MICROFAILURE MECHANISMS AND INTERFACIAL EVALUATION OF SINGLE FIBER REINFORCED EPOXY COMPOISTES AT CRYOGENIC TEMPERATURES

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1 Introduction

Epoxy resins have been widely used as the matrix of composites because of their good electric insulating, mechanical, and easy fabricating properties. Composites have also been used in a large number of cryogenic applications because of their unique and highly tailorable properties [1, 2]. While fundamental mechanical, electrical, and thermal requirements generally serve to help dictate the selection of material constituents and processes, it is often necessary to make compromises [3]. Material selection is further complicated by the specific operating conditions and environments, including extreme of temperature, close dimensional tolerances, exposure to radiation etc. Difficult fabrication scenarios required for some applications may also effect material selection. Reliability is another very important issue, for example, composites used in cryogenic applications are often inaccessible for inspection or repair, and adequate performance may be critical during the entire life cycle of the device. The thermal and mechanical properties of the epoxy resin, used as the composite matrix, are known to have a strong influence on the mechanical behavior of fiber reinforced composites. For epoxy resins to remain tough in cryogenic applications, it is essential that low temperature crack propagation can be repressed.

The thermal contraction associated the decrease in temperature to cryogenic conditions, can induce significant internal stresses in a composite matrix. This can result in dramatic changes in the composite's structure and associated properties. Matrix cracking is likely to occur if the stress intensity factor, induced by these thermal stresses, exceeds the fracture toughness of the resin. Since most epoxy resins readily crack at low temperature, it is important to select appropriate epoxy resins as both matrix materials and adhesives, for cryogenic applications.

In the research reported here, micromechanical techniques were used to investigate interfacial properties of fiber reinforced two kinds of epoxy composites at ambient, low and cryogenic temperatures.

2 Experimental

2.1 Materials

Carbon fiber (T700S, Toray Inc., Japan) with average diameter of 8 μm and glass fiber (RS2200KT-111A, Owens Corning Inc., U.S.A.) with average diameter of 16 μm were used as reinforcing fibers. Epoxy (YD-114, Kukdo Chemical Co., Korea) based on diglycidyl ether of bisphenol A and epoxy (YDF-175, Kukdo Chemical Co., Korea) based on Diglycidyl ether of bisphenol F were used as matrices, methyl tetrahydrophthalic anhydride (KBH-1089, Kukdo Chemical Co., Korea) and polyamide (G-0331, Kukdo Chemical Co., Korea) were used as curing agents of epoxy resins.

2.2 Curing reaction of epoxy resin

The matrices used in this study were: (1) Epoxy YD-114 with curing agent KBH-1089 mixed 1:1, and cured at 120ºC for 2 hours. (2) Epoxy YDF-175 with curing agent G-0331 mixed 7:3 and cured at 80ºC for 2 hours. The epoxies exhibited very different optical properties after curing. Epoxy YD-114 was clearly transparent with a yellow color similar to that of the uncured resin whereas epoxy YDF-175 was semi-transparent and light yellow.

2.3 Apparent Young's modulus measurement

Figure 1 shows schematically the experimental specimen used to measure the apparent Young's modulus under constant strain-amplitude cyclic loading. The reinforcement effects of carbon and glass fibers embedded in the two different epoxy resins were measured in a cyclic loading test. The combined effects of interfacial bonding and resin reinforcement of the single fiber reinforced epoxy specimen was evaluated based on determination of its apparent Young's modulus and tensile strength during five strain cycles. The change in this associated reinforcement as a function of the two different temperatures was of particular interest.

Fig.1. cryogenic chamber and test system

2.4 Measurement of interfacial shear strength

Interfacial shear strength (IFSS) of the carbon and glass fibers/epoxy composites was measured by a microdroplet pull-out test. The cryogenic chamber and test system are shown in figure 1, and this experimental system designed for microdroplet pull-out test at low temperature. Fibers were fixed in a steel frame at regular separated distances. Microdroplets of epoxy resin were formed on each fiber using a tip-pin and fiber. The microdroplet specimen was fixed by a microvice using a specially-designed micrometer. The IFSS was calculated from the measured pullout force, F, using the following equation:

$$\tau = \frac{F}{\pi D_f L} \qquad (1)$$

where D_f and L are fiber diameter and fiber embedded length in the matrix, respectively.
The double layer chamber supplied a closed and homothermal conditions during the test, low temperature chamber connected with refrigerating system. There are two different temperature for comparison, room temperature as 25ºC and low temperature as -10ºC.

2.5 Wettability measurement

Dynamic contact angles of fibers and epoxy resins were measured using Wilhelmy plate technique (Sigma 70, KSV Co., Finland). Four dipping liquids double purified water, formamide, ethylene glycol and diiodomethane were used. Dynamic contact angle, surface energies, donor and acceptor components, polar and dispersive free energy terms of carbon fiber with different conditions and CNT-phenol composites were measured.
A commonly-used approach in considering solid surface energies is to express them as a sum of dispersive and polar components which can influence the work of adhesion, W_a between the surface of the reinforcement material and the matrix. To determine the polar and dispersive surface free energies, the Owens-Wendt equation is used, expressed as:

$$W_a = \gamma_L(1+\cos\theta) = 2\left(\gamma_S{}^d \gamma_L{}^d\right)^{\frac{1}{2}} + 2\left(\gamma_S{}^p \gamma_L{}^p\right)^{\frac{1}{2}} \qquad (2)$$

3 Results and Discussion

3.1 Interfacial shear strength

Figure 2(a) shows results from the microdroplet test for carbon fibers in YD-114 epoxy, whereas Figure 2(b) shows similar results but for glass fibers in YD-114 epoxy. The results are shown for tests conducted at -10°C and 25°C. In both cases, the IFSS decreased significantly when the temperature was reduced from 25°c to -10°C, for the carbon fiber the decrease was from approximately 50 MPa to 25 MPa, while for the glass fibers the increase was from approximately 62 MPa to 42 MPa.
Figure 3 shows results from the microdroplet test for carbon and glass fibers in YDF-175 epoxy. In both cases, the IFSS increased significantly when the temperature was reduced, for the carbon fiber the increase was from approximately 45 MPa to 98 MPa,

while for the glass fibers the increase was from approximately 57 MPa to 82 MPa. At 25°C the IFSS of glass fibers in YDF-175 epoxy was higher than the IFSS of carbon fibers in YDF-175 epoxy, which is thought to be due to more chemical functional groups, such as silanol on the glass fiber. However, at the lower temperature interfacial adhesion behavior was very different.

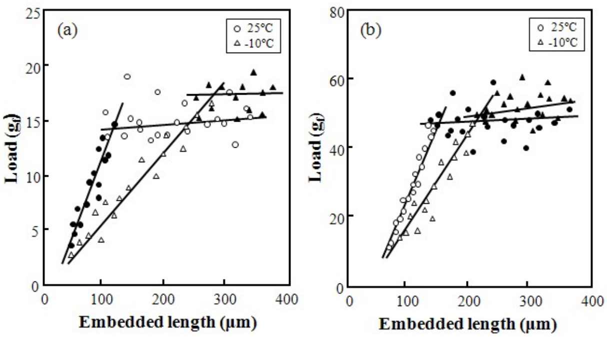

Fig.2. Comparison of IFSS of fiber with epoxy YD-114

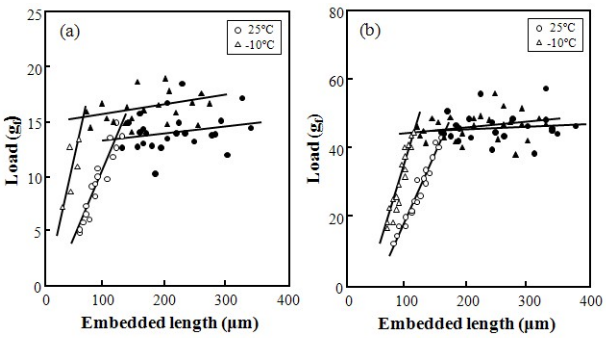

Fig.3. Comparison of IFSS of fiber with epoxy YDF-175

From the results shown in these figures, it is clear that there are two distinct patterns or regions of behavior, dependent on difference in Young's modulus and interfacial adhesion of the epoxies. These different patterns might be simply explained as that, microdroplet slippage occurred when the applied force exceeded the value of interfacial adhesion force and fiber fracture occurred when the value of the interfacial adhesion force exceeded the fiber's tensile strength. Compare to the worse interfacial adhesion between fibers and YD-114 epoxy at -10°C, in YDF-175 epoxy case, while the IFSS increased dramatically for both fiber types the increase for the carbon fibers was much larger such that its IFSS was significantly higher than that for the glass fiber at -10°C. This difference is attributed to an increase in the tensile strength of the carbon fibers.

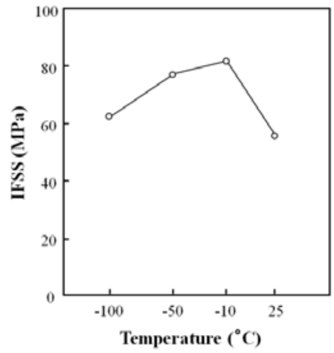

Fig.4. IFSS between glass fiber and epoxy YDF-175

The force to cause the microdroplet to slip was higher at -50°C than at -100°C, indicating that interfacial adhesion was less at -100°C. Figure 4 shows a comparison of IFSS between glass fiber and epoxy YDF-175 at 4 different temperatures. As the temperature is reduced from room temperature (25°C), the interfacial shear strength first increased went through a maximum and then exhibited a downward trend to -100°C.

3.2 Failure patterns of microdroplet test

From typical curves of pull-out force versus cross-head extension for glass fiber/YD-114 epoxy microdroplet tests, at the two different temperatures. These results illustrate that the microdroplet's pull-out or slippage force was larger at ambient temperature than that at low temperature. The results are typical of all the tests at low temperature, in that at the first occurrence of any slippage the load dropped immediately to zero, somewhat analogous to brittle fracture. On the other hand for microdroplet pull-out tests conducted at 25 ºC, the first slippage was accompanied by a sudden drop in load to nearly zero, followed by subsequent increases and drops in load somewhat analogous to 'slip-stick' behavior often observed in adhesive peel tests.

The photos illustrate the difference in the pull-out failure patterns after microdroplet pull-out test at the two different temperatures. The pullout patterns illustrated in these photos are consistent with the test curves and previous discussion of the curves. At lower temperature, the slippage of the microdroplet appears to be accompanied by more brittle like cracking than did the specimen tested at room

temperature. Although the sizes of two microdroplets were almost same, the slippage force was larger at ambient temperature.
For comparison with YD-114, typical curves of pull-out force versus cross-head extension for glass fiber/YDF-175 epoxy microdroplet tests were investigated at the two different temperatures. Quite the contrary with YD-114 epoxy, the microdroplet's slippage force was larger at low temperature than that at ambient temperature. At lower temperature, since the better interfacial adhesion between fibers and epoxy resin, the slippage force was larger than that at ambient temperature, and the microdroplet exhibited a modified interfacial failure pattern.

3.3 Work of adhesion measurement

Figure 5 shows the plots of dynamic contact angle test for two epoxy resins. Figure 5(a) shows the different contact angle of YD-114 epoxy at 0ºC and 25ºC. YD-114 epoxy exhibits hydrophobic properties at lower temperature, and the advancing contact angle at 25ºC was lower. It means that there were different surface energies of epoxy resin at different temperature. On the contrary, the advancing contact angle of YDF-175 epoxy at 0ºC was lower as figure 5(b) shown.

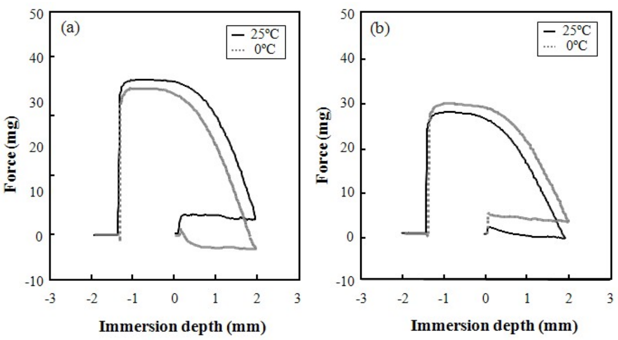

Fig.5. Dynamic contact angles measurement: (a) YD-114 epoxy, and (b) YDF-175 epoxy

Figure 6 shows the work of adhesion between two types of fibers (carbon and glass) and the two epoxy resins at temperatures between -10^0 C and 30°C. The work of adhesion between both fibers and epoxy resin were higher at 30°C than -10^0 C. The YDF-175 exhibited a different trend, in that work of adhesion between both fibers and the epoxy were higher at the lower temperatures. The interfacial adhesion between fibers and the YDF-175 epoxy was higher than that between fibers and the YD-114 epoxy.

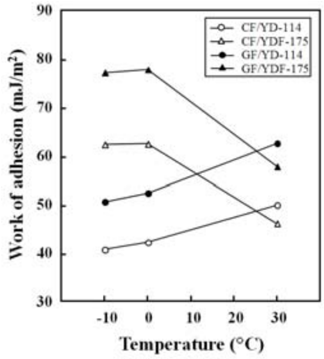

Fig.6. Work of adhesion between fiber and epoxy

4 Conclusions

Microdroplet tests combined with wettability test were investigated to obtain the interfacial properties of carbon or glass fibers reinforced epoxy composites. In low temperature case, both carbon fiber and glass fiber reinforced epoxy YDF-175 composites showed higher interfacial adhesion and apparent modulus than room temperature. The IFSS increased significantly between fibers and epoxy YDF-175 at low temperature environment, whereas the IFSS between fibers and epoxy YD-114 decreased at low temperature. In addition, Wettability test also exhibited the work of adhesion between carbon or glass fibers and epoxy YDF-175 were higher than epoxy YD-114.

Acknowledgments

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