Incorporation of TiO_2 Nanoparticles, Formed via Sol–Gel Process in Micelle of Block Copolymer, into Poly(methyl methacrylate) to Fabricate High Refractive and Transparent Hybrid Materials

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Tiatanium dioxide (TiO_2) nanoparticles, of around 20 nm in diameter, were synthesized within the hydrophilic core of micelles, formed using poly(acrylic acid-*block*-methyl methacrylate) in toluene solution, via sol–gel process using titanium isopropoxide. Hybrid films of poly(methyl methacrylate) (PMMA) containing TiO_2 nanoparticles exhibit high transparency in the visible light region even at 30 wt % TiO_2. The refractive index of the hybrid films at 633 nm linearly increased with TiO_2 to attain 1.579.

The development of organic–inorganic hybrid material has received great attention as a new class of advanced material because of potential application to optical or electrical devices providing processability, flexibility, and transparency.[1,2] To date, optical materials exhibiting high or low refractive index and high transparency have been prepared by incorporation of inorganic particles such as SiO_2, Al_2O_3, TiO_2, and ZrO_2 into a transparent polymer matrix.[3,4] In these hybrid materials, homogeneous dispersion of inorganic particles with a diameter less than one-tenth the wavelength of visible light is necessary for high transparency,[5,6] because large aggregates usually cause stronger light scattering inhibiting transparency. Thus, effective control of the interaction between inorganic particles and polymer matrix to attain highly homogeneous dispersion is essential. On the other hand, amphiphilic block copolymers are known to assemble into spherical reverse micelles with a hydrophilic core and hydrophobic corona in organic solvents. Therefore, formation of TiO_2 nanoparticles in the hydrophilic core via hydrolysis of titanium alkoxide, and successive incorporation of particles into PMMA could give highly transparent TiO_2-dispersed PMMA hybrid films. In this study, formation of poly(acrylic acid-*block*-methyl methacrylate) (PAA-*b*-PMMA) micelle including TiO_2 nanoparticles in toluene and hybridization of TiO_2 and PMMA to fabricate highly refractive and transparent hybrid films were investigated.

Block copolymer, poly(*tert*-butyl acrylate-*block*-methyl methacrylate) was synthesized by living anionic polymerization with sequential addition of methyl methacrylate followed by *tert*-butyl acrylate, using (1,1-diphenylhexyl)lithium as an initiator in the presence of lithium chloride according to a method reported by Teyssie et al.[7,8] Hydrolysis of the poly(*tert*-butyl acrylate) moiety in the block copolymer was carried out by the addition of 12 M aqueous HCl solution in a 1,4-dioxane solution of poly(*tert*-butyl acrylate-*block*-methyl methacrylate). The resulting poly(acrylic acid-*block*-methyl methacylate) (PAA-*b*-PMMA), M_n(PAA) = 6700 g mol^{-1}, M_n(PMMA) = 35000 g mol^{-1}, PDI = 1.10, was dissolved in toluene to make a concentration of 12 mg mL^{-1}. Sol–gel precursor solution was prepared by the addition of 12 M HCl (37%, 0.12 g) into a mixture of 2-propanol (2.5 mL) and titanium tetraisopropoxide (TTIP) (0.37 g) and then stirred over 1 h, until the solution became clear. The sol–gel precursor was added to the polymer micelle solution to make the molar ratio range of Ti^{4+} to carboxyl groups in the block copolymer from 1.0 to 4.0. The polymer micelle solution was mixed with a 2 wt % toluene solution of PMMA (M_n 30000) that was synthesized by usual radical polymerization as to make content of TiO_2 in the range from 0 to 30 wt % in the resulting PMMA hybrid films. After stirring for 1 h, these toluene solutions were poured into a petri dish and then dried at 333 K for 12 h to remove the solvent completely. The thickness of resulting hybrid films was around 20 µm. Transmission electron microscope (TEM) observation was carried out on a Hitachi H-9000NAR, Japan, with acceleration voltage of 100 kV. Particle size and distribution were determined by dynamic light scattering (DLS) and static light scattering (SLS) measurements using a He–Ne laser on a DLS 7000 Otsuka Electronics Co., Ltd., Japan. Atomic force microscope (AFM) image observation was carried out on a Digital Instruments Nanoscope by tapping mode. Refractive index was determined by a prism coupler on a Metricon Corp. model 2010.

Formation of polymer micelles in toluene was confirmed by the appearance of scattering signals corresponding to 80 nm of hydrodynamic radius (R_h) in DLS. Also, radius of gyration (R_g) of polymer micelles determined from Zimm plot analysis by SLS was evaluated to be 60 nm. The ratio of R_g to R_h, 0.75, suggested the polymer micelles to be spherical shape.[9] An AFM image of polymer micelles deposited on Si substrate also showed spherical polymer micelles 20 nm in the diameter (Figure 1), which probably corresponds to the core size of the polymer micelles. The addition of sol–gel precursor to the polymer micelle solution, corresponding to equimolar Ti^{4+} to carboxyl groups, led to slightly increasing the size of R_h to 120 nm in DLS. Furthermore, the addition of much sol–gel precursor at a mole ratio of 2.5 and 4.0 gave significant increase of R_h to 130 and 135 nm, respectively. These results therefore suggested that sol–gel precursor was loaded within hydrophilic cores formed by PAA chains, which resulted in increasing micelle size with the amount of sol–gel precursor. Figures 2a and 2b are TEM images of polymer micelles formed at the mole ratio of 1.0 and 4.0, which were deposited and dried on a carbon-coated copper grid. From TEM images, it was observed that the size of TiO_2 particles is around 20 nm, and then the shape of particles is spherical. Fabrication of PMMA/TiO_2 hybrid films was carried

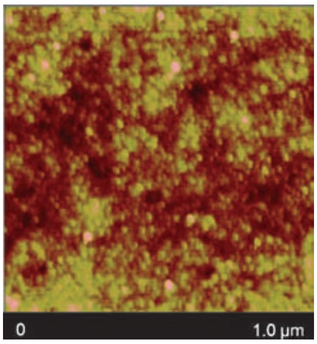

Figure 1. AFM image of polymer micelle deposited on Si substrate.

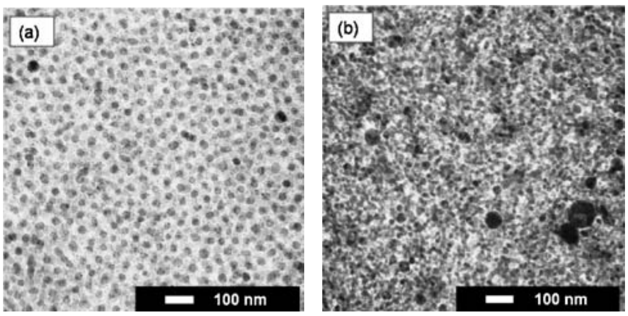

Figure 2. TEM images of polymer micells loaded with sol–gel precursor, mole ratio of Ti^{4+}/carboxyl group, (a) 1.0 and (b) 4.0.

out using a polymer micelle solution of Ti^{4+}/carboxyl group mole ratio of 4.0. Thermogravimetric analysis of PMMA/TiO_2 hybrid films resulted in increasing decomposition temperature compared to PMMA film. As shown in Figure 3, transmittance of hybrid films at 500 nm slightly decreased with increasing TiO_2 content, but the hybrid film even 30 wt % TiO_2 showed high transmission over 87% at 500 nm (Figure 4). The refractive index of hybrid films at 633 nm linearly increased with content of TiO_2 to give 1.579 at 30 wt % and well agreed with the values calculated by the Lorentz–Lorenz equation,[10]

$$(n^2 - 1)/(n^2 + 2) = \sum v_i(n_i^{\,2} - 1)/(n_i^{\,2} + 2) \qquad (1)$$

where n is the refractive index of hybrid film, v_i and n_i are the volume fraction and refractive index of component i, respectively. In this case, refractive indexes of anatase TiO_2 and PMMA, 2.52 and 1.49, were employed, respectively. These results of the transparency and refractive index of PMMA/TiO_2 films suggested that TiO_2 particles were homogeneously dispersed in PMMA matrix without the aggregation of TiO_2 particles during preparation of the hybrid film. In the X-ray diffraction analysis of PMMA/TiO_2 hybrid film, the significant peaks attributed to anatase or rutile phase of TiO_2 were not observed, indicating that TiO_2 particles incorporated into PMMA matrix were amorphous. In a typical process for crystallization of TiO_2 synthesized in aqueous solution via sol–gel method, the thermal treatment involving autoclave heating was performed at 200 °C to get highly crystalline TiO_2.[11,12] The development of a crystallization method for TiO_2 particle in PMMA matrix is now in progress.

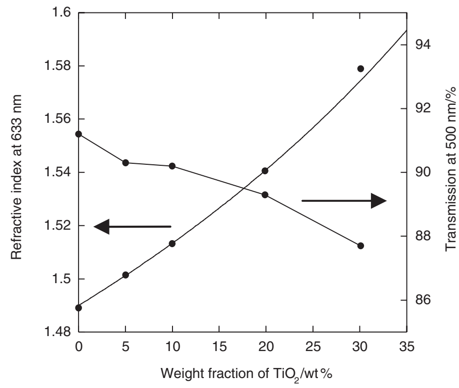

Figure 3. Plots of TiO_2 content vs. refractive index and transmittance of hybrid films prepared using polymer micelle solution: solid line represents calculated values of refractive index.

Figure 4. Photograph of 30 wt % TiO_2-contained hybrid film.

In conclusion, TiO_2 particles, formed in reversed micelles of PAA-*b*-PMMA in toluene solution, were homogeneously incorporated into PMMA matrix to give high transparency. The refractive index of resulting hybrid films proportionally elevated with TiO_2 content to afford 1.579 at 30 wt %, which is 0.1 higher than that of PMMA. The present strategy for preparation of hybrid films could be utilized to enhance refractive index of optical polymer materials ($n \approx 1.7$) containing sulfur, aromatic ring, or halogen except for fluorine.

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