Preparation of High Refractive index Materials using ZrO\textsubscript{2} Nanoparticles and Glyceryl-N-(2-methacryloyloxyethyl)urethane and Its Properties\textsuperscript{a}

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We established the metal-oxide nanoparticles dispersion technology using Glyceryl-N-(2-methacryloyloxyethyl)urethane (GLYMOU\textsuperscript{R}®) with high affinity for the inorganic materials, such as zirconia (ZrO\textsubscript{2}), titania (TiO\textsubscript{2}), and silica (SiO\textsubscript{2}). The high refractive index optical films were prepared by using ZrO\textsubscript{2} nanoparticles (grain size: 3 nm) and GLYMOU\textsuperscript{R}®. The films were colorless and transparent. As a ZrO\textsubscript{2} 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\textsuperscript{R}® was strongly coordinated to the ZrO\textsubscript{2} surfaces with hydroxyl groups and urethane bond. The dispersion state of ZrO\textsubscript{2} 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, ZrO\textsubscript{2} nanoparticles were finely dispersed in the poly-GLYMOU\textsuperscript{R}® matrices.

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\textsuperscript{R}/ZrO\textsubscript{2} hybrid hydrogel achieved finely dispersion of ZrO\textsubscript{2} nanoparticles by utilizing hydrogen bonding between Zr–OH groups of the ZrO\textsubscript{2} nanoparticles and the hydroxyl groups and the urethane groups of poly-GLYMOU\textsuperscript{R} [3]. In this work, we synthesized ZrO\textsubscript{2}/GLYMOU\textsuperscript{R} hybrid thin films, and evaluated the dispersion state of ZrO\textsubscript{2} nanoparticles in hybrid. We also evaluated interaction with GLYMOU\textsuperscript{R} and ZrO\textsubscript{2} nanoparticles.

II. EXPERIMENTAL

Prepare ZrO\textsubscript{2}/GLYMOU\textsuperscript{R} hybrid thin films, first the coating solutions were prepared by dissolving

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FIG. 1: Reflective index of the hybrid films.

ZrO\textsubscript{2} dispersions (grain size: 3 nm), GLYMOU\textsuperscript{R}, dipentaerythritol penta-/hexa-acrylate (DPHA), 2,4,6-trimethylbenzyldiphenylphosphine 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, SiO\textsubscript{2}) 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\textsuperscript{-2}) under N\textsubscript{2} 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, SiO\textsubscript{2} layer and Cauchy layer (Si/SiO\textsubscript{2}/Cauchy layer). The dispersion state of ZrO\textsubscript{2} nanoparticles in the hybrid films was investigated by combination of grazing incidence small angle X-ray scattering (GISAXS) and transmission
III. RESULTS AND DISCUSSIONS

We successfully prepared the ZrO$_2$/GLYMOU® hybrid thin films (ZrO$_2$ 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 on the Lorentz-Lorenz equation shown in Fig. 1. The Lorentz-Lorenz equation is represented by the following formula:

\[
\frac{(n^2 - 1)}{(n^2 + 2)} = \sum n_i \frac{(n_i^2 - 1)}{(n_i^2 + 2)},
\]

where \( n \) is the refractive index of hybrid film, \( n_i \) and \( n_{DPHA} \) are the volume fraction and refractive index of component \( i \), respectively. In this case, \( n_{ZrO_2}=2.10 \), \( n_{GLYMOU}=1.48 \), and \( n_{DPHA}=1.48 \) were employed, respectively. The refractive index at 589 nm of the ZrO$_2$/GLYMOU® hybrid films increased from 1.53 to 1.70 with the ZrO$_2$ 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 ZrO$_2$/GLYMOU® hybrid films at 589 nm. However, at higher ZrO$_2$ concentration deviated from the Lorentz-Lorenz equation.

Figure 2 shows the GISAXS profiles I(q) corresponding to the hybrid materials containing different contents of ZrO$_2$ nanoparticle. As the ZrO$_2$ nanoparticle content increased up to 80 wt%, the peak maximum became clearly and its position shifted toward higher 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 ZrO$_2$ nanoparticles, and this peak position indicates the center-to-center ZrO$_2$ nanoparticle distance in the hybrid film. To get further insights of these hybrids, TEM analysis was utilized.

Figure 3 shows Cross-Sectional TEM images of hybrid thin film 70-90 wt% of ZrO$_2$ nanoparticles. At the ZrO$_2$ content of 70 and 80 wt%, ZrO$_2$ nanoparticles dispersed finely in the organic matrices. At the ZrO$_2$ 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-ZrO$_2$(101) surface with acetic acid adsorption and GLYMOU®, and (b) schematic representation of interaction with GLYMOU® and tetragonal-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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