A STUDY OF THE EFFECT OF POLYDIMETHYLSILOXANE ON LOW TEMPERATURE PROPERTIES OF EPOXY RESIN

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1 Introduction

Fiber-reinforced polymer (FRP) composites have been taken into consideration as a promising material in the applications such as aerospace, next generation transportation system, superconductivity, and military parts. Due to their good mechanical properties and thermal barrier characteristics under severe conditions, there have been increasing demands for FRP composites, especially, in cryogenic applications. 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. Inorganic particles of micro or nano size such as SiO_2 [2-4], Al_2O_3 [5], ZrW_2O_8 [6], and montmorillonite (MMT) [7] can decrease the thermal contraction of matrix resin. 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. Moreover, surface treatment to enhance the interfacial adhesion between the resin and the fillers is additionally necessary.

Toughened epoxy resins contain, in general, the rubber-type additives such as CTBN (Carboxyl-terminated butadiene acrylonitrile, ATBN (Amine-terminated butadiene acrylonitrile), HTBN (Hydroxyl-terminated butadiene acrylonitrile), silicone-modified resin and urethane-modified resin [8]. These materials show better toughness and mechanical properties than neat epoxy resin at the low temperature as well as room temperature condition [9-11]. Therefore, they have been applied as a potential material and have realized in the cryogenic applications. However, there are still some drawbacks when they are used as a matrix resin of fiber-reinforced composites. For instance, since the thermal contraction of the resins is very high due to the rubber additives, the mismatch of the thermal contraction with the reinforced fiber can give rise to additional deterioration of the mechanical properties.

In this work, general epoxy resin was mixed with some organic additives to improve mechanical properties of the blend resin under the low temperature condition. Several resin blends including silicone-type [12-13] additives were compounded to develop an optimal formulation which could have good mechanical properties and maintain thermal contraction at the low temperature. In addition, the reinforcement mechanism of organic additives was also investigated.

2 Experimentals

2.1 Materials

YD-128 (EEW: 184~190, room temperature viscosity: 11,500~13,500cps), a diglycidyl ether of bisphenol A (DGEBA)-based epoxy resin, was supplied by Kukdo Chemical. KBH-1089, anhydride-type 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.

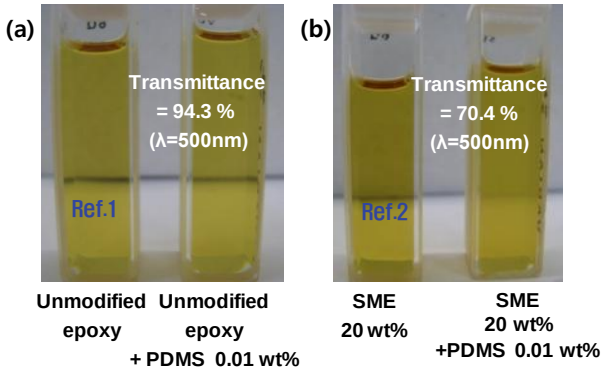

Fig. 1 Transmittance of the blend resins: (a) epoxy resin containing PDMS, and (b) epoxy resin containing both SME and PDMS.

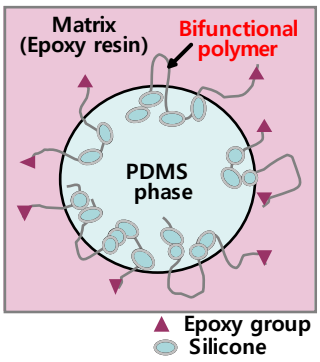

Fig. 2 Explanatory schematic diagram for the compatibilization of SME.

2.2 Blend preparation and characterization

The base resin (YD-128), curing agent (KBH-1089) and some additives were mixed with the stoichiometric balance. The mixtures were agitated vigorously for 20 minutes at room temperature by a mechanical stirrer and were degassed for 60 minutes at 60℃ under vacuum condition to remove trapped air. After degassing, the mixtures were cured at 120℃ for 120 minutes.

Tensile properties of the blended resin were evaluated at 25℃ and -100℃ 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 blend resins was measure by the reported method [14]. Analysis of fracture morphology of the blend resin was conducted by SEM. In order to estimate the miscibility of additives, transmittance of the blend resin was measured at the wavelength of 500nm by UV-Vis spectroscopy.

3 Results and discussion

3.1 Effect of SME resin on compatibilization

It is known that general epoxy resin and PDMS liquid are not compatible because of relatively hydrophobic characteristic of PDMS. Therefore, although epoxy resin and PDMS seem to be well dispersed in early stage of mixing, eventually phase separation occurs. Figure 1(a) shows transmittance of the epoxy resin containing 0.01wt% of PDMS after degassing. Transmittance of unmodified epoxy resin was set as a baseline. The result showed that since the two materials were phase-separated, there was no noticeable difference of transmittance between reference resin and PDMS-containing epoxy resin. However, transmittance of the blend resin containing both SME and PDMS decreased significantly shown in Figure 1(b). This drop is attributed to the difference of refractive index. The result indicated that SME acted as a compatibilizer because SME resin stabilized the PDMS droplets in epoxy resin. Possible explanation for the reason is that SME possesses silicone and epoxy functional group simultaneously. Figure 2 shows a schematic diagram for the explanation of the compatibilization.

3.2 Effect of PDMS on mechanical properties

Due to the high viscosity of SME resin, an optimal concentration should be determined. Therefore, 20wt% of SME was selected considering the processability and compatibilization. Figure 3 shows the effect of PDMS on the tensile strength and modulus. In case of room temperature condition, tensile strength of SME-containing epoxy resin slightly increased compared to the unmodified epoxy resin. Significant improvement of the room temperature properties was not observed regardless of the addition of PDMS.

In case of -100℃ testing condition, as the content of PDMS increased, the tensile strength substantially increased. Tensile strength of the blend resin with 0.05wt% of PDMS was increased by about 41% compared to that of unmodified resin. When 0.1 wt% of PDMS was added, the tensile strength

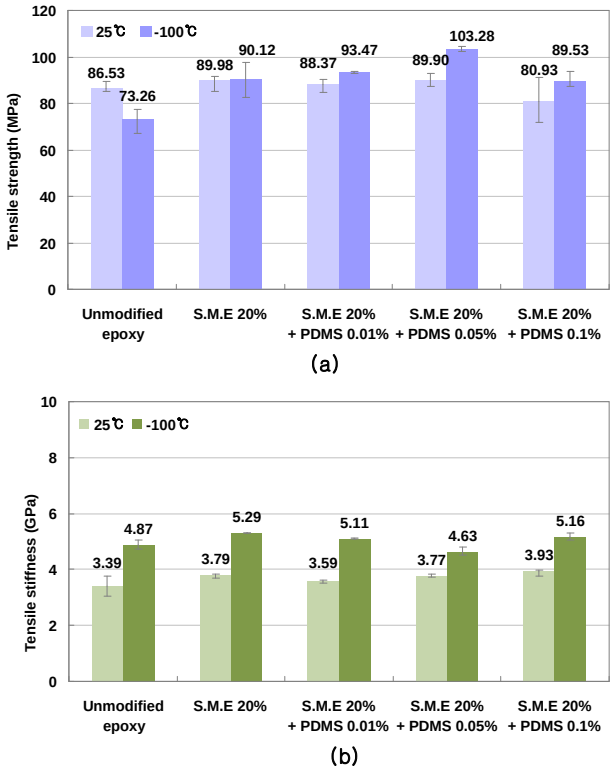

Fig. 3 Effect of PDMS on the ultimate tensile strength at 25℃ and -100℃: (a) Strength and (b) modulus.

decreased. This result can be explained simply by the fact that the amount of PDMS is beyond the ability of SME compatibilization. Tensile modulus of all resin blends was maintained due to no difference of stiffness among base epoxy resin and additives

3.3 Reinforcement mechanism

In order to verify the reinforcement mechanism of PDMS at the low temperature, analysis of fracture morphology was carried out by SEM. Figure 4 shows the fracture surfaces of the blend resins after tensile test at -100℃. As shown in Figure 4(a) and 4(b), a crack initiation point was observed at each sample and then the cracks propagated through the smooth fracture surface. On the other hand, in case of the resin with 20wt% of SME and 0.05 wt% of PDMS (Figure4(c)), it was seen that the crack propagation was obstructed resulting in the rough facture surface which can increase the tensile strength. It is also observed that PDMS droplets in a diameter of 10~20 ㎛ were well distributed

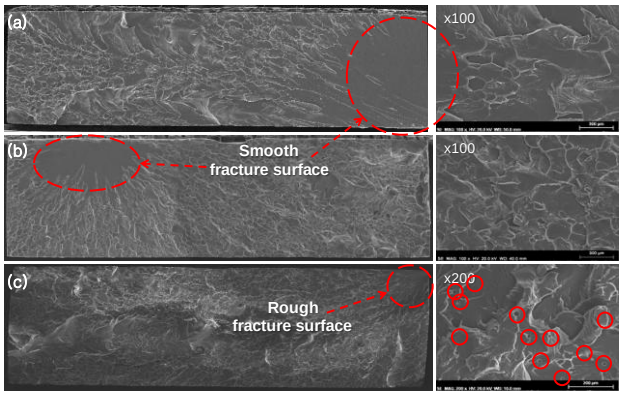

Fig. 4 SEM micrographs of fracture surface morphology after tensile testing at -100℃: (a) unmodified epoxy resin, (b) 20wt% of SME and (c) 20wt% SME and 0.05wt% of PDMS.

throughout the epoxy resin. According to the above results, it is possibly concluded that the reason why an epoxy sample with PDMS only exhibits a rough surface is because of the PDMS droplets which can disperse the localized stress and interrupt the propagation of cracks during the fracture at the low temperature. This accelerates deformation mechanism such as cavitation of PDMS droplets followed by multiple generation of numerous micro-deformations.

In order to ascertain the effect of size of PDMS droplets on the mechanical properties, we decreased the droplet size by controlling a shear rate during the mixing. Another epoxy resin sample for tensile test was fabricated by the same process except that resin mixing was performed by a high-shear homogenizer. Figure 5 shows the comparison of tensile strength with different mixing methods. According to the results, the tensile strength was elevated by decreasing the droplet size and improving the distribution of the droplets. This result confirms the effect of PDMS droplets in the epoxy resin.

3.4 Measurement of CTE

Figure 6 exhibits the CTEs of the blend resins. The results indicated that there was no significant decline of CTE compared to the reference epoxy resin when SME or PDMS were added. This can be explained by very small amount of adding quantity. In the future, CTE of the epoxy blend should be evaluated at very low temperature (~10K).

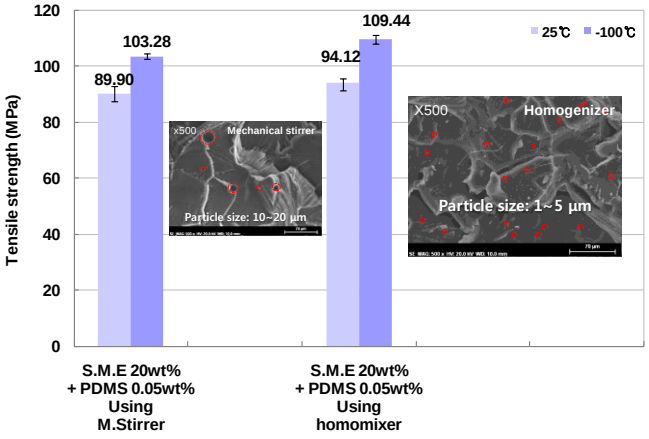

Fig. 5 Comparison of tensile strength of the blend resins fabricated by different mixing methods.

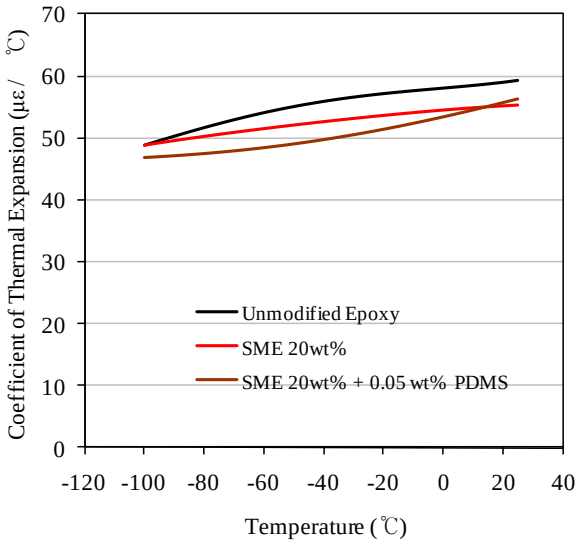

Fig. 6 CTE of the blend resins.

4 Conclusion

In order to improve the mechanical properties of epoxy resin and simultaneously maintain its thermal contraction under the low temperature condition, general epoxy resin was blended with a liquid-type additive, polydimethylsiloxane (PDMS). Silicon-modified epoxy resin was added to the blend as a compatibilizer. It is concluded that PDMS has no detrimental effect on the thermal contraction of the blend if a very small amount of PDMS is properly mixed. In case of an addition of PDMS (0.05 wt%) coupled with the compatibilizer (20 wt%), the tensile strength have been drastically improved by up to 41 % 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 through the promoting deformation mechanism such as cavitation of PDMS particles and multiple generation of numerous micro-deformation.

Acknowledgement

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