CRYOGENIC THERMAL EXPANSION AND MECHANICAL PROPERTIES OF EPOXY RESIN MODIFIED WITH POLYDIMETHYLSILOXANE

J. W. Yi[1*], Y. J. Lee[1], W. Lee[1], S. B. Lee[1], M. K. Um[1]

[1]Composites Research Center, Korea Institute of Materials Science (KIMS), 797 Changwondaero, Seongsan-gu, Changwon city, Gyeongnam, South Korea
**yjw0628@kims.re.kr*

Keywords: Cryogenic, Thermal expansion, Polydimethylsiloxane, Epoxy matrix

Abstract

In order to improve the mechanical properties and simultaneously reduce the thermal expansion coefficient (CTE) of epoxy resins under low temperature, a study of the effect of a liquid-type additive, polydimethylsiloxane (PDMS) on the cryogenic properties was performed. Phenol novolac-based epoxy resin was blended with an aromatic amine curing agent, silicone-modified epoxy resin (SME) and PDMS liquid. In particular, SME was added to the blend as a compatibilizer because it was a critical factor to increase the mechanical properties. It is also expected that a very small amount of PDMS liquid has no detrimental effect on the CTE of the resin mixture. In case of an addition of 0.05wt% PDMS coupled with the compatibilizer (20 wt%), the tensile strength has been drastically improved by up to 11 % at 173 K compared to that of unmodified epoxy. It was thought that both PDMS and the compatibilizer favorably affected the strength and toughness of the epoxy resin by dispersing the localized stress and interrupting the propagation of cracks. In addition, relationship between the glass transition temperature and CTE of the epoxy resin was investigated to find out the optimal cure process conditions.

1 Introduction

Composites materials have been applied in various fields, especially, a cryogenic environment such as aerospace, next generation transportation system, superconductivity, LNG/LPG storage vessels, and military parts due to their excellent mechanical properties. One of critical factors to be considered in the low-temperature usage of the composites is that the discrepancy of the thermal contraction between reinforcing fibers and matrix resin should be reduced. The difference of the contraction which corresponds to coefficient of thermal expansion (CTE) can lead to interfacial failure resulting in the deterioration of mechanical properties [1]. It is also important to improve the toughness of matrix resin at low temperature conditions.

Many researchers have reported the results about the improvement of toughness of matrix resin using organic additives and inorganic or fillers [2-11]. However, at least more than 10wt% of the fillers should be added into matrix resin to obtain practically positive effect on the CTE and mechanical properties. In case of rubber additives, since the thermal contraction of a resin mixture containing them increases drastically under a cryogenic condition, the CTE mismatch with reinforced fibers may give rise to additional deterioration of the mechanical properties.

In this study, general epoxy resin was mixed with organic additives to improve mechanical properties under the low temperature and the reinforcement mechanism of the organic additives was also suggested. Furthermore, to secure the optimal cure process for minimizing the CTE of the resin, not only the relation between glass transition temperature and CTE, but also behavior of the volume change during the post cure were studied.

2 Experimentals

2.1 Materials

The phenol novolac-based epoxy resin (YDPN-631, EEW: 165~185) was supplied by Kukdo Chemical. 4,4’-diaminodiphenyl sulfone (DDS) as a curing agent was also purchased from Kukdo Chemical. Polydimethylsiloxane (PDMS, KSR-1000) liquid provide by Dow Corning was added to enhance the mechanical properties of epoxy resin blends. Silicone-modified epoxy resin (SME, Kukdo Chemical) was used to increase the compatibility between epoxy resin system and PDMS liquid.

2.2 Blend preparation and characterizations

YDPN-631, SME, DDS, and PDMS were mixed with the stoichiometric balance. The mixture was agitated vigorously at 135℃ by a mechanical stirrer until DDS and SME were clearly dissolved into the base resin. And then, the mixture was degassed for 60 minutes at 80℃ under vacuum condition to remove trapped air. After being degassed, the mixtures were cured at 100℃ for 60 minutes, then at 150℃ for 90 minutes and finally at 180℃ for 120 minutes. Post curing was performed for 120 minutes at 200℃ and 220℃, respectively.

The curing behavior of the mixtures was studied using a DSC (DSC 7, Perkin Elmer). Approximate 2 mg of each sample was sealed in an aluminum pan and was dynamic-scanned from 50℃ to 300℃ at a heating rate of 10℃/min. The isothermal scanning for each curing temperature was also carried out. The heat of curing reaction was obtained from the DSC curves of the mixtures. The degree of cure (α) was calculated by the equation shown in (1).

$$\alpha = \Delta H_i / \Delta H_t = \frac{1}{\Delta H_t} \int_0^t \left(\frac{\partial Q}{\partial t} \right)_T dt \quad (1)$$

where ΔH_t is the total heat of curing reaction, ΔH_i is the heat of curing reaction at each isothermally-scanned temperature. To measure the glass transition temperature (T_g) and coefficient of thermal expansion (CTE) of the resin mixtures, a thermomechanical analysis was conducted using a thermomechanical analyzer (TMA 7, Perkin Elmer). The cured samples were cut into $8 \times 8 \times 8 mm^3$ and then placed in a temperature-controlled chamber equipped with an expansion type probe. T_g data were obtained at a heating rate of 5℃/min.

Tensile properties of the blended resin were evaluated at 298K and 173K according to the ASTM standard D638. Modulus of specimens was measured using a strain gauge (FCA-5-11-1L, Tokyo Sokki Kenkyuio). Data were taken from an average of at least five specimens. Coefficient of thermal expansion of the resins under the cryogenic condition was measure by the reported method [12]. The cryogenic CTE of the resins were measured by the equipment consisting of a temperature controller, a temperature monitor, and a temperature sensor (DT-670, LakeShore). First, the specimen to which a strain gauge was attached was put in a chamber and the ambient temperature was lowered to 4K. And then the apparent strain was measured while slowly rising the temperature. The CTE was calculated through the calibration with a standard material, titanium silicate.

3 Results and discussion

3.1 Effect of PDMS on the mechanical properties

It is known that phenol novolac-based epoxy resin is not compatible with PDMS liquid due to the relatively hydrophobic characteristic of PDMS. According to our previous work [13], SME resin acted as an effective compatibilizer with PDMS for the resin system of a DGEBA-based epoxy resin and anhydride curing agent. Possible explanation for the reason was that SME possesses silicone and epoxy functional group simultaneously. Because of the high viscosity of SME resin, an optimal concentration of SME was 20wt%. Figure 1 shows a schematic diagram for the explanation of the compatibilization.

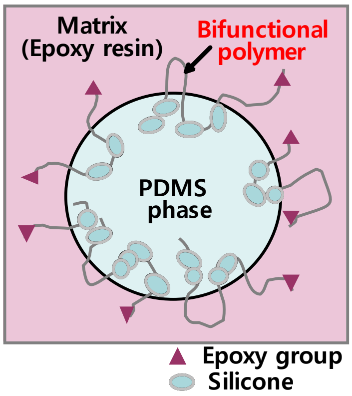

Figure 1. Explanatory schematic for the compatibilization of SME.

In addition, PDMS improved the low temperature properties because the PDMS droplets were capable of dispersing the localized stress and interrupt the propagation of cracks during the fracture at the low temperature. This accelerated a cavitation of PDMS droplets followed by multiple generation of numerous micro-deformations. Therefore, it is expected that the SME can stabilize the PDMS droplets and the PDMS can also enhance the low temperature properties for the mixture of phenol novolac-based epoxy resin and DDS.

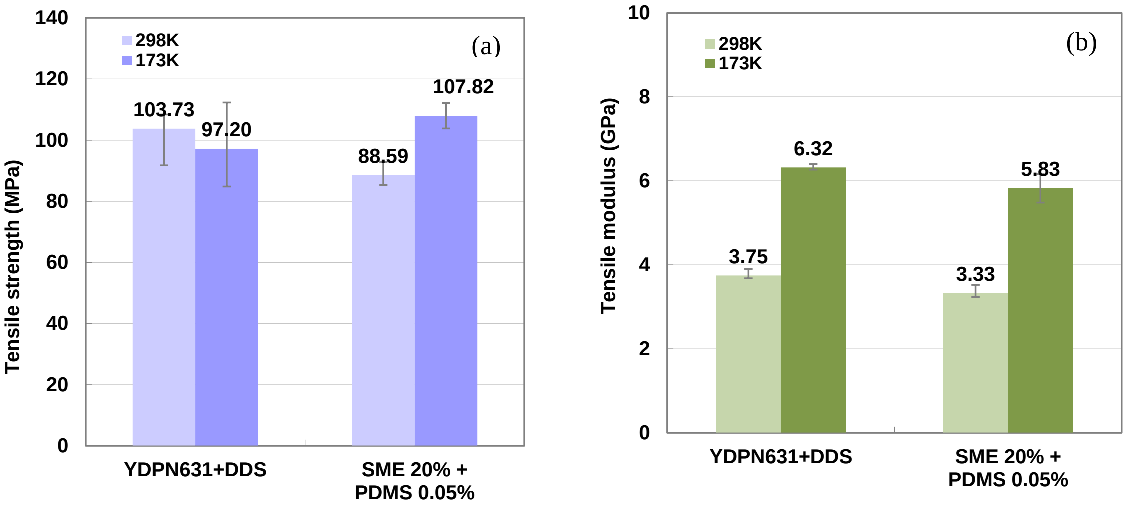

Figure 2. Effect of PDMS on the ultimate tensile strength at 298K and 173K: (a) Strength and (b) modulus.

Figure 2 shows the effect of PDMS on the tensile strength and modulus. In case of room temperature, the tensile strength of PDMS-containing epoxy resin decreased compared to the unmodified epoxy resin which only included the base resin (YDPN-631) and curing agent (DDS). This is because of the low stiffness of SME resin while a very small amount of PDMS has no effect on the stiffness. In case of 173K testing condition, the tensile strength of the resin with 0.05wt% of PDMS was increased by about 11% compared to that of unmodified resin. Noticeable thing is that despite the lower modulus, the modified epoxy resin showed a higher strength indicating the higher elongation at the low temperature.

3.3Relationship between glass transition temperature and CTE

In order to fabricate resin samples with different T_g, the post-curing temperature was varied: 200℃ and 220℃. Figure 3 showed the T_g of each resin sample cured at different temperatures. The T_g of each resin was 455K, 480K and 491K, respectively and they were increased with the post cure temperature. Furthermore, the corresponding degree of cure had a similar tendency. This means that additional cross-linking reaction by the post cure leads to the increase of T_g.

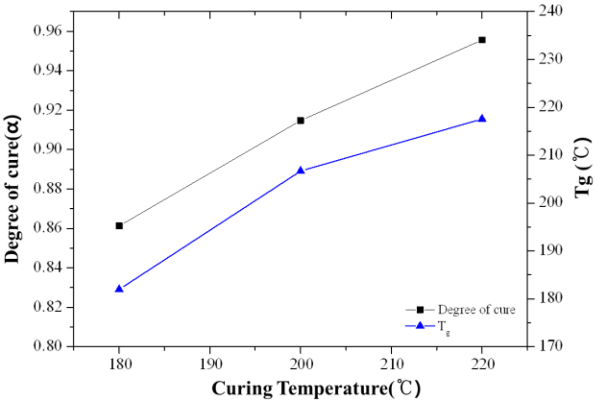

Figure 3. Degree of cure and T_g of pre-cured and post-cured epoxy resins.

CTE of the resin with different T_g was measured and the results were shown in figure 4. According to the result, a resin with a higher T_g showed a higher CTE and this was also observed in the same way with a TMA measurement. The high CTE originating from the post cure can cause a deterioration of mechanical properties of fiber-reinforced epoxy composites used in the cryogenic applications. Moreover, these experimental results are completely contrary to a general expectation that the higher T_g a resin has, the lower CTE.

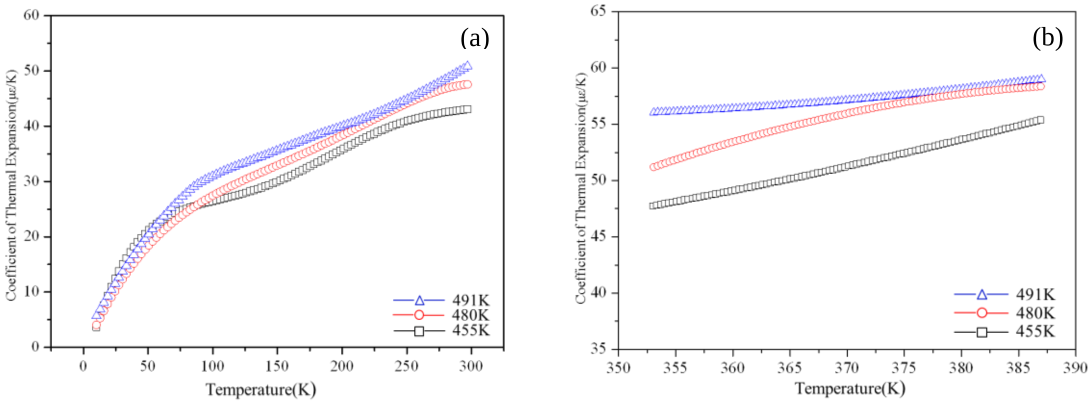

Figure 4. CTE of pre-cured and post-cured epoxy resins: (a) 4~298K and (b) 353~388K.

This contradictory trend of T_g can be explained by a generation of residual stresses induced by the post curing. The volume change of a resin sample with T_{g1} starting from T_o to T_{g2} can be depicted as shown in figure 5. At first, the volume expansion below T_{g1} follows the path ① and then rapid volume expansion takes places along with the path ②. However, since an additional cross linking is induced by a post cure resulting in a volume contraction, the path ③ become dominant. At this point, residual tensile stress can remain inside the sample when the ambient temperature directly comes down to T_o (Path ④). If the ambient temperature increase again without mitigation of the residual tensile stress, the volume change may follow the path ⑤ resulting in a higher CTE. This result suggests that it is necessary to release the residual stress inside epoxy composites post-cured at a high temperature.

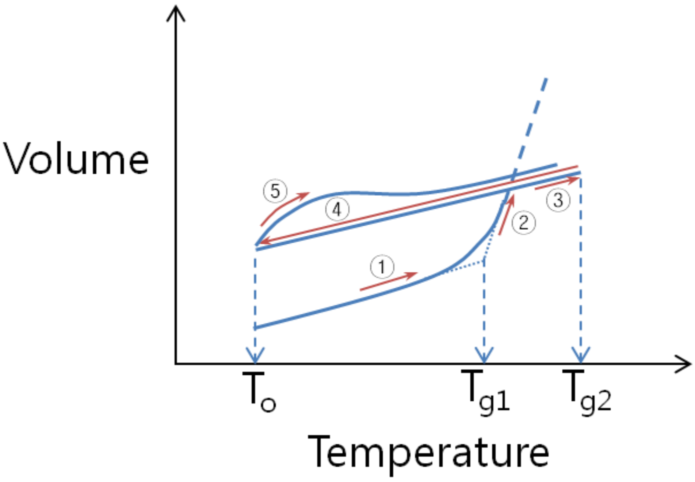

Figure 5. Schematic of the volume change for the explanation of the CTE change.

4 Conclusions

Phenol novolac-based epoxy resin was blended with a liquid-type additive, PDMS to improve the low temperature mechanical properties. The experimental results showed that the addition of PDMS (0.05 wt%) coupled with the compatibilizer (20 wt%), the tensile strength have been improved by up to 11 % at 173 K compared to that of unmodified epoxy. It was thought that PDMS dispersed the localized stress and interrupting the propagation of cracks. Through the study about relationship between T_g and CTE, the optimal cure process condition to minimize CTE of the resin was suggested.

Acknowledgement

This work was supported by a grant from the general research program supported by Korea Institute of Materials Science (KIMS).

References

[1] Kim M. G., Kang S. G., Kim C. G., Kong C. W. Tensile properties of CFRP composite with different resin composition under cryogenic temperature. *Journal of the Korean Society for Composite Materials*, **Vol. 20**, No. 1, pp. 1-8(2007).

[2] Jin H. Y., Yang Y. Q., Xu L., Hou S. E. Effects of spherical silica on the properties of an epoxy resin system. *Journal of Applied Polymer Science*, **Vol. 121**, pp. 648-653(2011).

[3] William K., Kessler M. R. Thermal expansion of fumed silica/cyanate ester nanocomposites. *Journal of Applied Polymer Science*, **Vol. 109**, pp. 647-653(2008).

[4] Veena M. G., Renukappa N. M., Raj J. M., Ranganathaiah C., Shivakumar K. N. Characterization of nanosilica-filled epoxy composites for electrical and insulation applications. *Journal of Polymer Science Part A: Polymer Chemistry*, **Vol. 121**, pp. 2752-2760(2011).

[5] Cho J., Joshi M. S., Sun C. T. Effect of inclusion size on mechanical properties of polymeric composites with micro and nano particles. *Composites Science and Technology*, **Vol. 66**, pp. 1941-1952(2006).

[6] Chu X., Huang R., Yang H., Wu Z., Lu J., Zhou Y., Li L. The cryogenic thermal expansion and mechanical properties of plasma modified ZrW_2O_8 reinforced epoxy. *Materials Science and Engineering A*, **Vol. 528**, pp. 3367-3374(2011).

[7] Yang J. P., Yang G., Xu G., Fu S. Y. Cryogenic mechanical behaviors of MMT/epoxy nanocomposites. *Composites Science and Technology*, **Vol. 67**, pp. 2934-2940(2007).

[8] Jansen B. J. P., Tamminga K. Y., Meijer H. E. H., and Lemstra P. J. Preparation of thermoset rubbery epoxy particles as novel toughening modifiers for glassy epoxy resins. *Polymer*, **Vol. 40**, pp. 5601-5607(1999).

[9] Chen Z. K., Yang G., Yang J. P., Fu S. Y., Ye L., Huang Y. G. Simultaneously increasing cryogenic strength, ductility and impact resistance of epoxy resins modified by n-butyl glycidyl ether. *Polymer*, **Vol. 50**, pp. 1316-1323(2009).

[10] Kim B. C., Park S. W., Lee D. G. Fracture toughness of the nano-particle reinforced epoxy composite. *Composite Structures*, **Vol. 86**, pp. 69-77(2008).

[11] Yang J. P., Chen Z. K., Yang G., Fu S. Y., Ye L. Simultaneous improvements in the cryogenic tensile strength, ductility and impact strength of epoxy resins by a hyperbranched polymer. *Polymer*, **Vol. 49**, pp. 3168-3175(2008).

[12] Lee W., Lee S. B., Yi J. W., Um M. K. Calibration of strain gauge for thermal expansion coefficient of fiber reinforced composites at cryogenic temperature. *Journal of the Korea Institute of Applied Superconductivity and Cryogenics*, **Vol. 12**, No. 3, pp. 1-6(2010).

[13] Yi, J. W., Ban C. S., Lee S. B., Lee W., Um M. K. *A study of the effect of polydimethylsiloxane on low temperature properties of epoxy resin* in Proceeding of ICCM-18, Jeju ICC, South Korea, (2011).