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Anionic Surfactant with Hydrophobic and Hydrophilic Chains for Nanoparticle Dispersion and Shape Memory Polymer Nanocomposites

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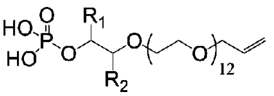
Nanoparticles have already became indispensable materials for industries, because of their unique size-dependent properties such as electrical, magnetic, mechanical, optical, and chemical properties, which largely differ from those of their bulk materials.[1−5] Polymer nanocomposites are one of the most attractive materials because they combine the advantages of polymeric materials, such as flexibility, and the functional properties of nanoparticles. Thus far, numerous nanoparticles such as oxides, semiconductors, carbon-related particles, and clays have been dispersed in polymeric materials to design composites with novel optical, mechanical, thermal, and electromagnetic properties.[6−12] To obtain homogeneous polymer nanocomposites with good properties, it is important to improve the dispersion stability of nanoparticles in polymers.

Various processes have been developed for maintaining the stability of nanoparticles in polymers.[6−8] One example is an in situ method by which functional nanoparticles are synthesized in the polymer matrix. Typically, in the case of oxide nanoparticles, a silane-terminated polymer is spin-coated with metal alkoxides and nanoparticles can be generated by the subsequent mild heat treatment of the polymer. While transparent nanocomposites with well-dispersed nanoparticles can be obtained by this method when the solid content is low, it is very difficult to obtain dense nanocomposites by this method. Furthermore, the species of nanoparticles are restricted to several oxides and metals. Another example is the direct dispersion of nanoparticles in polymers after surface modifications.[9−12] Many researchers have synthesized well-dispersed functional nanoparticles and then modified their surface with an adequate modifier. This modifier was designed for each polymer species to maintain the stability of nanoparticles during the entire fabrication process of nanocomposites. Though several nanocomposites with high solid contents have been reported, there are still some difficulties in the prevention of nanoparticle aggregations. The first difficulty is that the capping agents should be designed for each polymer species. The second difficulty is that the solvent that can be used during material processing is restricted because the nanoparticles capped with the designed modifier can be dispersed only in selected solvents. In this communication, we designed a novel anionic surfactant for ensuring the complete dispersion of nanoparticles in various organic solvents and polymers with high solid contents. Furthermore, we found that nanocomposites with nanoparticles modified by the developed surfactant possessed unique temperature-induced shape memory properties.

Figure 1 shows the structure of the novel anionic surfactant. This surfactant was designed to have an anionic headgroup and organic chains that branched into a hydrophobic alkyl chain and a hydrophilic poly(ethylene glycol) (PEG) chain. Furthermore, it was designed to have a polymerizable vinyl group at the end of the hydrophilic PEG chain. The purpose of including the hydrophobic chain, hydrophilic chain, and the polymerizable groups was to increase the affinity of nanoparticles modified with this surfactant for low polar solvents, polar solvents, and polymerizable polymers, respectively. From NMR analysis (see Supporting Information), it was found that the purity of the surfactant containing organic chains shown in Figure 1 was 63%. Further, the ratios of phosphoric acid, monomers, and dimers were characterized to be 13%, 74%, and 13%, respectively.



$R_1 = C_nH_{2n+1}$ (n=10,12), R_2=H
and
R_1=H, $R_2 = C_nH_{2n+1}$ (n=10,12)

Figure 1. Anionic surfactant (**1**) designed to have a hydrophobic alkyl chain, hydrophilic PEG chain, and polymerizable group.

The surface structure of TiO_2 nanoparticles modified by surfactant (**1**) was characterized by FT-IR spectroscopy (see Supporting Information). From the spectrum of TiO_2 nanoparticles before modifications, absorbance related to the O−H bending mode was observed at 1645 cm^{-1}.[13] In the case of the spectrum of surfactant (**1**), absorbances at 3006, 2962, 2933, 2852, 1350, 1280, 1108, and 969 cm^{-1} were observed, which were attributed to vinyl groups, $\nu_{as}CH_3$, $\nu_{as}CH_2$, ν_sCH_2, CH_2 wag, CH_2 twist, C−O−C stretch, and CH_2 rock, respectively.[14,15] It is clear that surfactant (**1**) was adsorbed onto TiO_2 nanoparticles since absorbances related to both TiO_2 nanoparticles and surfactant (**1**) were detected from surface-modified TiO_2 nanoparticles. From the TG-DTA analysis of surface-modified TiO_2 nanoparticles (see Supporting Information), the adsorbed content of surfactant (**1**) was calculated to be 1.3 mmol/g of TiO_2.

The stabilities of surface-modified TiO_2 nanoparticles in various organic solvents with various polarities are shown in Figure 2. The surface-modified TiO_2 nanoparticles were dispersed in various organic solvents to 3.0 wt %. The corresponding average aggregate size, measured by the dynamic light scattering method as a z-average diameter, is also shown in the figure. It can be observed that the particles modified by **1** can be dispersed in a wide range of organic solvents such as alcohols, nitriles, ketones, and acetates. Furthermore, their average aggregated size was several tens of nanometers, which was sufficiently small to obtain a transparent suspension. The obtained suspension was stable over several months.

The TiO_2 nanoparticles modified by **1** were dispersible not only in various solvents but also in polymers. Figure 3 shows photographs of TiO_2 nanoparticles dispersed in epoxy resin and poly(methylmethacrylate) (PMMA) resin. It can be observed that the surface-modified TiO_2 nanoparticles were dispersible in epoxy resin

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without strong aggregation and turbidities even when the content of modified TiO_2 nanoparticles was increased up to 18.4 wt % (5.2 vol%). Furthermore, the TiO_2 nanoparticles were dispersible in completely different kinds of polymers such as radical polymerized PMMA without strong aggregations. TEM analysis (see Supporting Information) shows that the aggregate size of these TiO_2 nanoparticles in polymers was below 30 nm.

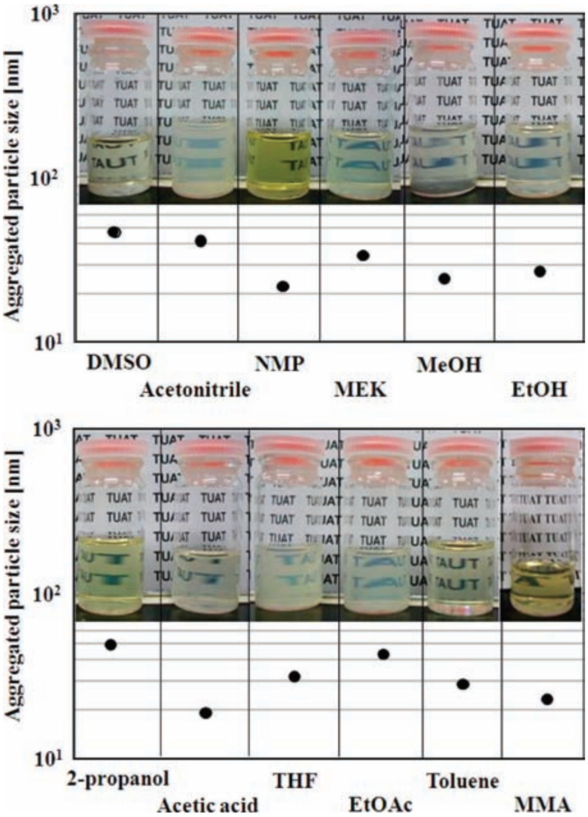

Figure 2. Suspension of TiO_2 nanoparticles modified by surfactant (**1**) dispersed in various organic solvents and corresponding z-average diameter measured by dynamic light scattering method.

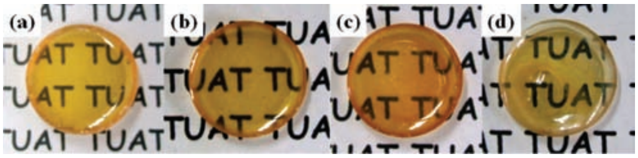

Figure 3. TiO_2 nanoparticles dispersed in epoxy and PMMA resins. (a) 2.4 wt % (0.6 vol %) in epoxy, (b) 13 wt % (3.8 vol %) in epoxy, (c) 18 wt % (5.2 vol %) in epoxy, and (d) 6.4 wt % (1.8 vol %) in PMMA. The diameter and thickness of the pellet were 25 and 2 mm, respectively.

It was also found that the TiO_2/epoxy composites possess unique shape memory properties. Figure 4a shows the initial structure of TiO_2/epoxy composites whose shape was fixed during the hardening procedure. At room temperature, the composite was in the hard state. However, as the temperature was increased up to 60 °C, the composite became flexible, and as a result, its shape could be changed into any structure due to the partial melting of the PEG moiety. The changed structure can then be fixed by reducing the temperature to room temperature again, because of the solidification of the PEG chain. In this state, the epoxy networks are under bending stress; however, if the temperature is again increased up to 60 °C, the structure of the composites gradually goes back to the initial structure because of the melting and relaxation of the PEG moiety. We confirmed that this process was reversible at least 50 times.

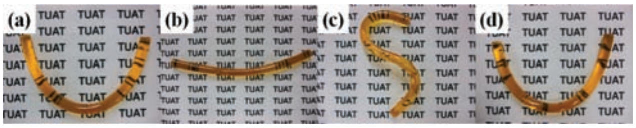

Figure 4. Shape memory properties of 18 wt % (5.2 vol %) surface-modified TiO_2/epoxy composites. (a) Initial structure, (b) (c) examples of changed shapes, and (d) shape recovery after second heating process. The diameter and length of the composite tube were 4.0 and 100 mm, respectively.

In summary, we synthesized an anionic surfactant that comprises a hydrophobic chain and hydrophilic chain. TiO_2 nanoparticles capped with this surfactant could be successfully dispersed in various organic solvents and polymers in relatively high concentrations. Further, we prepared nanoparticle-loaded transparent polymer composites by using the developed surfactant and found that this composite material can possess unique shape memory properties.

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Supporting Information Available: Experimental details, TG-DTA, FT-IR spectra, and TEM of surface-modified TiO_2; and ^{1}H, ^{13}C, and ^{31}P NMR spectra of surfactant **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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