Molecular Crystals and Liquid Crystals

ISSN: 1542-1406 (Print) 1563-5287 (Online) Journal homepage: http://www.tandfonline.com/loi/gmcl20

Fabrication and Properties of Hybrid Thin Film with Epoxy Resin and Methyltrimethoxy Silane-modified ZrO_2

Young Taec Kang, Dong Jun Kang, Dong Pil Kang & Ildoo Chung

To cite this article: Young Taec Kang, Dong Jun Kang, Dong Pil Kang & Ildoo Chung (2015) Fabrication and Properties of Hybrid Thin Film with Epoxy Resin and Methyltrimethoxy Silane-modified ZrO_2, Molecular Crystals and Liquid Crystals, 622:1, 25-30, DOI: 10.1080/15421406.2015.1096499

To link to this article: http://dx.doi.org/10.1080/15421406.2015.1096499

Published online: 16 Dec 2015.

Mol. Cryst. Liq. Cryst., Vol. 622: pp. 25–30, 2015

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2015.1096499

Fabrication and Properties of Hybrid Thin Film with Epoxy Resin and Methyltrimethoxy Silane-modified ZrO_2

YOUNG TAEC KANG,[1,2] DONG JUN KANG,[1]
DONG PIL KANG,[1] AND ILDOO CHUNG[2,*]

[1]Advanced Materials & Application Research Division, Korea Electrotechnology Research Institute, Changwon, Korea
[2]Department of Polymer Science and Engineering, Pusan National University, Busan, Korea

The ZrO_2-sol was prepared with zirconium acetate and water below 60°C followed by the modification with 0, 0.5 and 5 mol of methyltrimethoxysilane(MTMS) via sol-gel method. The epoxy system was consisted of 1,1,1-(triglycidyl-oxyphenyl) methane, (3-4-epoxycyclohexane) methyl-3-4-epoxycyclohexyl carboxylate, methyl-2,3-norbornanedicarboxylic anhybride, ethyl triphenyl phosphonium iodide and N,N-dimethylacetamide (DMAc). The epoxy system and MTMS-modified ZrO_2-sols were mixed to be solid contents of 90 : 10 weight percentages. ZrO_2 particles synthesized from sol-gel method were amorphous phase in XRD patterns. FE-SEM images showed MTMS-modified ZrO_2 particles were dispersed with excellent homogeneity in hybrid system. The FT-IR spectra of MTMS-modified ZrO_2 particle identified the methyl and silica groups formed from MTMS on the surface of ZrO_2 particle. It is considered that epoxy-ZrO_2 hybrid materials have the potential to be used as the hybrid thin film due to their high refractive index and excellent hybridization stability.

Keywords Sol-gel; Refractive index; ZrO_2; Epoxy; Nano hybrid

1. Introduction

ZrO_2 has been widely studied for a long time because of its high refractive index in optical applications and its low thermal conductivity at high temperature [1–5]. The nano-sized ZrO_2 particle has a significant effect on the optical and mechanical properties of its hybrid or nanocomposite materials [6, 7]. Though various methods have been used such as ball-mill, hydro-thermal and super-critical process for the synthesis of nano-sized particle, the sol-gel process is the most popular process. The nano-sized particle with a narrow-size distribution has been fabricated using the same method [8–13]. In this reason, the particle size and size distribution of ZrO_2 can be controlled via the sol-gel method [14–16].

Epoxy is a widely used material especially for coatings, adhesives and composite materials such as those used for ceramic reinforcements. Some transparent epoxy with

*Address correspondence to Professor Ildoo Chung, Department of Polymer Science and Engineering, Pusan National University, Busan 609-735, Korea. E-mail: idchung@pusan.ac.kr

Color versions of one or more of the figures in the article can be found online at www.tandfonline.com/gmcl.

Table 1. Fabrication of ZrO_2 sol and epoxy-ZrO_2 hybrid film.

ZrO_2 sol					Epoxy-ZrO_2 hybrid film	
Code1	ZA	Water	DMAc	MTMS	Code2	Hybridization (Weight ratio 9/1)
M0				—	EM0	Epoxy/M0
M0.5	1 mol	2 mol	17 mol	0.5 mol	EM0.5	Epoxy/M0.5
M5				5 mol	EM5	Epoxy/M5
					Neat epoxy	—

discoloration resistance of high temperature has been studied as encapsulation materials for light-emitting diode(LED), liquid-crystal display(LCD) panels and optical lenses [17–19]. However, epoxy is limited in its application due to its low refractive index and mechanical properties. Recently, organic-inorganic hybrid materials have been studied to enhance the limited properties of epoxy [20–22]. The organic-inorganic hybrid materials can be easily prepared by hybridizing organic resins with inorganic particles [23].

The surface modification of inorganic particle is necessary for the hybridization of organic resins and inorganic particles, since they cannot be homogeneous phase due to different hydrophilicity. Such modified inorganic particles are usually obtained by sol-gel methods, involving hydrolysis and condensation of esters and/or alcoholates of the type $(RO)_{4\text{-}n}SiR_n$ as organic silane [24–27]. Also, the homogeneity of organic resins and inorganic increased with introducing organic group on surface of inorganic particles. Then, organic-inorganic hybrid materials combine the advantages of organic resins and inorganic particles. Furthermore, the chemical bonds of organic polymers and inorganic particles usually provide special properties compared with traditional composites. Accordingly, organic-inorganic hybrid materials have been used in various applications. In this study, surface modified ZrO_2 with organic silane was synthesized by sol-gel method and mixed with epoxy system, followed by the evaluation of their refractive index and hybridization stability.

2. Experimental

The chemicals were used in this study, zirconium acetate (ZA), water and N,N-dimethylacetamide (DMAc), were purchased from Sigma-Aldrich Co., Ltd. (USA). 1,1,1-(Triglycidyl-oxyphenyl) methane was obtained from Kukdo Chemical Co., Ltd. (Korea), (3-4-epoxycyclohexane) methyl-3-4-epoxycyclohexyl carboxylate and ethyl triphenyl phosphonium iodide were purchased from Kolon Industries Co., Ltd. (Korea). Methyl-2,3-norbornane dicarboxylic anhydride was supplied by New Japan Chemical Co., Ltd. (Japan). All other chemical reagents were of analytical grade and used without further purification.

The mixed solution of zirconium acetate (16 wt% in acetic acid), water and DMAc with the molar ratios of 1 : 2 : 17 was reacted for 24 h at 60°C with stirring rate at 800 rpm. As shown in Table 1, methyltrimethoxysilane (MTMS) was added to the above mixture with 0, 0.5 and 5 mol, and allowed to react for an additional 2 h at room temperature with same stirring rate and then finally distilled under vacuum to remove unneeded solvents(acetic

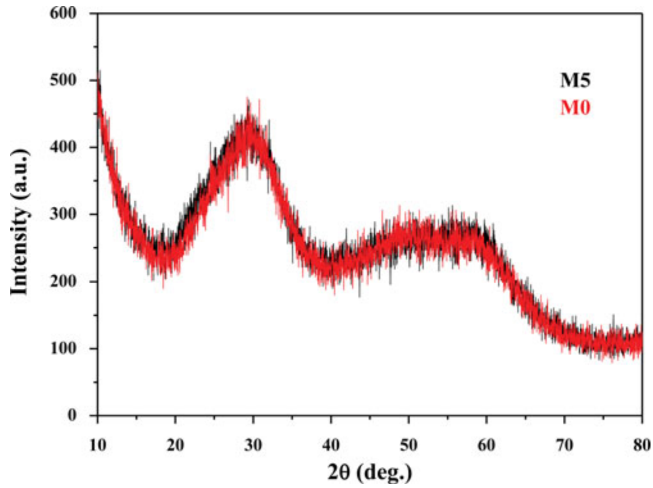

Figure 1. X-ray diffraction patterns of samples (M0) and (M5).

acid/alcohol/water) from mono-dispersed ZrO_2-sols in DMAc after sol-gel reaction. Epoxy system was consisted of 1,1,1-(triglycidyl-oxyphenyl) methane, (3-4-epoxycyclohexane) methyl-3-4-epoxycyclohexyl carboxylate as resin matrix and methyl-2,3-norbornane dicarboxylic anhydride as an hardener and ethyl triphenyl phosphonium iodide as an hardening accelerator with the weight ratios of 4 : 1 : 4 : 0.09, and it was diluted with DMAc to be solid content of 30wt%. Finally, MTMS-modified and MTMS-unmodified ZrO_2 sols were added to the epoxy solution with the weight ratio of 1 : 9. Samples M0 and M5 sols were heated at 200°C for 1 h to remove solvent for FT-IR analysis. The solutions of neat epoxy resin, EM0, EM0.5 and EM5 were coated on Si-wafer and pre-dried at 150°C for 1 h, cured at 180°C for 2 h and finally post-cured at 200°C for 30 min to prepare coating films. The refractive indices and FE-SEM images of coating films were investigated.

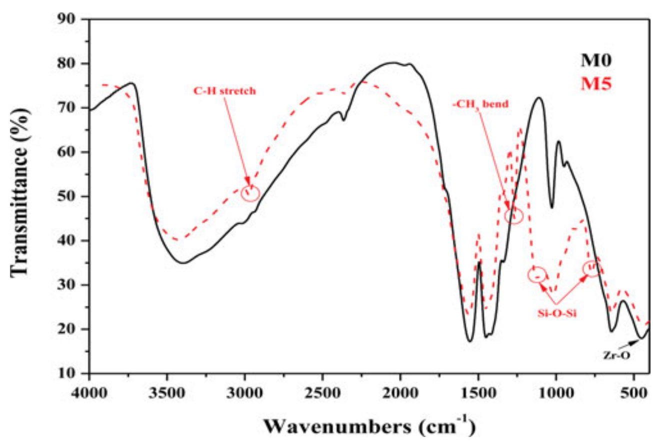

Figure 2. FT-IR spectra of samples (M0) and (M5).

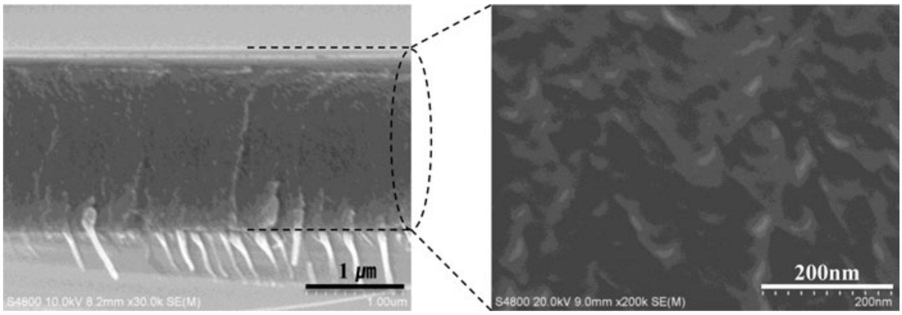

Figure 3. FE-SEM images of cross section of sample (M5): (a) entire film, (b) hybrid layer.

3. Results and Discussion

As shown in Figure 1, X-ray diffraction patterns of samples M0 and M5, a characteristic XRD peak of tetragonal zirconia at $2\theta = 30.2^{\circ}$ was clearly detected [28]. MTMS modified ZrO_2 sol(M5) showed similar XRD pattern to neat sol(M0) due to amorphous phase of networked interface area from MTMS.

Because ZrO_2 sol was prepared using zirconium acetate solution in acetic acid and water via sol-gel method, in this process, acetic acid also served as a chelating ligand at the molecular level. The chelated zirconium acetate was hydrolyzed to zirconium hydroxide by addition of water. This chelating ligand decreases the rate of hydrolysis, implying that very fine particles of zirconium hydroxide will be formed and suspended in solution [29]. In this reason, we understand that ZrO_2 particles have amorphous phases as shown in XRD pattern.

Figure 2 showed FT-IR analysis of samples of solventless M0 and M5 particles. The absorption band at 3390 cm^{-1} corresponds to the vibration of stretching of the O-H bond due to the absorption of water. Another important absorption band can be observed at 466 cm^{-1}, which is related to the vibration of Zr-O bond in ZrO_2 [30].

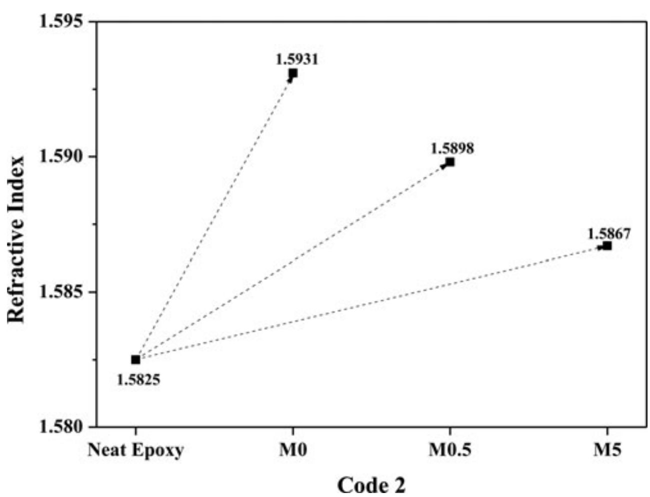

Figure 4. Refractive indices of samples (neat epoxy), (EM0), (EM0.5) and (EM5).

In FT-IR spectrum of sample M5, several bands are related to the vibrations of both ZrO_2 and MTMS. The most intensive bands, at about 770 and 1100 cm^{-1}, are connected with asymmetric stretching vibration of the Si-O-Si bridges. Bands related to the vibrations of the C-H groups in MTMS are usually found both at 1270 and 2940 cm^{-1}.

A cross sectional of FE-SEM images of sample M5(Figure 3(a)) showed excellent adhesion of the hybrid coating film on a Si-wafer substrate, and the interface between the epoxy and the ZrO_2 of the hybrid coating film(Figure 3(b)) was homogeneous due to their similar hydrophobicity between epoxy and MTMS-modified ZrO_2 particles.

As shown in Figure 4, the refractive indices of neat epoxy, EM0, EM0.5 and EM5 are 1.5825, 1.5931, 1.5898 and 1.5867. Though a sample of hybrid material EM0 has the highest refractive index among all samples, it was not homogeneous with epoxy resin due to the hydrophilicity of ZrO_2. For this reason, it may be concluded that the hybrid material of epoxy-ZrO_2 with 5 mol of MTMS (EM5) was optimal hybrid film due to its proper refractive index and the highest homogeneity.

4. Conclusions

The ZrO_2 was synthesized from zirconium acetate and water, and then its surface was modified with MTMS via sol-gel method. The hybrid films of ZrO_2-epoxy with or without MTMS-modification were fabricated by a special heating process. The addition of ZrO_2 particles increased the refractive index of hybrid coating film, while the mixing solution can be a gelation without MTMS-modification of ZrO_2 particles. The hybrid coating film prepared from epoxy and MTMS-modified ZrO_2 had higher refractive index than that of neat epoxy film and excellent blending solution stability.

Acknowledgments

This work was supported by a 2-Year Research Grant of Pusan National University.

References

[1] Johnson, D. W., Messing, G. L., Mazduyasni, K. S., McCauley, J. W., & Haver, R. A. (1987). *Ceram. Powder Sci.*, *21*, 3.
[2] Hass, D. D., Slifka, A. J., & Wadley, H. N. G. (2001). *Acta Mater.*, *49*, 973.
[3] Singh, J., & Wolfe, D. E. (2004). *J. Mater. Sci.*, *39*, 1975.
[4] Klinger, R. E., & Carniglia, C. K. (1985). *Appl. Optics*, *24*, 3184.
[5] Nicoloso, N., Lobert, A., & Leibold, B. (1992). *Sensor. Actuat. B-Chem.*, *8*, 253.
[6] Zhou, S., & Wu, L. (2008). *Macromol. Chem. Phys.*, *209*, 1170.
[7] Hu, Y., Zhou, S., & Wu, L. (2006). *Polym.*, *50*, 3609.
[8] Xia, Y. N., Gates, B., Yin, Y. D., & Lu, Y. (2000). *Adv. Mater.*, *12*, 693.
[9] Castelvetro, V., Devita, C. (2004). *Adv. Colloid Interfac.*, *108*, 167.
[10] Kickelbick, G., & Liz-marzan, L. M. (2003). *J. Nanosci. Nanotechno.*, *2*, 217.
[11] Caruso, R. A., & Antonietti, M. (2001). *Chem. Mater.*, *13*, 3272.
[12] Yaglioglu, B., Huang, Y. J., & Yeom, H. Y. (2006). *Thin soild Films*, *496*, 89.
[13] Kaya, C., He, J. Y., Gum, X., & Butler, E. G. (2002). *Micropor. Mesopor. Mat.*, *54*, 37.
[14] Brune, A., Lajavardi, M., Fisler, D., & Wagner, Jr. J. B. (1998). *Solid State Ionics*, *106*, 89.
[15] Joo, J., Yu, T., Kim, Y. Y., Park, H. M., Wu, F., Zhang, J. Z., & Hyeon, T. (2003). *J. Am. Chem. Soc.*, *125*, 6553.
[16] Huang, J. C., Chu, Y. P., Wei, M., & Deanin, R. D. (2004). *Adv. Polym. Tech.*, *23*, 298.
[17] Jung, S.C., Lee, J. E., & Chang, S. H. (2004). *Compos. Struct.*, *66*, 439.
[18] Berge, B., & Peseux, J. (2000). *Eur. Phys. J. E.*, *3*, 159.

[19] Choi, J., Kim, S. G., & Laine, R. M. (2004). *Macromolecules*, *37*, 99.
[20] Hsiue, G. H., Liu, Y. L., & Liao, H. H. (2001). *J. Polym. Sci. Polym. Chem.*, *39*, 986.
[21] Liu, H., Zheng, S., & Nie, K. (2005). *Macromolecules*, *38*, 5088.
[22] Kang, D. J., Han, D. H., & Kang, D. P. (2009). *J. Non-Cryst. Solids.*, *355*, 397.
[23] Kang, D. J., Han, D. H., Kang, D. P., Yoo, J. W., & Kim, B. U. (2008). *Opt. Express*, *16*, 18320.
[24] Schubert, U., Huesing, N., & Lorenz, A. (1995). *Chem. Mater.*, *7*, 2010.
[25] Wen, J., & Wilkes, G. L. (1996). *Chem. Mater.*, *8*, 1667.
[26] Schmidt, H. (1994). *J. Sol-Gel Sci. Techn.*, *1*, 217.
[27] Schmidt, H., Jonschker, G., Goedicke, S., & Mennig, M. (2000). *J. Sol-Gel Sci. Techn.*, *19*, 39.
[28] Ksapabutr, Gulari, E., Wongkasemjit, S. (2004). *Powder Technol.*, *148*, 11.
[29] Wu, J. C. S., & Cheng, L. C. (2000). *J. Memb. Sci.*, *167*, 253.
[30] Hao, Y., Li, J., Yang, X., Wang, X., & Lu, L. (2004). *Mater. Sci. Eng. A.*, *367*, 243.