

Thermal Expansion Coefficient and Young's Modulus of Silica-Reinforced Epoxy Composite

Hyu Sang Jo, Gyo Woo Lee

Abstract—In this study, the evaluation of thermal stability of the micrometer-sized silica particle reinforced epoxy composite was carried out through the measurement of thermal expansion coefficient and Young's modulus of the specimens. For all the specimens in this study from the baseline to those containing 50 wt% silica filler, the thermal expansion coefficients and the Young's moduli were gradually decreased down to 20% and increased up to 41%, respectively. The experimental results were compared with filler-volume-based simple empirical relations. The experimental results of thermal expansion coefficients correspond with those of Thomas's model which is modified from the rule of mixture. However, the measured result for Young's modulus tends to be increased slightly. The differences in increments of the moduli between experimental and numerical model data are quite large.

Keywords—Thermal Stability, Silica-Reinforced, Epoxy Composite, Coefficient of Thermal Expansion, Empirical Model.

I. INTRODUCTION

THE high adhesiveness to other substrates and good heat and chemical resistances of the epoxy resin make it the most widely used thermo-setting plastics in the world. Due to the better mechanical property than the other resins epoxy has lots of industrial applications such as reinforced-plastics, mold products, layered plates, adhesive materials, and so on. Besides its single use, epoxy resin has been used as a matrix of composites which are reinforced with several fillers. Numerous research works about the properties enhancement of composites have been carried out. The enhancement of mechanical, thermal, electrical, and viscoelastic properties has been done through the reinforcing filler such as carbon nanotubes, nanofibers, various particles, and so on.

In particular with the thermal property of the epoxy composite, Choi et al. [1] reported the control of the thermal expansion coefficient (CTE) of epoxy/inorganic composites by changing the amount of the inorganic additives such as talc and fused silica. Ku et al. [2] fabricated multi-walled carbon nanotube reinforced composite specimens by using shear mixing and ultra-sonication, and showed the measured CTEs to assess the thermal stability of the composites; while, the addition of silica nanoparticles (23 nm, 74 nm, and 170 nm) to a lightly cross-linked epoxyresin, was studied by Dittanet and Pearson [3]. They investigated the effect of silica nanoparticle

content and particle size on glass transition temperature, coefficient of thermal expansion, Young's modulus (E), yield stress, fracture energy, and fracture toughness. Also they reported some particle size dependency of CTEs of the composites.

Although the properties of resin, hardener and filler materials are well known, it is not easy to estimate exactly the composite properties. So, a lot of empirical or semi-empirical models to calculate the composite properties have been developed. A few representative models for the CTE are the rule of mixture (RoM) [4], Thomas' [4], Turner's [5] and Kerner's [6] model. However, the well-known models for Young's modulus of the composites are Kerner's [6], Mori-Tanaka's [7] and Halpin-Tsai's [8]. In this study, the volume-based simple models of RoM and Thomas' are investigated. Details of the models are described in the following section.

In this study, the evaluation of thermal stability of the micrometer-sized silica particle reinforced epoxy composite was carried out through the measurement of thermal expansion coefficient and Young's modulus of the specimen. Also the results from simple empirical models compared with those from the experiment.

II. EXPERIMENTAL DETAILS AND MODELS

A. Materials and Composite Fabrication

YDF-161 (Bisphenol-F type) epoxy resin purchased from Kukdo Chemical Co., Ltd. (Seoul, South Korea) was chosen as the matrix. Jeffamine D-230 manufactured by Huntsman International LLC was used as a curing agent for the epoxy resin. A commercial grade micrometer-sized (3 μm in mean diameter) silica powder, SILNOS 230 from ABC Nanotech Co. Ltd. (Daejeon, South Korea), was selected as a filler material to improve the thermal property of the epoxy composite. The fused silica powder was used as received without any further purification. Details about the matrix and filler material properties like density, Young's modulus, tensile strength and coefficient of thermal expansion are presented in Table I.

Composite samples were fabricated using YDF-161 resin along with the hardener at a weight ratio of 3:1. Before mixing with the nanotube filler, the air entrapped in the epoxy resin was released using a vacuum desiccator with an air release agent (BYK-A 500, BYK-Chemie GmbH) for two hours. The silica particles were then added to the resin in appropriate amounts to reach the desired loadings, and were then dispersed in the resin using a shear mixer (PDM-300 Paste mixer, Dae Wha Tech. Co., Ltd., Yongin, South Korea) and an ultrasonic bath sonicator (WUC-A03H, Daihan Scientific Co., 100 W

H. S. Jo, Graduate School Student, is with the Division of Mechanical DesignEngineering, Chonbuk National University, Jeonju, Jeonbuk 561-756, South Korea (e-mail: whgbtkd@jbnu.ac.kr).

G. W. Lee, Corresponding Author and Associate Professor, is with the Division of Mechanical DesignEngineering, Chonbuk National University, Jeonju, Jeonbuk 561-756, South Korea (e-mail: gwlee@jbnu.ac.kr).

peak out, 40 kHz frequency, Seoul, South Korea). After mixing with the filler, a curing agent was added and mixed with the epoxy resin using a paste mixer. When the mixing of epoxy resin with the filler and hardener was completed, the resin

mixture was poured into silicone molds and cured at 400 kPa pressure and room temperature for one day. This was followed by post curing in an oven at 80 °C for 6 hours. The detailed fabrication process is shown in Fig. 1.

TABLE I
PROPERTIES OF EPOXY MATRIX AND SILICA FILLER

| | Materials | Density (kg/m ³) | Young's Modulus (GPa) | Tensile Strength (MPa) | Coefficient of Thermal Expansion (x 10 ⁻⁶ /K) |
|--------|-------------------------------|------------------------------|-----------------------|------------------------|--|
| Matrix | Epoxy Resin (YDF-161) | 1,170[9] | 1.2[11] | 77.7[11] | 31.87[11] |
| | Curing Agent(D230) | 948[10] | | | |
| Filler | SiO ₂ (SILNOS 230) | 2,200[12] | 73.0[13] | 48.0[13] | 0.55[13] |

Specimens having different filler loadings were prepared from baseline (that is, neat epoxy) to 50 wt% filler content specimens with respect to the weight of the resin. 115 mm-long and more than 4 mm-thick dog-bone shaped specimens fabricated following the standard test method (ASTM D638-10) were used in the investigation of the tensile strength and stiffness. Rectangular-shaped specimens (45 mm (L) x 10 mm (W)) of 3 mm thickness were fabricated and used to determine the coefficient of thermal expansion.

of the specimens were calculated from measured thermal strain differences divided by temperature differences. The thermal strains were measured using strain gages (CEA-13-240UZ-120, Micro-measurements) and a strain indicator (P3, Micro-measurements) using a half bridge connection. Also, the temperatures of the specimens were measured using T-type thermocouples (TG-T-36-500, Omega Eng. Inc.) and an A/D converter (34970A, Agilent Technologies).

C. Empirical Models

As mentioned in Introduction, various empirical or semi-empirical models to estimate the properties of composites have been presented. In this study, two simple volume-based models were used to compare the numerical results with those of measurement. Volume fractions of the matrix and filler were calculated as in (1). In this equation f , ρ , and m denote the volume fraction, density, and mass, respectively. The subscript f and m stand for the filler and matrix, respectively.

$$f_f = \frac{\left(\frac{m_f}{\rho_f}\right)}{\left(\frac{m_f}{\rho_f}\right) + \left(\frac{m_m}{\rho_m}\right)} f_m = 1 - f_f \quad (1)$$

The data presented in Table I were used as the input data for the empirical models.

At first, a rudimentary model, the rule of mixture (RoM), was tried. In this simple model the mechanical interaction between matrix and filler was ignored. Equation (2) is showing the RoM model. In this equation f and α denote the volume fraction and thermal expansion coefficient, respectively. The subscript c , f and m stand for the composite, filler and matrix, respectively.

$$\alpha_c = f_f \alpha_f + f_m \alpha_m \quad (2)$$

The second empirical model, the Thomas model, for the composite properties was modified from the RoM model. It uses the arbitrary index, as seen in (3), ranging from -1 to +1 to follow the experimental results. In this study the arbitrary index, a , was selected as 0.75 to allow the best fit with the experimental results.

$$\alpha_c^a = f_f \alpha_f^a + f_m \alpha_m^a \quad (3)$$

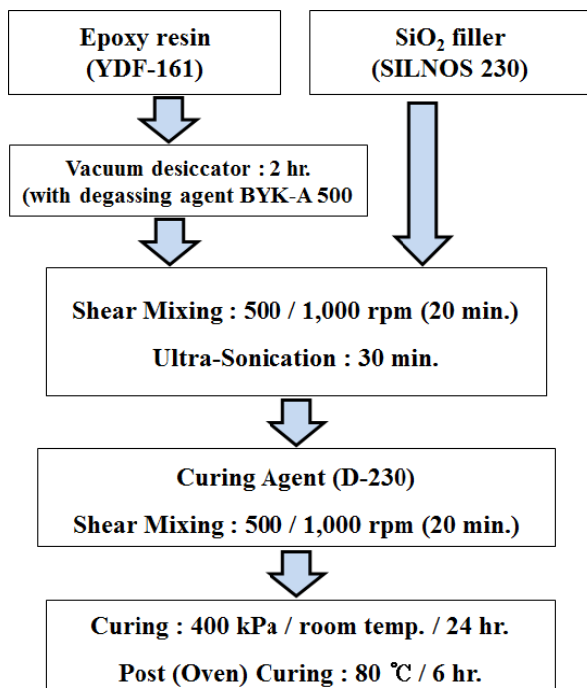


Fig. 1 Fabrication process of specimen

B. Measurements

In this study, a field emission scanning electron microscope (FE-SEM, S-4700, Hitachi Ltd., in KBSI (Korea Basic Science Institute) Jeonju Center, Jeonju, South Korea) was used to qualitatively assess the dispersion of the silica filler in a matrix, using high and low magnified images. A tensile test, using a universal testing machine (RB 301 Unitech T, R&B Inc., Daejeon, South Korea), was used to measure the tensile strengths and stiffnesses. The coefficients of thermal expansion

III. RESULTS AND DISCUSSION

A. Coefficient of Thermal Expansion

The fracture surfaces of the specimens were magnified and are shown in Fig. 2. Figs. 2 (a) and (c) show 500 and 5,000 times magnified fracture surface images, respectively, of the specimen containing 10 wt% silica filler. The images of the right hand side (Figs. 2 (b) and (d)) show the fracture surface of the composite specimen having 30 wt% silica filler. From these low and highly magnified images it is believed that the dispersion of silica filler in the epoxy matrix is fairly good.

Thermal strains with temperature increase were measured and are plotted in Fig. 3. The temperature increment was 1°C per 3 minutes from room temperature to 67°C. The temperature of the specimen surface and the thermal strain were measured and stored at one second increments using a data logger and computer. From these raw data, linear sections were selected from 30 to 50°C to calculate the coefficients of thermal expansion as seen in the small figure in Fig. 3. Three groups of thermal strain measurements were performed and the coefficients of thermal expansion (CTEs) were calculated. The CTEs were then averaged and normalized with respect to those of the baseline, as shown in Fig. 4. The specimens containing 50 wt% silica shows lower thermal expansions than those of the other specimens. A thermal stability enhancement of approximately 20% was obtained. The CTEs of baseline samples were measured and averaged as $31.9 \times 10^{-6}/K$. The averaged CTE of the baseline specimens was used as the material property of the matrix as seen in Table I. The results of the two empirical models, RoM model and Thomas model, are also presented in Fig. 4. The RoM model shows only 5 % overestimation with respect to the experiment at the case of 50 wt% silica content. The results from Thomas model which has an arbitrary index of 0.75 was well fitted with the experimental data. From the coinciding tendencies of CTEs in the experiment data and the volume-based empirical models, it is believed that the thermal expansion property of this silica-reinforced composite is volume-dependent.

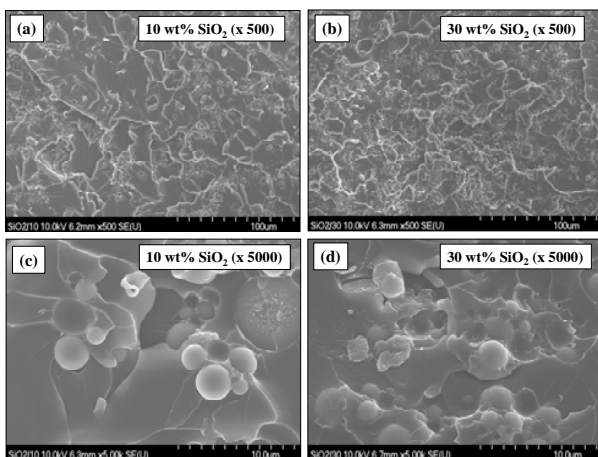


Fig. 2 SEM images of the fracture surfaces of specimens for 10 wt% (a) and (c), images of the left hand side) and 30 wt% ((b) and (d), right hand side) silica filler concentrations

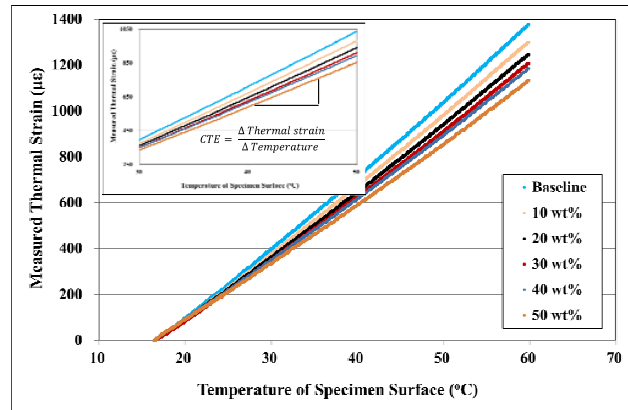


Fig. 3 Measured thermal strains of several specimens containing silica filler with temperature of specimen surface

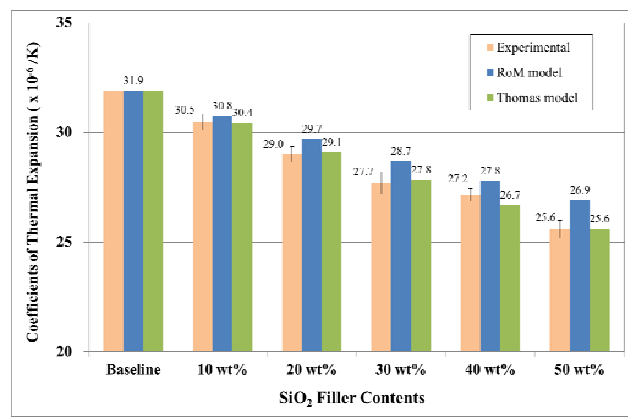


Fig. 4 Coefficients of thermal expansion of specimens with concentrations of silica filler

B. Tensile Strength and Young's Modulus

The tensile strength and stiffness of the composite specimens are seen in Fig. 5 and 6, respectively. For the experimental data, more than 5 specimens were tested in each case, and the data were averaged. Data labels in both figures are the strengths and moduli. In the case of baseline specimens, tensile strength and the Young's modulus were obtained as 77.7 MPa and 1.23 GPa, respectively. These strength and stiffness for the neat epoxy were used as the input properties, as seen in Table I, for the empirical models. In Fig. 5, differ from the estimation by the models; it is unclear to see the decreasing tendency of the tensile strength in the experimental result with respect to the silica contents. Compared with the small standard deviations of CTEs in Fig. 4, the deviations of tensile strength in Fig. 5 are quite large. The similar values of the tensile strength of matrix and filler material as seen in Table I might be the reason of this unclear result. However, the measured result for Young's modulus in Fig. 6 tends to be increased slightly. The differences in increments of the moduli between experimental and numerical model data are quite large. From this big differences of the Young's moduli between the experiment and the empirical models, we believe that these kinds of volume-based models want to estimate the Young's modulus of the composite

need an additional terms related with the interfacial area between matrix and filler and size of the filler materials.

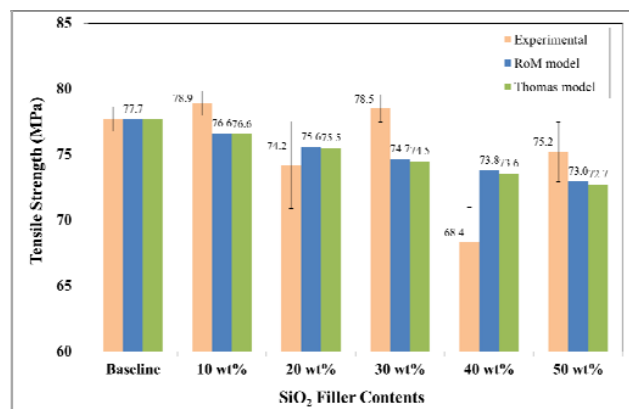


Fig. 5 Averaged tensile strengths and standard deviations with respect to the concentrations of silica filler

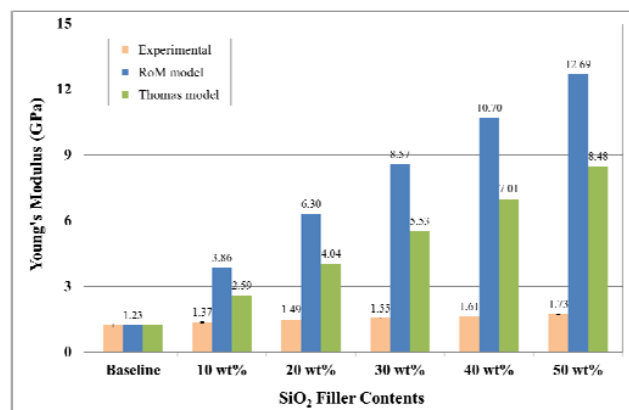


Fig. 6 Averaged Young's moduli and standard deviations with respect to the concentrations of silica filler

IV. CONCLUSION

In this study, the evaluation of thermal stability of the micrometer-sized silica particle reinforced epoxy composite was done through the measurement of thermal expansion coefficient and Young's modulus of the specimens. For all the specimens in this study from the baseline to those containing 50 wt% silica filler, the thermal expansion coefficients and the Young's moduli were gradually decreased down to 20% and increased up to 41%, respectively. The experimental results were compared with filler-volume-based simple empirical relations. The experimental results of thermal expansion coefficients correspond with those of Thomas's model which is modified from the rule of mixture. However, the measured result for Young's modulus tends to be increased slightly. The differences in increments of the moduli between experimental and numerical model data are quite large. From this big differences of the Young's moduli between the experiment and the empirical models, we believe that these kinds of volume-based models want to estimate the Young's modulus of the composite need an additional terms related with the interfacial

area between matrix and filler and size of the filler materials.

ACKNOWLEDGMENT

This research was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (Grant No. NRF-2011-0009109).

REFERENCES

- [1] Choi, Y. S., Chae, I. S., Kang, Y. S., Won, J. G., Kim, J. J., and Kim, S. D., "Tuning Thermal Expansion Coefficient of Composites Containing Epoxy Resin/Inorganic Additives for Stone Conservation," *Journal of Conservation Science*, Vol. 27, No. 4, pp. 431~440, 2011.
- [2] Ku, M. Y., Kim, J. H., Kang, H. Y., and Lee, G. W., "Measurement of Mechanical Property and Thermal Expansion Coefficient of Carbon-Nanotube-Reinforced Epoxy Composites," *Trans. of the KSME(B)*, Vol. 37, No 5, pp. 657~664, 2013.
- [3] Dittanet, P., and Pearson, R. A., "Effect of Silica Nanoparticle Size on Toughening Mechanisms of Filled Epoxy," *Polymer*, Vol. 53, No 9, pp. 1890~1905, 2012.
- [4] Ehrenstien, G. W., Riedel G., and Trawiel P., "Thermal Analysis of Plastic: Theory and Practice," Hanser, 2004.
- [5] Turner, P. S., "Thermal-Expansion Stresses in Reinforced Plastics," *Research of the National Bureau of Standards*, Vol. 37, No 4, pp. 239~250, 1946.
- [6] Kerner, E. H., "The Elastic and Thermo-Elastic Properties of Composite Media," *Proc. Phys. Soc. B*, Vol. 69, pp. 808~813, 1956.
- [7] Mori, T., and Tanaka, K., "Average Stress in the Matrix and Average Elastic Energy of Materials with Misfitting Inclusions," *Acta metall.*, Vol. 21, pp. 571~574, 1973.
- [8] Halpin, J. C., "Stiffness and Expansion Estimates for Oriented Short Fiber Composites," *Composite Materials*, Vol. 3, pp. 732~734, 1969.
- [9] General description of YDF-161 from Kukdo Chem. Co., Ltd.
- [10] Technical bulletin of Jeffamine D230 from Huntsman Corp.
- [11] From the measurement of baseline specimens of this study
- [12] Technical data sheet of SILNOS 230 from ABC Nanotech Co.,Ltd.
- [13] www.accuratus.com