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SHORT COMMUNICATION

# Interaction between Poly(glyceryl-*N*-(2-methacryloyloxyethyl)-urethane) and $ZrO_2$ Nanoparticles: Formation of Hybrid Hydrogel

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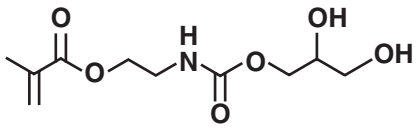
Organic-inorganic hybrid materials have been extensively studied during the past two decades because of their unique optical, mechanical, and physicochemical properties.[1–4] These organic-inorganic hybrid materials were usually prepared by two methods. The first method is hybrid using the sol-gel process of metal alkoxides, and the other method is hybrid by incorporating inorganic nanoparticles into the polymer matrices. In general, the polymer hybrids are prepared by utilizing physical interactions such as hydrogen bonding, ionic and aromatic $\pi$-$\pi$ interactions. From the viewpoint of the formation of hydrogen bonding both polymer and inorganic metal oxide such as silica, zirconia, titania and alumina plates, we synthesized the novel vinyl monomer, glyceryl-*N*-(2-methacryloyloxyethyl)urethane (GLYMOU), with several hydrogen bonding sites (Scheme 1).[5–9] In the previous reports, we studied the preparation and characteristics of GLYMOU/silica hybrid materials.[7] In that study, GLYMOU/silica hybrid materials exhibited high transparency and excellent mechanical properties.

Recently, several research groups have studied the preparation and properties of organic-inorganic hybrid hydrogel.[10–12] Takahara *et al.* prepared the hybrid hydrogel composed of imogolite and pepsin, and examined their enzyme activity.[10] Akiyoshi *et al.* reported the preparation of organic-inorganic hybrid nanogel with dual network structure of both chemically crosslinked points with siloxane bonds and physically crosslinked hydrophobic association points.[11] Haraguchi *et al.* reported the preparation and the properties of nanocomposite hydrogel composed of clay and poly(*N*-isopropylacrylamide).[12] We found that poly(glyceryl-*N*-(2-methacryloyloxyethyl)urethane) (pGLYMOU) forms the hybrid hydrogel with zirconium oxide ($ZrO_2$) nanoparticles in aqueous solution. In this paper, the preparation and the phase behavior of novel pGLYMOU/$ZrO_2$ hybrid hydrogel are described.

For the preparation of pGLYMOU/$ZrO_2$ hybrid hydrogel, pGLYMOU ($M_w$ 116,000 $M_w/M_n = 3.4$) prepared by the free radical polymerization as previously reported.[6] 30 wt % aqueous $ZrO_2$ nanoparticles (average diameter = 3 nm) solutions were donated by Sumitomo Osaka Cement Co. Ltd. In a typical experiment, the pGLYMOU/$ZrO_2$ hybrid hydrogel was prepared by adding 0.5 g of 10.0 wt % aqueous pGLYMOU solution to the 0.5 g of 10.0 wt % aqueous $ZrO_2$ solution (pH = 4.18). Figure 1 shows a photograph of 10.0 wt % aqueous $ZrO_2$ solution and pGLYMOU/$ZrO_2$ hybrid hydrogel. Generally, the outermost surface of metal oxide nanoparticles has several hydroxyl groups and lewis acid sites or lewis base sites in aqueous solution.[13,14] The surfaces of $ZrO_2$ nanoparticles have several hydroxyl groups and lewis acid sites. The $ZrO_2$ nanoparticles are positively charged and dispersed by the electrostatic repulsion in acidic aqueous solution (pH < 5) (Figure 1a). The pGLYMOU/$ZrO_2$ hybrid hydrogel was formed due to the hydrogen bonding interaction between Zr-OH groups of the $ZrO_2$ surface and the hydroxyl groups and the urethane groups of pGLYMOU (Figure 1b).

For field-emission scanning electron microscopic (FE-SEM) observation, the pGLYMOU/$ZrO_2$ hybrid hydrogel was quickly frozen in liquid nitrogen, and then dehydrated under vacuum. The dehydrated hydrogel was fixed onto a stage for SEM observation. Platinum was sputtered onto the sample at a thickness of approximately 20 nm. The surface was then analyzed with a HITACHI S-5000 (Hitachi) at an accelerated voltage of 6 kV. Figure 2 shows typical SEM observation of pGLYMOU/$ZrO_2$ hybrid hydrogel. The three-dimensional network structure of the pGLYMOU/$ZrO_2$ hybrid hydrogel composed of pGLYMOU and $ZrO_2$ nanoparticles as a hydrogel component could be clearly observed. The average pore size of the pGLYMOU/$ZrO_2$ hybrid hydrogel was about 6 μm.




**Scheme 1.** Chemical structure of GLYMOU.

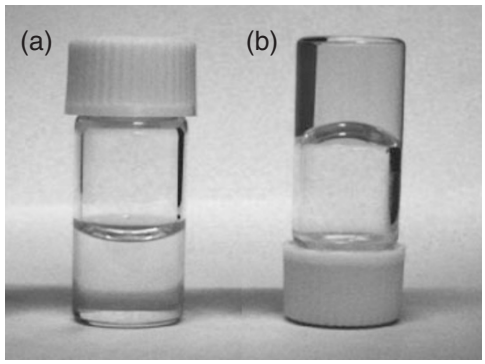



**Figure 1.** Photograph of (a) 10.0 wt % aqueous $ZrO_2$ solution and (b) pGLYMOU/$ZrO_2$ hybrid hydrogel (pGLYMOU/$ZrO_2$/water = 5/5/90 by wt %).

For transmission electron microscopic (TEM) observation, the pGLYMOU/$ZrO_2$ hybrid hydrogel was quickly frozen in liquid nitrogen, and then dehydrated under vacuum. The dehydrated hybrid hydrogel with $OsO_4$ were fixed onto a stage for TEM observation. The surface was then analyzed with a JEM-4000EX (JEOL) at an accelerated voltage of 200 kV. Figure 3 shows typical TEM observation of pGLYMOU/$ZrO_2$ hybrid hydrogel. $ZrO_2$ nanoparticles were found to be finely dispersed in the pGLYMOU/$ZrO_2$ hybrid hydrogel.

An appropriate amount of a 20 wt % aqueous pGLYMOU solution was mixed with water and a 30 wt % aqueous $ZrO_2$ solution in a vial, which was then sealed. In most cases, the total sample weight was kept constant at 1.0 g. The sample solution was mixed by inverting the vial 30 times until the solution became visually homogeneous. Once the sample solution became homogeneous, the phase behavior was investigated after 1 hr at

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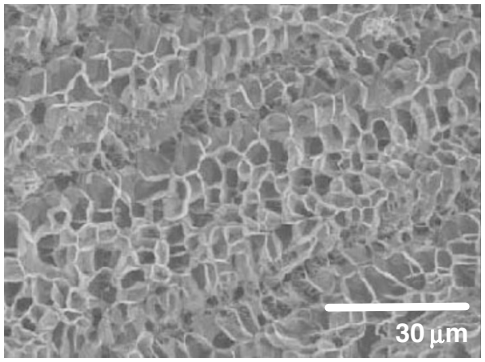


**Figure 2.** SEM observation of pGLYMOU/$ZrO_2$ hybrid hydrogel (pGLYMOU/$ZrO_2$/water = 5/5/90 by wt%).

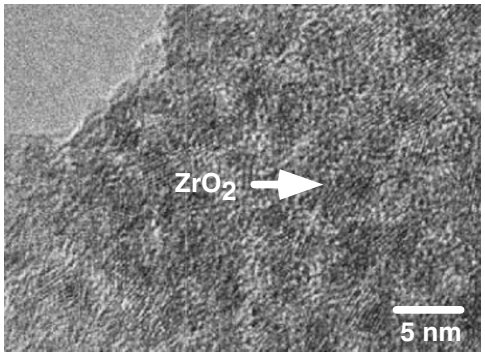


**Figure 3.** TEM observation of pGLYMOU/$ZrO_2$ hybrid hydrogel (pGLYMOU/$ZrO_2$/water = 5/5/90 by wt%).

25 °C. Gel formation was checked by the tilting method. Namely, if the sample solution did not flow immediately when the test tube was turned upside down, it was considered to be a gel. Otherwise, it was considered to be a sol. Totally 100 samples were prepared to obtain phase diagram. Figure 4 shows the phase diagram of pGLYMOU/$ZrO_2$/water ternary system at 25 °C. When the pGLYMOU concentration was lower than 3.0 wt%, no gel formation was observed at all even if $ZrO_2$ was added in any concentration.

In conclusion, we successfully prepared a pGLYMOU/$ZrO_2$ hybrid hydrogel utilizing hydrogen bonding interaction between Zr-OH groups of the $ZrO_2$ nanoparticles and the hydroxyl groups and the urethane groups of pGLYMOU. The three-dimensional network structure of pGLYMOU/$ZrO_2$ hybrid hydrogel could be clearly observed by FE-SEM. $ZrO_2$ nanoparticles were found to be finely dispersed in the hybrid hydrogel by TEM. Further studies concerning the physical properties of pGLYMOU/$ZrO_2$ hybrid hydrogel are now in progress.

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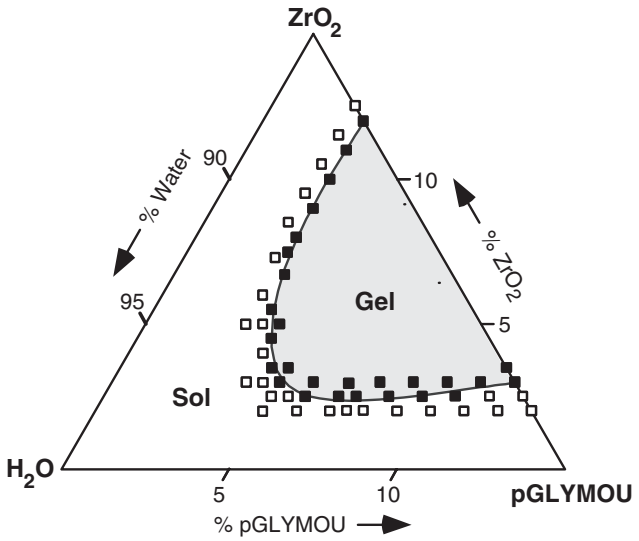


**Figure 4.** Phase diagram of pGLYMOU/$ZrO_2$/water system at 25 °C. Sol and gel are indicated by open and closed square, respectively.

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REFERENCES

1. Y. Chujo and T. Saegusa, *Adv. Polym. Sci.*, **100**, 11 (1992).
2. C. M. Brick, Y. Ouchi, Y. Chujo, and R. M. Laine, *Macromolecules*, **38**, 4661 (2005).
3. T. Sanji, Y. Nakatsuka, and H. Sakurai, *Polym. J.*, **37**, 1 (2005).
4. T. Otsuka and Y. Chujo, *Polym. J.*, **40**, 1157 (2008).
5. E.-C. Kang, A. Ogura, T. Iwata, and S. Kataoka, *Polymer Materials Form Preprints, Japan*, **14**, 72 (2005).
6. E.-C. Kang, A. Ogura, T. Iwata, S. Kataoka, and Y. Maruhashi, *Polym. J.*, **38**, 1205 (2006).
7. S. Kataoka, K. Ito, A. Ogura, and E.-C. Kang, *Polymer Materials Form Preprints, Japan*, **15**, 52 (2006).
8. Y. Sekine, H. Ohkawa, T. Fujita, and H. Fukui, *Fragrance J.*, **35**, 81 (2007).
9. H. Fukui and E.-C. Kang, *Expected Materials for the Future*, **8**, 44 (2008).
10. N. Inoue, H. Otsuka, S.-I. Wada, and A. Takahara, *Chem. Lett.*, **35**, 194 (2006).
11. S. Yamane, Y. Sasaki, and K. Akiyoshi, *Chem. Lett.*, **37**, 1282 (2008).
12. K. Haraguchi, T. Takehisa, and S. Fan, *Macromolecules*, **35**, 10162 (2002).
13. K. Shimizu, "Metal Oxide and its Catalytic Ability," Kodansha, Japan, 1978, chap. 3, p 102.
14. M. Watanabe, M. Osada, H. Inomata, K. Arai, and A. Kruse, *Appl. Catal., A*, **245**, 333 (2003).