

Research Article

Preparation of Oleyl Phosphate-Modified TiO_2 /Poly(methyl methacrylate) Hybrid Thin Films for Investigation of Their Optical Properties

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TiO_2 nanoparticles (NPs) modified with oleyl phosphate were synthesized through stable Ti–O–P bonds and were utilized to prepare poly(methyl methacrylate)- (PMMA-) based hybrid thin films via the *ex situ* route for investigation of their optical properties. After surface modification of TiO_2 NPs with oleyl phosphate, IR and ^{13}C CP/MAS NMR spectroscopy showed the presence of oleyl groups. The solid-state ^{31}P MAS NMR spectrum of the product revealed that the signal due to oleyl phosphate (OP) shifted upon reaction, indicating formation of covalent Ti–O–P bonds. The modified TiO_2 NPs could be homogeneously dispersed in toluene, and the median size was 16.1 nm, which is likely to be sufficient to suppress Rayleigh scattering effectively. The TEM images of TiO_2 /PMMA hybrid thin films also showed a homogeneous dispersion of TiO_2 NPs, and they exhibited excellent optical transparency even though the TiO_2 content was 20 vol%. The refractive indices of the OP-modified TiO_2 /PMMA hybrid thin films changed higher with increases in TiO_2 volume fraction, and the hybrid thin film with 20 vol% of TiO_2 showed the highest refractive index ($n = 1.86$).

1. Introduction

Transparent materials with high refractive indices have been extensively required for numerous applications, including optical devices, lenses, antireflective coatings, and waveguides [1–3]. In these applications, synthetic polymers have been employed as optical materials exhibiting excellent formability and tunable chemical and physical properties. However, refractive indices of common polymers are limited to the range from 1.3 to 1.7 [4]. Recently, functional polymer-based hybrids incorporating inorganic fillers with high refractive indices have attracted increasing attention for their ability to improve the optical properties of conventional polymers [5]. TiO_2 is an attractive inorganic component for preparation of hybrid materials because of such characteristics as its high refractive index ($n = 2.5$ – 2.7), nonadsorption

of visible light, nontoxicity, and low cost [6]. One important issue in the preparation of transparent TiO_2 /polymer hybrids is the suppression of Rayleigh scattering at the interfaces between inorganic components and polymer matrices. In general, the diameters of inorganic fillers should be smaller than 40 nm, which is one-tenth the minimum wavelength of visible light, to suppress Rayleigh scattering [7]. Thus, TiO_2 nanoparticles (NPs) of desirable size, below 40 nm, as high refractive inorganic fillers, should be employed in the preparation of transparent polymer-based hybrids. In addition, homogeneous dispersion of TiO_2 NPs in a polymer matrix is also required to maintain the transparency after formation of the hybrids. TiO_2 NPs easily aggregate in hydrophobic polymer matrices because their surfaces are covered with hydrophilic hydroxyl groups [8]. Surface modification of TiO_2 NPs with organic groups is consequently an important

technique for improving their affinity with polymer matrices [7] to suppress their aggregation.

Carboxylic acids [9, 10], silane coupling reagents [11, 12], and phosphorus coupling reagents [13, 14] have been generally used for surface modification of various metallic oxides including TiO_2 because of their high reactivity to the surfaces. In the case of inorganic fillers in polymer-based hybrids for optical applications, monolayered stable surface modification is strongly desired to maintain their uniform and stable dispersion in the polymer matrix. For modification with carboxylic acids, the drawback is instability of Ti–O–C bonds with respect to hydrolysis. It is well-known that silane coupling reagents undergo inter- and intramolecular condensation (namely, homocondensation) in the presence of a trace of water to form multilayers comprising silane coupling molecule moieties on their surfaces. Phosphorus coupling reagents react with the TiO_2 surfaces easily to form Ti–O–P bonds, on the other hand, which are stable with respect to hydrolysis, and no homocondensation of phosphorous coupling reagents proceeds under mild conditions [15]. Among phosphorus coupling reagents, phosphoric acid esters are attractive, since they can be easily prepared from commercially available phosphoric acids and alcohols [16]. Another advantage is the flexibility of their structures, leading to facile introduction of desirable functional groups, which play an important role in their compatibility with both polymer matrices and solvents [17–21].

Poly(methyl methacrylate) (PMMA) is a typical optical polymer exhibiting high transparency and excellent formability. Since the refractive index of PMMA is relatively low for optical applications ($n = 1.49$) [22], incorporation of TiO_2 NPs in PMMA matrices has been investigated extensively for preparation of PMMA-based hybrid materials exhibiting high refractive indices [10, 23–34]. Yuwono et al. prepared transparent TiO_2 /PMMA hybrid films via an *in situ* sol-gel route [24]. The refractive index of the hybrid film increased to 1.780 with incorporation of 60 mass% TiO_2 into PMMA. Lee and Chen also investigated the *in situ* sol-gel route for preparation of hybrids using titanium(IV) *n*-butoxide and PMMA-based polymers bearing trimethoxysilyl residues [25]. The refractive indices of the hybrid films increased linearly from 1.508 to 1.867 with TiO_2 contents in the range from 2.9 to 70.7 mass% TiO_2 . In both studies, the *in situ* sol-gel route was used to generate anatase TiO_2 NPs ($n = 2.5$) in the polymer matrices. In the *in situ* method, it is difficult to control the precise amount of TiO_2 content and the dispersion of NPs in PMMA. An *ex situ* route in which inorganic fillers are incorporated into polymer matrices after surface modification, on the other hand, enables easier adjustment of the refractive indices of TiO_2 /PMMA hybrids than the *in situ* route. Thus, the *ex situ* route enables us to achieve excellent dispersion of well-defined rutile TiO_2 NPs ($n = 2.7$) into polymer matrices.

In this study, we report the preparation of PMMA-based hybrid thin films by incorporating TiO_2 NPs modified with oleyl phosphate (OP) via the *ex situ* route. It has been demonstrating that an oleyl group is an attractive group for surface modification of TiO_2 NPs, though stability is not sufficient for modifications with oleic acid and oleylamine

[35] with respect to hydrolysis. The surfaces of the TiO_2 NPs were modified with OP, and a stable dispersion of the resulting modified TiO_2 NPs in organic solvent was achieved [36]. It should be noted that stability of resulting Ti–O–P bonds is important when TiO_2 NPs are used as nanofillers via the *ex situ* route. In this study, an aqueous dispersion of rutile TiO_2 was used as a starting material and was reacted with OP to achieve surface modification. The resultant OP-modified TiO_2 NPs were dispersed in a PMMA matrix to prepare TiO_2 /PMMA hybrid thin films, and their optical properties were investigated as a function of the TiO_2 content.

2. Materials and Methods

2.1. Materials. A 15 mass% aqueous TiO_2 dispersion and OP (monoester and diester mixture) were kindly supplied by Sakai Chemical Co., Ltd. (Osaka, Japan). All reagents were used as received without further purification. Poly(methyl methacrylate) (PMMA) was purchased from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan).

2.2. Analyses. Infrared (IR) spectra were recorded on a JASCO FT-IR-460 Plus spectrometer using the KBr disk technique. X-ray diffraction (XRD) patterns were obtained with a Rigaku RINT-2500 diffractometer (monochromated $\text{CuK}\alpha$ radiation). Solid-state ^{13}C and ^{31}P nuclear magnetic resonance (NMR) spectroscopy was performed using a JEOL CMX-400 spectrometer at 99.55 and 160.25 MHz, respectively. Solid-state ^{13}C NMR spectra were obtained with cross-polarization (CP) and magic angle spinning (MAS) techniques (pulse delay 5 s, contact time 1.5 s, spinning rate 8 kHz). Solid-state ^{31}P NMR spectra were obtained with a MAS technique only (pulse delay 20 s, spinning rate 8 kHz). Thermogravimetric analysis (TG) was performed with a PERKIN ELMER TGA7 thermobalance in the temperature range from 30 to 800°C at a heating rate of 10°C/min under an air flow. A transmission electron microscopy (TEM) image was obtained with a JEOL JEM-1011 microscope operating at 100 kV accelerating voltage. The distribution of particle sizes was measured by dynamic light scattering (DLS) technique using a NIKKISO Nanotracer Wave-EX150 at a wavelength of 780 nm. In obtaining TEM image of TiO_2 /PMMA hybrids, the sample was prepared on a Si wafer and an ultrathin section of the film was cut by a focused ion beam instrument (SEIKO EG&G SMI 2050). Ultraviolet-visible (UV-Vis) spectra were recorded on a JASCO V-630 spectrometer in the transmittance mode. The refractive indices were determined using an Otsuka Electronics FE-3000 refractive film thickness monitor. The resultant refractive indices of hybrid films were reported as a function of volume fraction of TiO_2 ($=[\text{volume of } \text{TiO}_2 \text{ NPs}]/[\text{volume of PMMA}]$) using density of rutile TiO_2 (4.23 g/cm³) [37] and PMMA (1.18 g/cm³) [38].

2.3. Surface Modification of TiO_2 NPs. OP moiety was covalently bound to the surface of TiO_2 NPs using an aqueous dispersion diluted with 15 mL of methanol, based on a previous study [36]. Briefly, 0.49 mL of OP dissolved in 20 mL of methanol was added to the TiO_2 dispersion and stirred

for 18 h at room temperature. The precipitate was separated by centrifugation at 3500 rpm for 10 min and redispersed in 5 mL of toluene. The precipitate was washed twice with 15 mL of ethanol by the dispersion-precipitation process using super-centrifugation at 13500 rpm for 5 min to remove unreacted OP. The precipitate was then dispersed in 10 mL of toluene, following evaporation of the solution in vacuo. Finally, the remaining OP-modified TiO_2 NPs (OP-TiO_2) were redispersed in 20 mL of toluene.

2.4. Preparation of TiO_2 /PMMA Hybrid Thin Films. Prescribed amounts of the OP-TiO_2 /toluene dispersion and toluene were added to a vial containing 200 mg of PMMA. In all the PMMA-based hybrid samples (0–20 vol% TiO_2 content), the total dispersion volume was 10 mL. After stirring for 5 h at 40°C , a dispersion of OP-TiO_2 and PMMA was obtained. Hybrid thin films were prepared by spin-coating of the dispersion on glass substrates at 2000 rpm for 20 s and subsequent heating at 100°C for 1 h.

3. Results and Discussion

3.1. Characterization of TiO_2 NPs. The FTIR spectra of OP-TiO_2 , OP, and bare TiO_2 NPs are shown in Figure 1. In the spectrum of OP-TiO_2 , absorption bands assignable to oleyl groups are present: stretching vibrations of $-\text{HC}=\text{CH}-$ appear at 3001 cm^{-1} , $\nu_{\text{as}}(\text{CH}_3)$ at 2954 cm^{-1} , $\nu_{\text{s}}(\text{CH}_3)$ at 2871 cm^{-1} , $\nu_{\text{as}}(\text{CH}_2)$ at 2921 cm^{-1} , $\nu_{\text{s}}(\text{CH}_2)$ at 2851 cm^{-1} , and $\delta(\text{CH}_2)$ at 1458 cm^{-1} . These bands are also present in the spectrum of OP [39]. Notable differences among these IR spectra are observed in the P–O stretching region. Although a $\nu(\text{P}=\text{O})$ absorption band at 1151 cm^{-1} is clearly observed in the spectrum of OP, the corresponding band disappears in the spectrum of OP-TiO_2 . P–O stretching absorption bands, which are not observed in the spectrum of TiO_2 NPs, are present at 1029 and 1008 cm^{-1} in the spectrum of OP-TiO_2 . These observations suggest that the OP moiety is bound to the TiO_2 surface [13].

The solid-state ^{13}C CP/MAS NMR spectrum of OP-TiO_2 is shown in Figure 2. The carbon signals of free OP in the liquid-state ^{13}C NMR spectrum (Figure 2(a)) are observed at 129.9, 67.9, 32.6, 31.9, 29.3, 27.2, 27.2, 25.4, 22.7, and 14.1 ppm. In the spectrum of OP-TiO_2 , therefore all the signals at 130, 68, 33, 31, 28, 27, 24, and 15 ppm are assignable to the oleyl groups. Thus, the solid-state ^{13}C CP/MAS NMR and FTIR results demonstrate the presence of oleyl groups in the OP-TiO_2 .

The solid-state ^{31}P MAS NMR spectrum of OP-TiO_2 is shown in Figure 3. In the liquid-state ^{31}P NMR spectrum of free OP (Figure 3(a)), the signals of free mono- and diesters are observed at 4.3 and 3.1 ppm, respectively. In the OP-TiO_2 , the signals are observed at 4.5, 2.1, and -1.3 ppm after the modification reaction. Guerrero et al. reported that the NMR signal of organophosphorous compounds shifted upfield after dehydration condensation between Ti-OH and P-OH [13]. In addition, the phosphorous signals shifted downfield with the coordination of the phosphoryl oxygen with Lewis acid sites because of an increase in the electrophilicity of phosphorous atoms. The disappearance of the $\nu(\text{P}=\text{O})$ absorption

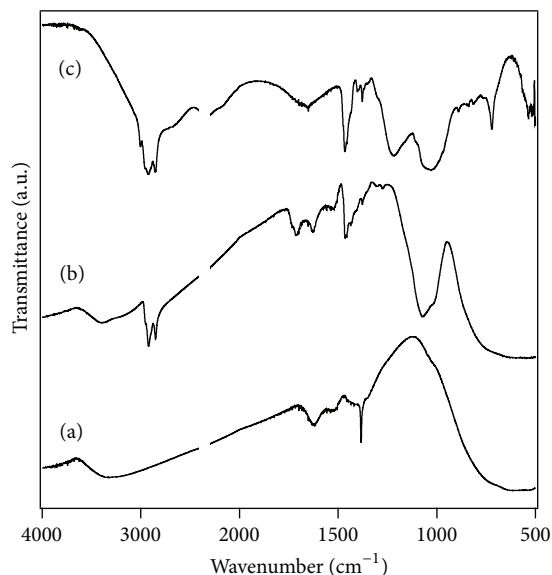


FIGURE 1: FTIR spectra of (a) TiO_2 NPs, (b) OP-TiO_2 , and (c) OP.

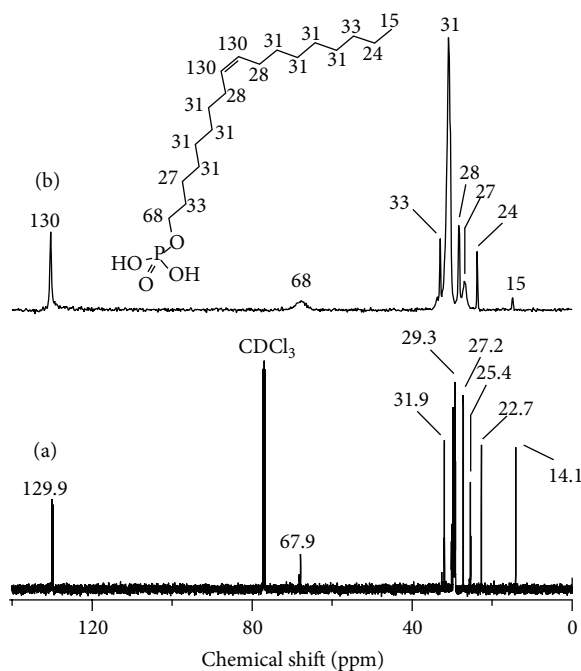


FIGURE 2: (a) ^{13}C NMR spectrum of OP and (b) ^{13}C CP/MAS NMR spectrum of OP-TiO_2 .

band from FTIR suggests that the phosphoryl oxygen in OP may react preferentially with the Lewis acid sites of the TiO_2 surfaces. Thus, the signal at -1.3 ppm is assignable to the tri- and bidentate environments of mono- and dioleil phosphate moieties, respectively. The signal at 2.1 ppm is likely to be due to the bidentate environment of a monooleil phosphate moiety produced by a reaction involving $\text{P}=\text{O}$ and Lewis acid sites. The formation of monodentate binding by a reaction between Lewis acid sites on TiO_2 NPs and

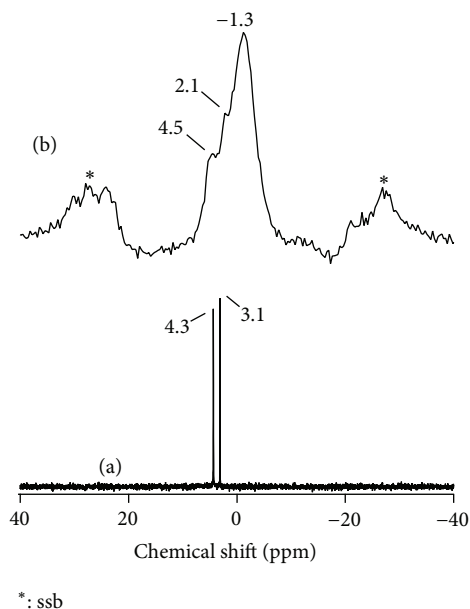


FIGURE 3: (a) ^{31}P NMR spectrum of OP and (b) ^{31}P MAS NMR spectrum of OP-TiO_2 .

phosphoryl oxygens of OP seems to result in the appearance of the signal at 4.5 ppm.

In XRD patterns of TiO_2 NPs and OP-TiO_2 (see Figure S1 in Supplementary Material available online at <http://dx.doi.org/10.1155/2015/297197>), all diffraction lines in the patterns of both samples correspond to rutile TiO_2 (JCPDS card 21-1276), indicating that the crystal structure is retained after the reaction. The crystallite size of the TiO_2 NPs is estimated at 5.5 nm using the Scherrer equation.

In the TEM image of OP-TiO_2 (Figure S2), TiO_2 NPs can be observed as a large number of dark spots in the range of 4–20 nm. Almost all of the TiO_2 NPs are individually divided by border lines with a few nm thickness, and they appear to correspond to OP layers on the surface. Considering the length of the oleyl groups (≈ 2.3 nm) [40], OP moieties could be present as monolayers on the surfaces of the TiO_2 NPs. The particle size distribution is determined by DLS using dispersion of OP-TiO_2 in toluene (Figure S3 in Supplementary Material). The size distribution of the OP-TiO_2 NPs is shown to be relatively narrow with the monodispersion, and the median size is 16.1 nm. In contrast, bare TiO_2 NPs exhibit a 4.9 nm median size for the starting aqueous dispersion. Since individual particle shapes of OP-TiO_2 are clearly observed in the TEM images, aggregation comprising a limited number of TiO_2 NPs could be modified with OP. Thus, it is demonstrated that OP-modified TiO_2 NPs are successfully prepared as nanofillers for optical applications because their size can be controlled at below 40 nm to suppress Rayleigh scattering effectively.

3.2. Optical Properties of $\text{OP-TiO}_2/\text{PMMA}$ Hybrid Thin Films. $\text{OP-TiO}_2/\text{PMMA}$ hybrid thin films are transparent even though they contain 20 vol% TiO_2 NPs (Figure S4 in

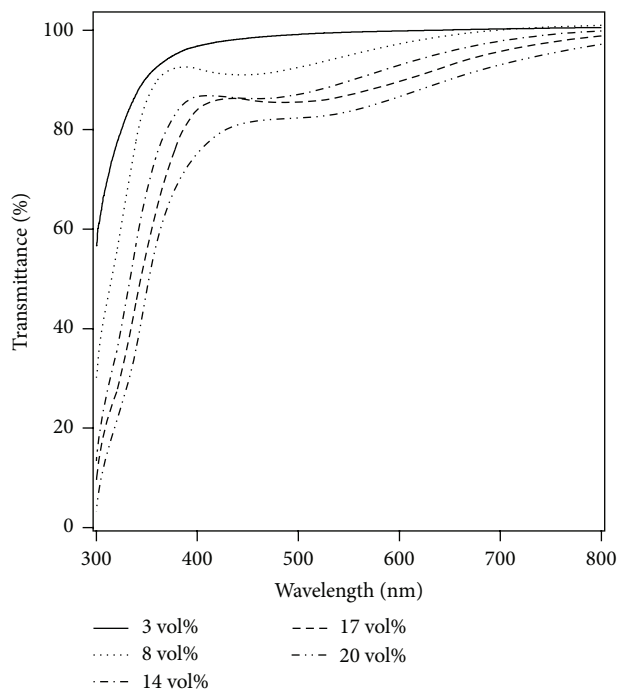


FIGURE 4: UV-Vis spectra of $\text{OP-TiO}_2/\text{PMMA}$ hybrid films.

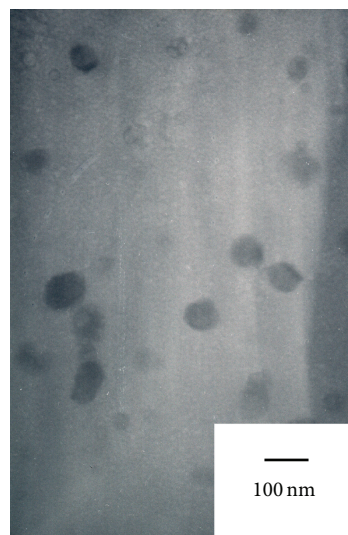


FIGURE 5: TEM image of $\text{OP-TiO}_2/\text{PMMA}$ hybrid film (14 vol% TiO_2).

Supplementary Material). UV-Vis spectra of $\text{OP-TiO}_2/\text{PMMA}$ hybrid thin films containing 3, 8, 14, and 20 vol% TiO_2 are shown in Figure 4. It is clearly demonstrated that the transmittance value at 633 nm is higher than 89.0% for all $\text{OP-TiO}_2/\text{PMMA}$ hybrid thin films. In the TEM image of $\text{OP-TiO}_2/\text{PMMA}$ containing 14 vol% TiO_2 shown in Figure 5, dark circles with diameters of 10–40 nm are homogeneously dispersed in the PMMA matrices. Although some aggregated TiO_2 NPs larger than 40 nm are observed in the TEM image, the dispersion of TiO_2 NPs of a desirable size

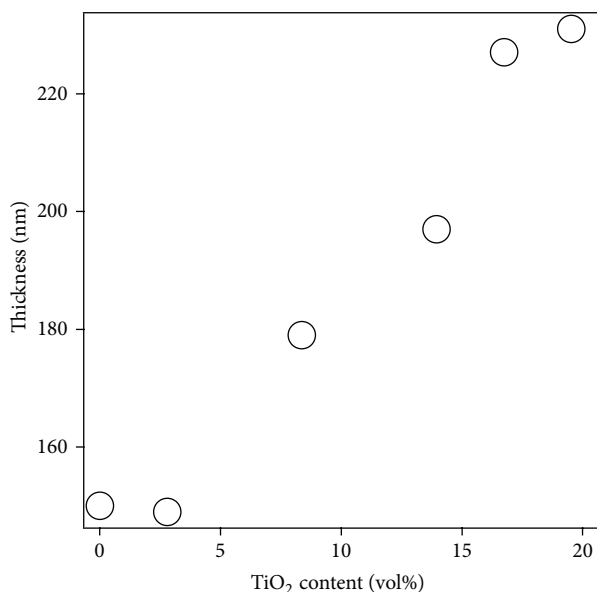


FIGURE 6: Changes in thicknesses of TiO₂/PMMA hybrid films as a function of their TiO₂ content.

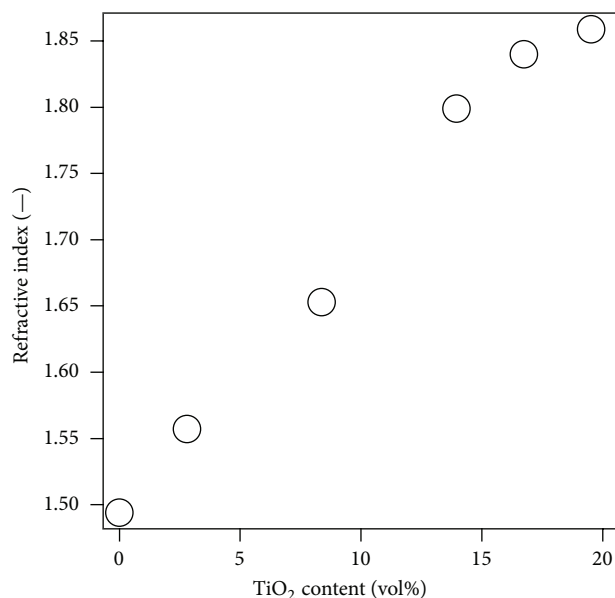


FIGURE 7: Changes in refractive indices of TiO₂/PMMA hybrid films as a function of TiO₂ content.

for suppression of Rayleigh scattering therefore leads to high transparency of the OP-TiO₂/PMMA hybrid thin films.

The thicknesses of the OP-TiO₂/PMMA hybrid thin films are shown in Figure 6. The film thickness increases in the range of 150–260 nm with increases in TiO₂ volume fraction. In general, the thickness of spin-coated polymer film depends mainly on the viscosity and density of a polymer solution at a certain spin speed [41]. TiO₂ NPs have a greater density than PMMA, and PMMA is diluted with a low viscosity OP-TiO₂ dispersion. The effect of density seems to dominate and the addition of the OP-TiO₂ dispersion to the PMMA solution results in the formation of a thicker film than neat PMMA.

The refractive indices of the OP-TiO₂/PMMA hybrid thin films at 633 nm are plotted against the TiO₂ volume fraction, as shown in Figure 7. The refractive index of the neat PMMA film is 1.49, and the indices of OP-TiO₂/PMMA hybrid thin films increase linearly with increases in the TiO₂ volume fraction, suggesting that the refractive indices of hybrid thin films can be controlled by adjusting the TiO₂ volume fraction. At 20 vol% TiO₂ content, the refractive index rises to 1.86. This value is comparable with those of flint glass ($n = 1.4$ – 2.0) [42] and sapphire crystal ($n = 1.77$) [43], suggesting the potential usefulness of the OP-TiO₂/PMMA hybrids in the present study for various optical applications.

In a previous report on TiO₂/PMMA hybrids, Lee and Chen reported the preparation of anatase TiO₂/PMMA hybrid films using titanium butoxide and a PMMA derivative bearing trialkoxysilane in the side chains via the *in situ* sol-gel route [25]. The refractive indices of the hybrid films increased linearly between 1.508 and 1.867 for 2.9–70.7 mass% TiO₂ content. In the present study, rutile TiO₂ NPs, which have a higher refractive index than that of anatase, were dispersed in PMMA via the *ex situ* route. The refractive indices of the hybrid thin films in the present study are slightly higher

than those in the previous report using anatase in the TiO₂ content range between 0.9 and 21.6 vol%. In this study, OP used as a surface modifier has a relatively low refractive index ($n = 1.45$ – 1.48), and surface modification with OP should decrease the volume fraction of TiO₂ NPs compared with the hybrid film comprising only PMMA and TiO₂ in the previous report. Thus, the refractive indices of hybrid thin films using OP-TiO₂ were similar to those in the previous report in spite of the dispersion of rutile TiO₂ NPs.

4. Conclusions

OP was covalently bound to the surfaces of TiO₂ NPs to prepare TiO₂/PMMA hybrid thin films with high refractive indices. After the surface modification of TiO₂ NPs, IR and the solid-state ³¹P MAS NMR results revealed the formation of Ti–O–P bonds, and the oleyl groups on the surfaces played an important role in suppressing the aggregation of TiO₂ NPs in toluene. The particle sizes of the OP-modified NPs were smaller than 40 nm and were homogeneously dispersed in PMMA. The OP-TiO₂/PMMA hybrid thin films exhibited excellent optical transparency, and their transmittance values were larger than 89.0% at 633 nm. The refractive indices of the hybrid thin films increased with increases in the volume fraction of TiO₂ NPs, and their refractive index reached 1.86 at 20 vol% TiO₂ content. The present results demonstrate that the surface modification of TiO₂ NPs is an excellent method for the preparation of TiO₂ fillers applicable to the *ex situ* method for preparing various TiO₂/polymer hybrids.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

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