liquid-Crystal Composites

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EFFECTS OF PARTICLE MODIFICATION ON PROPERTIES OF PARTICLE/LIQUID-CRYSTAL COMPOSITES

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We investigated effects of particle modification on physical properties of particle/liquid-crystal composites by polarizing optical microscopy and rheology. The surface modification of particles (ZrO_2) was performed with an azobenzene carboxylic acid (8AB5COOH) in acetone. Surface coverage was evaluated as 56%. Under a polarizing microscope, the composites containing the surface-modified particle (8AB5COOH-ZrO_2/8CB) exhibited characteristic textures in both smectic A (SmA) and nematic (N) phases. These textures could be observed repeatedly by changing the phase structures (SmA ↔ N) indicating the presence of strong coupling between the particle surface and 8CB molecules. In the rheological measurements, we observed cooperative changes of steady shear viscosity associated with isotropic → N phase transition in 8AB5COOH-ZrO_2/8CB composites. With increasing the particle concentration, although the inherent discontinuous change of the viscosity around 42°C became small, a new characteristic change in the viscosity appeared around 46°C and became dominant. Effects of the shear rates on these changes suggest that structured regions may be formed with the modified particles. The viscosity change around 46°C would be attributable to the phase transition behavior of 8CB coupled with the particle surface in the structured regions. In addition, the morphology of the system can be reversibly modulated with the aid of the isomerization of the azobenzene moieties.

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Keywords: azobenzene; heterogeneous liquid-crystal systems; phase transition behavior; surface modification; suspensions

INTRODUCTION

Over recent decades, extensive research attention has been paid to particle/liquid-crystal (LC) composites [1–5]. Dispersions of small silica particles in nematic LCs (NLCs) called *filled nematics* have been studied as a new class of light-scattering materials for electro-optical switches [1–3]. In the dispersions, the particles form internal interfaces with a large specific surface making it possible to stabilize different director configurations. Small domains with the different configurations and the birefringence of host LCs develop the strong light scattering. By applying an electric field, the scattering state can be switched to transparent one due to reorientation of LC molecules. For strong anchoring, the particles create topological defects and exhibit a novel colloidal interaction in homogeneous director field, arising from orientational elastic energy of host LCs. Consequently, intriguing colloidal structures and properties are found in the systems. Chain-like structures were reported for water droplets suspended in NLCs [4]. Recently, an open cellular structure formed with small polymer particles in NLCs exhibited a remarkably high elastic modulus [5]. In all cases, surface properties of the particles will be a crucial factor to determine the scattering effects and colloidal properties of the systems. Therefore, surface modification of particles is essential to control the properties. In general, coupling reactions of silane couplers on silica or of thiols on gold are applied to modulation of the surface properties. However, these methods often restrict the variety of chemical structures of compounds due to strict conditions of the coupling reactions. Recently, long-chain alkanoic acids were found to form monolayers on zirconium oxide (ZrO_2) powder *via* a chelating bidentate zirconium carboxylate surface bond [6]. The layers were formed under mild conditions and exhibited high stability against to heat and chemicals. Furthermore, materials having a carboxyl group are readily synthesized compared to the synthesis of corresponding silane couplers or thiol derivatives. Therefore, this allows us to introduce a rich variety of functionality into the materials in the surface modification. Here we investigated effects of surface modification of ZrO_2 particles with a mesogenic azobenzene carboxylic acid on phase transition behavior of particle/LC composites by rheology and microscopy. In addition, we performed morphology changes of the composites by the use of photoisomerization of the azobenzene moiety.

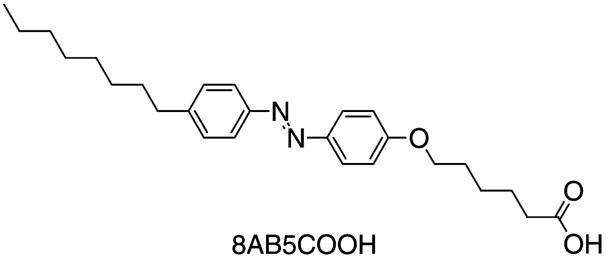

FIGURE 1 Azobenzene carboxylic acid used in this study.

EXPERIMENTAL

We employed ZrO_2 (monoclinic, Nippon Denko Co., LTD) and 8CB as a particle and a host LC, respectively. The reported particle sizes is 1.1 μm and the surface area is $32\,m^2/g$. Surface modification was performed, according to a literature [6], with an azobenzene carboxylic acid (8AB5COOH) shown in Figure 1. The modification was confirmed by IR spectroscopy. The surface coverage was calculated from a carbon content of the modified particle (8AB5COOH-ZrO_2), the surface area of ZrO_2, and a $0.47\,nm^2$/molecule of the azobenzene derivative [7]. Rheological properties of the particle/LC composites were examined with a rheometer (SR-5000-PE, Rheometric Scientific) on cooling from homogeneously mixed state. Microscopic observation was conducted with a polarizing optical microscope after the rheological measurements. Photochemical morphology changes of the composites were carried out on irradiation of 365- or 435-nm light during the rheological measurement.

RESULTS AND DISCUSSION

After thorough washing, the particles showed light yellow color indicating the presence of azobenzene moieties on the surface. The adsorption of 8AB5COOH on ZrO_2 surface was confirmed by IR spectroscopy according to the literature [6]. Surface coverage was estimated as 56% in an average value. It would be speculated relatively loose packing of the azobenzene moieties on the surface.

Figure 2 shows rheological property of 8CB containing 8AB5COOH-ZrO_2 (8AB5COOH-ZrO_2/8CB). The composites were sandwiched between aluminum plates treated with no alignment layers, and then sheared at a rate of $100\,s^{-1}$. To investigate the coupling of 8CB molecules with the particle surface, we performed the rheological measurements on cooling from the homogeneously mixed state. The mixed state was prepared by

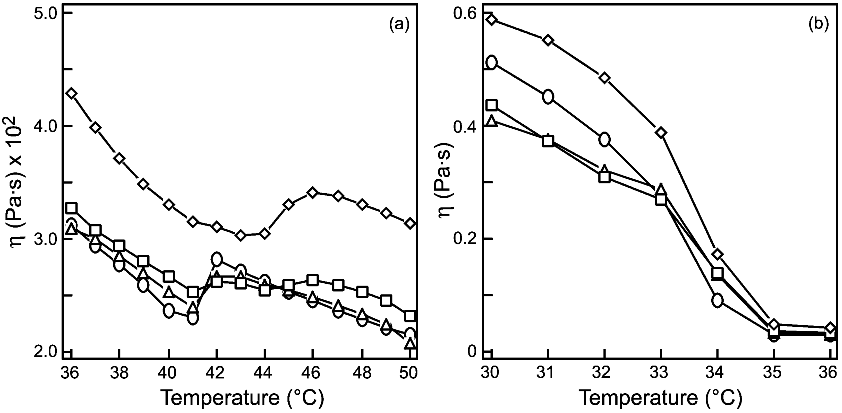

FIGURE 2 Steady shear viscosity of 8AB5COOH-ZrO_2/8CB composites: (a) I-to-N; (b) N-to-Sm A phase transitions; circle, [8AB5COOH-ZrO_2] = 0 wt%; triangle, 1 wt%; square, 3 wt%; rhombus, 5 wt%. Rheological measurements were performed on cooling from homogeneously mixed state (shear rate: $100\,s^{-1}$).

pre-shear treatment at the rate of $\sim$1,800 s^{-1} for 10 min at 50°C. The pure 8CB (circle, [8AB5COOH-ZrO_2] = 0 wt%) exhibited inherent discontinuous changes of steady shear viscosity around 42 and 35°C assigned to I-to-N (Fig. 2(a)) and N-to-SmA (Fig. 2(b)) phase transitions, respectively. In the I-to-N phase transition, with increasing the particle concentration, the discontinuous change around 42°C became small and a new characteristic change appeared around 46°C cooperatively. At 5 wt% of the modified particle, the composite has relatively larger viscosity than the other composites and the discontinuous viscosity change around 46°C was dominant. In addition, it is found that the change around 46°C is broadened compared to that around 42°C. It is suggested that structured regions, in which 8CB is expected to show different properties from bulk, would be created with the modified particles. On the other hand, no significant effects of the addition of the modified particle can be confirmed in the N-to-SmA phase transition. These results indicate that the modified particles participate in the "*disorder-to-order*" orientational change rather than the "*order-to-order*" change. In composites containing non-modified ZrO_2 particle (ZrO_2/8CB), the phase transition temperatures were hardly influenced by the addition of the particle (data not shown).

Effects of the surface modification were also confirmed with texture observation of composites under a polarizing optical microscope. Figure 3 shows optical textures of ZrO_2/8CB (upper) and 8AB5COOH-ZrO_2/8CB (lower) after the rheological measurements. In order to observe the inter-

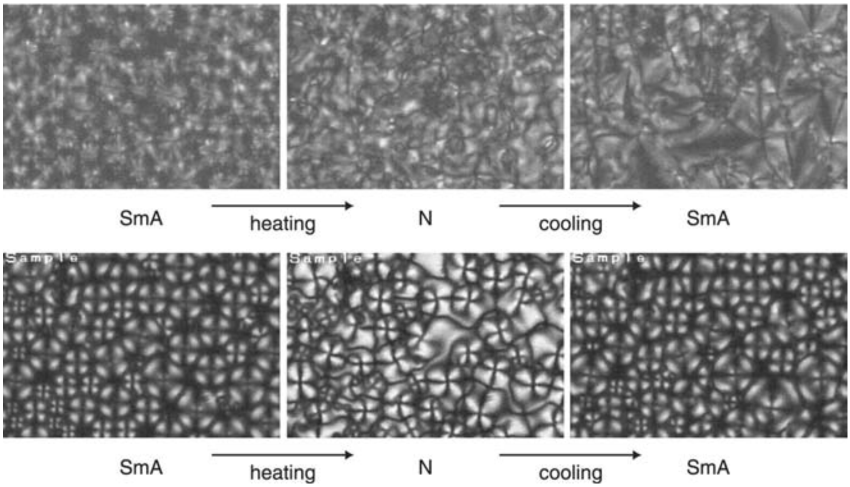

FIGURE 3 Optical textures of ZrO_2/8CB (upper) and 8AB5COOH-ZrO_2/8CB (lower) composites after shear treatments: $[ZrO_2] = [8AB5COOH\text{-}ZrO_2] = 1\,wt\%$. Heating and cooling processes were performed at 1°C/min. Samples were sandwiched between glass substrates without alignment layers.

action between the particles and 8CB molecules, we used the composites with a small particle concentration ($[ZrO_2] = [8AB5COOH\text{-}ZrO_2] = 1\,wt\%$). Both the composites exhibited orientational domains in circular shape centered with the particles in initial state (left pictures, SmA phase). Especially, the clear domains could be observed in 8AB5COOH-ZrO_2/8CB. 8CB. Then, by heating the composites to N phase slowly, these textures melted each other. Although ZrO_2/8CB could not recover the circular domains on cooling from N to SmA phase, 8AB5COOH-ZrO_2/8CB could acquire the clear domains repeatedly (right pictures). This obviously indicates the presence of strong coupling between the particle surface and 8CB molecules in 8AB5COOH-ZrO_2/8CB.

From these findings, we suggest here that the characteristic change of the steady shear viscosity around 46°C (Fig. 2(a)) will be attributable to phase transition behavior of 8CB coupled with the modified surface in structured region. Next, we measured the rheological profiles of 8AB5COOH-ZrO_2/8CB ($[8AB5COOH\text{-}ZrO_2] = 5\,wt\%$) at different shear rates (Fig. 4). The shear rate of $100\,s^{-1}$ is a standard condition in this study. The discontinuous change of the viscosity around 46°C was not shifted at the rate of $10\,s^{-1}$. The absolute values of the viscosity generally depend on the shear rates. At the rate of $1{,}000\,s^{-1}$, the change around 46°C disappeared and the change around 42°C emerged. At the larger rate, structured regions with the modified particles will be destroyed. However,

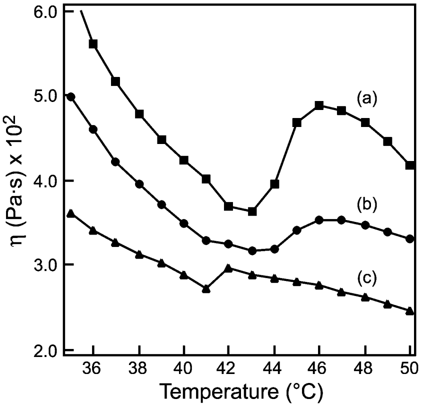

FIGURE 4 Effects of the shear rate on the viscosity profiles of 8AB5COOH-ZrO_2/8CB composite ([8AB5COOH-ZrO_2] = 5 wt%): (a) shear rate = $10\,s^{-1}$; (b) $100\,s^{-1}$; (c) $1{,}000\,s^{-1}$. Measurements were performed on cooling from homogeneously mixed state.

we could not observe a yield stress in this study. Therefore, there are no ordered structures of the modified particles.

By means of *trans-cis* photoisomerization of azobenzene derivatives, photochemical modulation of LC properties has been extensively studied with the intention of developing tunable photonic materials [8–11]. In this study, we also employed the azobenzene derivative for the surface modification. The morphology of 8AB5COOH-ZrO_2/8CB will be modulated with the photoisomerization. Figure 5 shows the viscosity profiles of the composite ([8AB5COOH-ZrO_2] = 5 wt%) at initial state (a) and during photoirradiation of 365-nm light (b). On photoirradiation, the viscosity profile was shifted to lower temperature. Although this profile is similar to that of pure 8CB (see Fig. 2(a), circle), the absolute values of the viscosity was still larger. The *trans-cis* photoisomerization on the substrate surface is known to affect bulk LC alignment [12]. Therefore, it is considered that the shift of the viscosity profile would be ascribed to generation of new coupling state between *cis*-azobenzene residues and 8CB molecules rather than the disappearance of the coupling.

Figure 6 exhibits photochemical morphology change of 8AB5COOH-ZrO_2/8CB ([8AB5COOH-ZrO_2] = 5 wt%). Alternative irradiation of 365- or 435-nm light was conducted at 41°C. On photoirradiation of 365-nm light (*trans*-to-*cis* isomerization), the viscosity increased rapidly. On the other hand, the viscosity went back to the initial state on irradiation of 435-nm light (*cis*-to-*trans* isomerization). Although, the *cis*-to-*trans* isomerization can also be induced thermally, the decrease of the viscosity

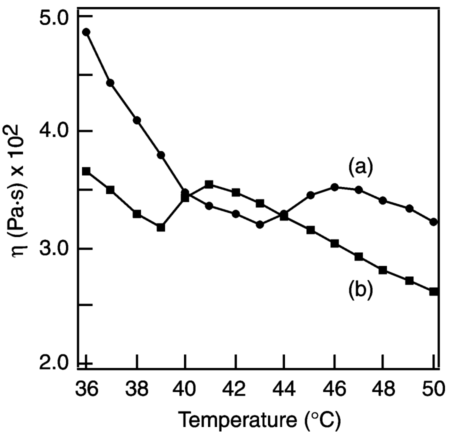

FIGURE 5 Effects of photoirradiation on the viscosity profile of 8AB5COOH-ZrO_2/8CB composite ([8AB5COOH-ZrO_2] = 5 wt%): (a) initial state; (b) during irradiation ($\lambda = 365$ nm). Shear rate was $100\,s^{-1}$.

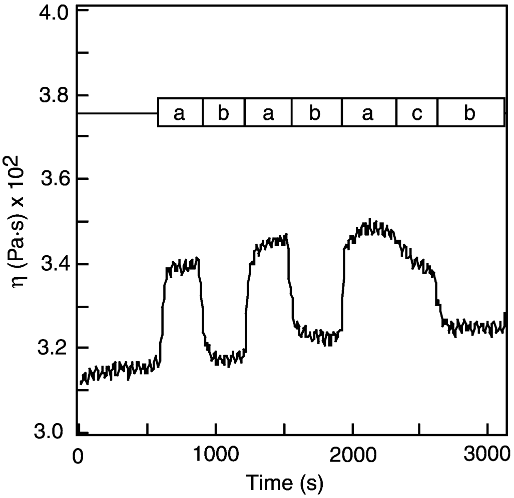

FIGURE 6 Photochemical morphology change in 8AB5COOH-ZrO_2/8CB composite ([8AB5COOH-ZrO_2] = 5 wt%) at 41℃: a, irradiation of 365-nm light; b, 435-nm light; c, no irradiation. Light intensities were 80 and 20 mW/cm^2 for 365-nm and 435-nm light, respectively.

with irradiation of the 435-nm light was faster than thermal manner. This clearly indicates that observed behavior is based on the photochemical process.

CONCLUSION

We investigated the effects of surface modification of ZrO_2 on phase transition behavior of particle/LC composites. The surface coverage of the particle with the mesogenic azobenzene derivative was evaluated as 56%. With increasing a concentration of the modified particle, 8AB5COOH-ZrO_2/8CB exhibited cooperative changes of the steady shear viscosity in the I-to-N phase transition. This would indicate strong coupling between 8CB molecules and the modified surface in structured regions. We also performed photochemical change of morphology of the composites by the use of *trans-cis* photoisomerization of the azobenzene residues bound on the surface. The viscosity could be modulated reversibly by alternative irradiation of UV and visible light.

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