



Effect of dimethylpolysiloxane liquid on the cryogenic tensile strength and thermal contraction behavior of epoxy resins



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ABSTRACT

Dimethylpolysiloxane liquid was blended with diglycidyl ether of bisphenol-A epoxy resin including anhydride curing agent to improve the tensile strength of the epoxy resin at 77 K without any increase in its coefficient of thermal expansion (CTE). A bifunctional polymer, silicone-modified epoxy resin (SME), was also added to the mixture as a compatibilizer. The results of UV transmittance for the blend resin showed that the incorporation of the SME could stabilize effectively spherical domains of the siloxane liquid which was immiscible with the epoxy matrix. The tensile strengths of the blend resins at both room temperature and 77 K were measured and SEM analysis for the fractured cross sections was carried out to verify the toughening behavior of the liquid droplets. The results indicated that even small amount of addition of the siloxane liquid (0.05 phr) coupled with SME (20 phr) could enhance the tensile strength at 77 K by 77.6% compared to that of the neat epoxy resin. This improvement is attributed to the fact that the solid and s droplets can disperse the localized stress and interrupt the crack propagation by cavitation mechanism followed by multiple generation of numerous micro-deformation. From the CTE measurement, the siloxane liquid has no influence on the thermal contraction behavior of the blend resin.

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1. Introduction

Fiber-reinforced polymer composites (FRPC) have been widely utilized in the various applications such as aerospace, leisure sports, automotive industry, and military parts. The FRPC also have been taken into consideration as a promising material in cryogenic applications due to their exceptional mechanical properties even under extreme low-temperature conditions [1–3]. One of critical factors to be considered for the usage in the severe environment is the discrepancy of the thermal contraction between reinforcing fibers and matrix resins. The difference of the contractions which directly correspond to the coefficient of thermal expansion (CTE) can lead to the interfacial failure resulting in deterioration of mechanical properties of the composites, in particular, reinforced with continuous fibers [4]. Another important point is the improvement of low temperature strength or toughness of the matrix resins itself. In general, highly cross-linked thermoset resins are mainly used as a matrix for FRPC. Since the resin has poor resistance to crack formation and propagation due to its brittle behavior at low temperature, it is necessary to increase the strength or toughness at low temperature conditions. Otherwise, the formed

cracks throughout the resin may decrease the barrier characteristics as well as the mechanical properties of the composites when they would be used as a composite outer shell of a hydrogen storage tank or structural materials for a liquefied nitrogen gas vessel [5].

Many researchers have reported the results about the improvement of mechanical properties of the resins using organic/inorganic additives and fillers. Inorganic particles of micro or nano size such as SiO₂ [6–8], Al₂O₃ [9,10], ZrW₂O₈ [11], nanoclay [12–14], AlN [15] and carbon nanotubes [16] can increase the mechanical properties and simultaneously decrease the CTE of the resins. However, the resins have some problems as matrix for continuous fiber-reinforced composites. At least more than 10 wt% of the fillers should be added into matrix resin to obtain practically positive effect on the CTE and mechanical properties. This high amount increases viscosity of the resin, which can make it difficult to infiltrate the resin into the reinforcement. Since most of the aggregated or undispersed filler are filtered by the reinforcement, the distribution state of the filler throughout the thickness is not uniform. Moreover, some surface treatments to enhance the interfacial adhesion between the resin and the fillers are additionally necessary.

Toughened epoxy resins contain, in general, the rubber-type additives such as carboxyl-terminated butadiene acrylonitrile

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(CTBN) [17–19], amine-terminated butadiene acrylonitrile (ATBN) [20], hydroxyl-terminated butadiene acrylonitrile (HTBN) [21], silicone-modified resin [22,23], urethane-modified resin [24], polydimethylsiloxane particle [25], and hyperbranched polymer [26–31]. These materials show better toughness and mechanical properties than neat epoxy resin at the low temperature as well as room temperature condition. 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 matrix resin of fiber-reinforced composites or as additive for the resin. For instance, since the thermal contraction of the resin becomes very high due to the rubber additives [17], the mismatch of the thermal contraction with the reinforced fibers can give rise to delamination of the fiber–matrix interface. Therefore, it is of great practical importance to find out a proper filler or additive for a matrix which is capable of improving the toughness at low temperature without significantly impairing the desirable engineering performance such as the thermal contraction and the composite fabrication process.

In this work, in order to improve the properties of matrix resin, we have focused on a dimethyl siloxane based liquid that has a very low T_g (Glass transition temperature) and small viscosity changes with variation in temperature, but incompatible with epoxy resin. Sometimes, the liquid has been compounded with some thermoplastic resins to improve the ambient and low temperature impact strength. The main purpose of this paper is to investigate the effect of the siloxane liquid on the mechanical and thermal behaviors at low temperatures of general epoxy resins. In addition, the toughening mechanism of the organic additive was also investigated.

2. Experiments

2.1. Materials

A diglycidyl ether of bisphenol-A type epoxy resin (YD-128, Kukdo Chemical Co., South Korea) with an epoxy weight equivalence (Weight in grams of resin containing 1 mol equivalent of epoxide, g/eq) in the range of 184–190 g/eq and a viscosity of 11,500–13,500 mPa s at 25 °C was used as a base resin. The anhydride type curing agent (KBH-1089, Kukdo Chemical Co., South Korea) was mixed with the base resin. Dimethylpolysiloxane based liquid (KF-96) with a viscosity of 1000 mPa s at 25 °C produced by Shin-Etsu Co. was used as an additive for the epoxy resin to enhance the properties. Silicone-modified epoxy resin (KSR-1000, Kukdo Chemical Co., South Korea) with an epoxy weight equivalence of 1100–1300 g/eq was used to increase the compatibility between the epoxy resin and the siloxane liquid. The chemical structures of the resin and the additives are shown in Fig. 1.

2.2. Preparation and characterization of the blend resin

In order to well disperse the siloxane liquid into the epoxy resin and control the droplet size, the epoxy blends were prepared by two different dispersing procedures: a mechanical stirrer and a homogenizer. At first, the base resin (YD-128) and the silicone-modified epoxy resin (SME) was pre-mixed and the mixture was agitated vigorously for 20 min at 60 °C by the mechanical stirrer until the mixture became clear. Next, 0.05 parts per hundred resin (phr) of siloxane liquid and 90 phr of curing agent (KBH-1089) were added to the mixture and subsequently it was dispersed by the mechanical stirrer or the homogenizer. The rotational speeds of each method were 500 rpm and 5000 rpm, respectively. The dispersed mixtures were degassed for 60 min at 60 °C under vacuum to remove trapped air during the dispersion because the air bub-

bles could have any effects on the property of samples. After the degassing, the mixtures were poured into an open rectangular mold and then cured at 120 °C for 120 min. The compositions of the blend epoxy resins were shown in Table 1.

Dog bone specimens of the blend resins were machined according to the ASTM standard D638. The tensile properties were evaluated on a universal tensile tester with a cross head speed of 5 mm/min. The temperature conditions were room temperature (RT) and 77 K respectively. In particular, the low temperature was achieved by spraying liquid nitrogen in a cryostat designed and manufactured in our laboratory. Data were taken from an average of at least five specimens.

Coefficient of thermal expansion (CTE) of the blend resins was measure by the reported method [32]. The equipment for the cryogenic CTE consists 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 173 K. And then the apparent strain was measured while slowly rising the temperature. The CTE was calculated through calibration with a standard material, titanium silicate. The strain gauge (FCA-5-11-1L) was purchased from Tokyo Sokki Kenkyuio. Analysis of the fracture morphologies of the blend resins was conducted by scanning electron microscopy (SEM). In order to estimate the dispersion state of the siloxane liquid in the epoxy resin, the percent transmittances of the blend resins were measured. The blend resins for the measurement were prepared by stirring mechanically at 500 rpm followed by being degassed for 60 min at 60 °C. These uncured blends were transferred to quartz cells and the transmittance was measured at the wavelength of 500 nm by UV–Vis spectroscopy.

3. Results and discussion

3.1. Effect of SME on the dispersion stability of siloxane liquid

It is known that general epoxy resin and siloxane liquid are completely immiscible each other due to the relatively non-polar and inactive characteristic of the liquid with siloxane groups compared to the epoxy resin including hydroxyl and epoxide groups. Therefore, even though they seem to be well dispersed in early stage of the mixing, a dispersed phase, for example the siloxane liquid, eventually coalesces and consequently a phase separation occurs. On the other hand, in order to stabilize the dispersed phase, a bifunctional polymer can reduce the interfacial tension between the continuous and the dispersed phase. With regards to this point, a silicone-modified epoxy resin (SME) has both alkyl siloxane and epoxide groups on the backbone as shown in Fig. 1. Each group on the SME can assist the siloxane liquid to form its spherical domain by placing SME at the interface. A schematic diagram in Fig. 2 depicts a concept of the stabilization. In order to confirm this effect, we compared the percent transmittances of the blend resins containing the siloxane liquid with or without the SME. Fig. 3a shows a picture of the neat epoxy resin and the resin with only 0.05 phr of the siloxane liquid. It is seen that these two resins are almost clear. When transmittance of the neat epoxy resin (Ref 1) was set as a baseline, the percent transmittance of the other was measured at 94.3% indicating that there was no noticeable difference in the transmittance. This result can be explained by the phase separation. Most of the siloxane liquid coalesce and float on the top due to its lower density (0.97 g/cm^3) resulting in no change of the transmittance. However, the blend resin containing SME and the siloxane liquid was relatively opaque shown in Fig. 3b. The percent transmittance significantly decreased to 70.4% compared to the clear reference resin only with the silicone-modified epoxy

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