Preparation of High Refractive index Materials using ZrO₂ Nanoparticles and Glyceryl-*N*-(2-methacryloyloxyethyl)urethane and Its Properties*

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We established the metal-oxide nanoparticles dispersion technology using Glyceryl-*N*-(2-methacryloyloxyethyl)urethane (GLYMOU®) with high affinity for the inorganic materials, such as zirconia (ZrO₂), titania (TiO₂), and silica (SiO₂). The high refractive index optical films were prepared by using ZrO₂ nanoparticles (grain size: 3 nm) and GLYMOU®. The films were colorless and transparent. As a ZrO₂ concentration increased up to 80 wt%, refractive index showed 1.70 at wavelength of 589 nm. Solid-state NMR and first density functional theory (DFT) study confirmed that GLYMOU® was strongly coordinated to the ZrO₂ surfaces with hydroxyl groups and urethane bond. The dispersion state of nanoparticles in the hybrid films was investigated by combination of grazing incidence small angle X-ray scattering (GISAXS) and transmission electron microscope (TEM). GISAXS measurements and TEM observations, ZrO₂ nanoparticles were finely dispersed in the poly-GLYMOU® matrices. [DOI: 10.1380/ejsnt.2012.85]

Keywords: Density functional calculations; Nuclear magnetic resonance; X-ray scattering

I. INTRODUCTION

Organic-inorganic hybrid materials have attracted special interest and various investigations have been conducted because of the novel properties arising from synergistic interaction of the individual constituents [1,2]. However inorganic nanoparticles are easily aggregate in the organic matrices because of the strong surface energy and thus the novel nanoproperties, which show up only in nanoscale region, are lost easily. Usually the surface of inorganic nanoparticles has hydroxyl groups, and adsorbed dispersant (e.g. acetic acid). To disperse the inorganic nanoparticles into organic matrices, the matrices should have hydrophilic functional groups that show high affinity to the surface of inorganics. In a previous paper, we described poly-GLYMOU®/ZrO₂ hybrid hydrogel achieved finely dispersion of ZrO₂ nanoparticles by utilizing hydrogen bonding between Zr-OH groups of the ZrO₂ nanoparticles and the hydroxyl groups and the urethane groups of poly-GLYMOU® [3]. In this work, we synthesized ZrO₂/GLYMOU® hybrid thin films, and evaluated the dispersion state of ZrO₂ nanoparticles in hybrid. We also evaluated interaction with GLYMOU® and ZrO₂ nanoparticles.

II. EXPERIMENTAL

Prepare ZrO₂/GLYMOU® hybrid thin films, first the coating solutions were prepared by dissolving

FIG. 1: Refractive index of the hybrid films.

ZrO₂ dispersions (grain size: 3 nm), GLYMOU®, dipentaerythritol penta-/hexa-acrylate (DPHA), 2,4,6-trimethylbenzoyl-diphenylphosphine oxide (initiator, 0.3 wt% to the total monomer) in propyl-glycol to the needed concentration. Then, the coating solution was spin-coated onto the substrates (Si, SiO₂) at 3000 rpm, and then dried at 150 for 15 min. The hybrid film was obtained by irradiation of 365 nm (about 1000 mJ cm⁻²) under N₂ flow.

The reflective index of hybrid films were measured with a reflective thickness monitor using a Cauchy [4] mode and a three-layer model, consisting of Si substrate, SiO₂ layer and Cauchy layer (Si/SiO₂/Cauchy layer).

The dispersion state of ZrO₂ nanoparticles in the hybrid films was investigated by combination of grazing incidence small angle X-ray scattering (GISAXS) and transmission

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FIG. 2: GISAXS intensity curve of the hybrid films.

FIG. 3: Cross-sectional TEM images of the hybrid films. (a) ZrO₂/GLYMOU®/DPHA hybrid (ZrO₂:70 wt%), (b) ZrO₂/GLYMOU®/DPHA hybrid (ZrO₂:80 wt%), (c) ZrO₂/GLYMOU®/DPHA hybrid (ZrO₂:90 wt%).

electron microscope (TEM). Interaction of ZrO₂ nanoparticles and GLYMOU® was investigated by combination of Solid-state NMR and Density functional calculations with periodic boundary conditions.

III. RESULTS AND DISCUSSIONS

We successfully prepared the ZrO₂/GLYMOU® hybrid thin films (ZrO₂ content: 30-90 wt%). The films were colorless and transparent. The refractive index of hybrid films measured by reflective thickness monitor was compared with refractive index calculated by using Lorentz-Lorenz equation shown in Fig. 1. The Lorentz-Lorenz equation is represented by the following formula:

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

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, n_{ZrO_2} =2.10, $n_{\text{GLYMOU®}}$ =1.48, n_{DPHA} =1.48 were employed, respectively. The refractive index at 589 nm of the ZrO₂/GLYMOU® hybrid films increased from 1.53 to 1.70 with the ZrO₂ concentration from 30 to 80 wt%. It could be confirmed the calculated refractive index on the Lorentz-Lorenz equation was in good agreement with the experimental value of ZrO₂/GLYMOU® hybrid films at 589 nm. However,

FIG. 4: ¹³C-CP/MAS spectra of ZrO₂/GLYMOU® hybrid (ZrO₂/GLYMOU®=70/30 wt%) and poly-GLYMOU®. FIG. 5: (a) Equilibrium structure of the GLYMOU®/tetragonal-ZrO₂ (101) surface with acetic acid adsorption. (b) Schematic representation of interaction.

at higher ZrO₂ concentration deviated from the Lorentz-Lorenz equation.

Figure 2 shows the GISAXS profiles $I(q)$ corresponding to the hybrid materials containing different contents of ZrO₂ nanoparticle. As the ZrO₂ nanoparticle content increased up to 80 wt%, the peak maximum became clearly and its position shifted toward larger q values. However, increased up to 90 wt%, the shape of the peak maximum became broader. This peak maximum is due to interference of the ZrO₂ nanoparticles, and this peak position indicates the center-to-center ZrO₂ nanoparticle distance in the hybrid film. To get further insight of these hybrids, TEM analysis was utilized.

Figure 3 shows Cross-Sectional TEM images of hybrid thin film with 70-90 wt% of ZrO₂ nano-particles. At the ZrO₂ content of 70 and 80 wt%, ZrO₂ nanoparticles dispersed finely in the organic matrices. At the ZrO₂ content of 90 wt%, decrease of dispersibility was observed.

Figure 4 shows ^{13}C -CP/MAS spectra of hybrid and poly-GLYMOU®. The peaks of acetic acid (ZrO_2 dispersant) were large and broad, and we suppressed acetic acid was strongly adsorbed on the surface of ZrO_2 . By hybridizing, the peaks of methine (the peak of f, $\delta = 71.2$ ppm) and methylene (the peak of e, $\delta = 64.6$ ppm) next to oxygen were increased. These results show that urethane group and hydroxyl groups of GLYMOU® interact strongly with ZrO_2 surface.

To better understand the interaction with GLYMOU® and ZrO_2 surface, DFT calculations with periodic boundary conditions were carried out by using DMol3 program. Figure 5 shows (a) interaction of tetragonal- $\text{ZrO}_2(101)$ surface with acetic acid adsorption and GLYMOU®, and (b) schematic representation of interaction with GLYMOU® and tetragonal- $\text{ZrO}_2(101)$ surface with acetic acid adsorption. Computational results show strong interaction with GLYMOU® and acetic acid adsorbed on ZrO_2 surface. This result is in good agreement with NMR result.

IV. CONCLUSIONS

In conclusion, we established the metal-oxide nanoparticles dispersion technology using GLYMOU® with high affinity for the inorganic materials. The high refractive index optical films were prepared by using ZrO_2 nanoparticles (grain size: 3 nm) and GLYMOU®. The films were colorless and transparent, and refractive index showed 1.70 at wavelength of 589 nm. As a ZrO_2 concentration increased up to 80wt%, ZrO_2 nanoparticles were finely dispersed in the poly-GLYMOU® matrices.

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- [1] Y. Chujo and T. Saegusa, *Adv. Polym. Sci.* **100**, 11 (1992).
 - [2] S. Katayama, Y. Kubo, and N. Yamada, *J. Am. Ceram. Soc.* **85**, 1157 (2002).
 - [3] E.-C. Kang, A. Ogura and T. Morishita, *Polym. J.* **41**, 356

- (2009).
- [4] F. A. Jenkins and H. E. White, *Fundamentals of the Optics*, 4th ed. (McGraw-Hill, Inc., 1981).