Thermoplastic vs. thermoset epoxy carbon textile composites

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Abstract. The main advantage of thermoplastic resins compared to thermoset counterpart are: increased toughness, better recyclability, and mainly the ability to deliver fast manufacturing processes. However, available thermoplastic resins (TP) have higher melt viscosity than thermoset ones. Due to high viscosity, the infusion process with conventional thermoplastic resins could lead to inappropriate impregnation of the fiber bundles. Recently, a thermoplastic epoxy resin (TP-EP) was developed with both advantages of thermoset and thermoplastic resins. The TP-EP couples the workability of thermoset, formability and recyclability of thermoplastic. The purpose of the present research is to comparatively assess the mechanical features of thermoplastic and thermoset epoxy carbon textile composites. As main outcome, the composite with highly polymerized thermoplastic epoxy has better mechanical performance than the conventional thermoset epoxy textile composite.

1. Introduction
Carbon fiber reinforced plastics (CFRP) have been studied because of excellent specific strength and specific rigidity. CFRPs have been widely used in aerospace and automotive industries. To take advantage of the recyclability and fast manufacturing process, carbon fiber reinforced thermoplastics (CFRTP) has been extensively studied ([1]-[5]). However, thermoplastic resins (TP) have higher melt viscosity than the thermoset ones. Hence, the infusion process with conventional thermoplastic resins could lead to inappropriate impregnation of the fiber bundles ([6], [7]). Recently, a new resin coupling the advantages of thermoset and thermoplastic was developed ([8], [9]). It has the good workability of thermoset and the post-formability and recyclability of thermoplastic. The CFRTP produced with in-situ resin had a lot of attention ([10], [11]).

In previous investigations, the effect of the weight-average molecular weight (Mw) on mechanical properties of thermoplastic epoxy carbon textile composites was measured. The result highlighted the better properties of high Mw (Mw$>$60,000) CFRTP ([12], [13]). However, to better understand its advantages for real industrial applications, it is necessary to assess and compare the effects of thermoplastic epoxy (TP-EP) and thermoset epoxy (TS-EP) on the main mechanical properties of CFRTP and carbon fiber reinforced thermoset (CFRTS) counterpart.

The purpose of the present research is to comparatively assess the mechanical features of CFRTP-EP and CFRTS-EP carbon textile composites. Micro droplet, quasi-static tensile, Izod impact, mode I and mode II inter-lamina fracture and inter-laminar shear tests were conducted.
2. Materials and Manufacturing

2.1. Reinforcement and Matrix
Plain weave carbon fiber fabric (Mitsubishi Rayon TR3110MS) was used as reinforcement (yarn TR30S 3L, linear density 1.79 g/cm³, pick and end counts 12.5 per inch, areal weight 200 g/m²). Thermoplastic epoxy resin (Denatite XNR 6850A, Accelerator XNH 6850B; supplied by Nagase ChemteX Corporation, Japan) [9] was used as matrix (Tg was approximately 100 degree-C). Thermoset epoxy resin (JER828, Mitsubishi Chemical Corporation) and amine (JER113, Mitsubishi Chemical Corporation) were used as resin and curing agent, respectively.

2.2. Manufacturing of CFRTP laminates
Plain weave CFRTP prepreg was made by the following procedure. The resin, ‘XNR6850A’, was heated by an electric oven at 120 degree-C. When the temperature of the resin reached 105 degree-C, the accelerator ‘XNH6850B’ was added to the resin with stirring. The plain weave carbon fabric was impregnated with the thermoplastic epoxy resin by hand lay-up. The molecular weight of prepreg was finally controlled by a predetermined time and temperature sequence. CFRTP prepreg impregnated with the thermoplastic epoxy resin in the state of oligomer was polymerized at a given temperature in an electric oven. The obtained prepreg was dried at 50 degree-C for 12 hours. CFRTP laminates were prepared by press molding at 175~195 degree-C and 6~12 MPa. The carbon fiber volume fraction of the CFRTP laminates was approximately 45%.

2.3. Fabrication of CFRTS laminates
The same plain weave carbon fiber fabric was used as reinforcement. The CFRTS plates were laminated by hand lay-up impregnation. The mold was cured in a hot press at 80 degree-C for 1 hour and then at 150 degree-C for 3 hours. The CFRTS laminates had approximately 45% fiber volume fraction, as the CFRTP ones.

3. Experimental Activities

3.1. Measurement of weight-average molecular weight
The weight-average molecular weight of the TP-EP matrix was measured for each batch by the gel permeation chromatography (GPC) adopting a CLASS-LC10 (Shimadzu Corporation) and a GPC column (Styragel HR4E, Styragel HR5E; waters). Tetrahydrofuran (THF) was used as solvent. The calibration curves were drawn based on the retention time and the Mw of standard polystyrene.

3.2. Micro-droplet tests
Figure 1 shows a scheme of the micro-droplet test setup. Both ends of a single carbon fiber were fixed on a sheet of paper using an epoxy-based adhesive. The droplets were attached to the single carbon fiber by a soldering iron. The interfacial shear strength was determined with a pullout loading speed of 0.12 mm/min. The average strength was obtained using at least 20 specimens for each resin. Equation (1) was used to calculate the interfacial shear strength (τ).

![Figure 1. Specimen for micro-droplet test.](image)
\[ \tau = \frac{F}{\pi DL} \]  

where \( \tau \) is the interfacial shear strength; \( F \) is the pull-out load; \( D \) is the fiber diameter; \( L \) is the adhesion length.

### 3.3. Quasi-static tensile tests

Tensile tests in the warp direction of CFRTP and CFRTS were conducted according to the standard ISO 527 at 1 mm/min (cross head speed) by using a universal material testing machine. Dimensions of the specimen were: length 200 mm, width 25 mm and thickness 2 mm. The distribution of strain on the surface of the specimen was estimated by the DIC (Digital Image Correlation) technique. The surface was painted with white and speckled with black acrylic paints for a length of about 4 cm (see Figure 2). During loading, digital images were recorded with a frequency of 1 Hz by a digital camera. Processing of images was performed by the software VIC-2D™.

![Figure 2. Specimen for quasi-static and fatigue tensile tests.](image)

### 3.4. End Notched Flexure (ENF) test

Figure 3 shows geometry of specimen for ENF test. Laminates had 20 layers of plain weave carbon fabric. The quasi-static three-point bending loading at 0.5 mm/min of cross-head speed allowed for the estimation of the Mode II inter-lamina fracture toughness. The length of pre-crack was 50 mm. Kapton film of approximately 30 \( \mu \)m thick (Kapton, Du Pont-Toray Corporation) was inserted between 10th and 11th ply of the laminate. Equation (2) was used to calculate the Mode II inter-lamina fracture toughness.

\[ G_{\text{IIc}} = \frac{9a_1^2R_2^2C_1}{2B(2L^3 + 3a_1^3)} \]  

where
In Eqs. (2, 3), $G_{IIc}$ is mode II inter-lamina fracture toughness; $a_i$ is initial crack length; $P_c$ is initial critical load; $C_0$ is load point compliance of the initial elastic part; $C_1$ is load point compliance at initial critical load; $a_1$ is estimated crack growth length at initial critical load; $L$ is supports span; $B$ is specimen width.

### 3.5. Double Cantilever Beam (DCB) test

Specimen with the size of 160 (length) x 25 (width) x 4 (thickness) mm (Figure 4) was loaded to measure the Mode I inter-lamina fracture toughness at 0.5 mm/min cross-head speed by a universal material testing machine (EZ-test, Shimadzu Corporation). The pin-blocks for loading were attached as shown in Figure 4. The length of pre-crack was 50 mm. Kapton film of approximately 30 μm thick (Kapton, Du Pont-Toray Corporation) was inserted between 10th and 11th ply of the laminate. Equation (4) was used to calculate the Mode I inter-lamina fracture toughness.

**Figure 4.** Specimen for DCB test.

\[
G_{IC} = \frac{3}{2(2H)} \left( \frac{P_c}{B} \right)^2 \left( \frac{B\lambda_0}{a_1} \right)^2
\]

where

\[
\frac{a}{2H} = \alpha_1 (B\lambda)^{1/3} + \alpha_0
\]

Symbols in Eqs. (4, 5) have the meaning: $G_{IC}$ is mode I inter-lamina fracture toughness; $2H$ is specimen thickness; $P_c$ is initial critical load; $B$ is specimen width; $\lambda_0$ is COD compliance of the initial elastic part; $\alpha_0$ is slope of straight line; $\alpha_1$ is intercept of the straight line; $a$ is crack length.

### 3.6. Inter-laminar shear strength (ILSS) test

Three point bending tests of short beam specimens were conducted by a universal material testing machine, following the recommendations of ISO 14130. Figure 5 shows geometry of specimen for ILSS test. The specimen had dimensions of 20 (length) x 5 (width) x 2 (thickness) mm. The span length was 10 mm. Bending load was applied with a displacement rate of 5.0 mm/min.
3.7. **Izod impact strength test**

Izod impact tests were conducted using an impact pendulum (Yonekura seisaku-sho, Co., Ltd., A1040). The izod impact test was according to ISO 180. Figure 6 shows geometry of specimen. The impact direction was edgewise and samples had dimensions of 80 (length) x 10 (width) x 2.5 (thickness) mm.

![Figure 5. Specimen for ILSS test.](image)

![Figure 6. Specimen for Izod impact strength test.](image)

4. **Results and discussion**

4.1. **Micro-droplet test**

The micro-droplet tests provided the interfacial shear strength compared in Figure 7. The interfacial shear strength of CFRTP depends on the weight-average molecular weight (Mw) of the matrix. The better strength was measured for Mw>60,000 by previous study ([12], [13]). For comparison, in Figure 7, the composite with Mw=90,000 was adopted. The interfacial shear strengths of CFRTS and CFRTP are comparable and in the same experimental scatter band. Figure 8 shows the SEM observations of carbon fiber surface after micro-droplet tests. Some resin still in contact demonstrate the good adhesion with carbon fiber of both resins.

![Figure 7. Interfacial shear strength.](image)
4.2. Quasi-static tensile tests
Figure 9 shows the quasi-static tensile test results in term of elastic modulus and strength. Previous study [13] highlights that the tensile strength of CFRTP depends on weight-average molecular weight (Mw) of the matrix and the better properties were for Mw>60,000. Therefore, here for comparison, the composite with of Mw=84,000 was considered. As a result, tensile strength and elastic modulus do not have considerable variations.

4.3. Inter-laminar properties
One of the main mechanical weaknesses of laminated composite materials is the inter-lamina fracture toughness. It is measured here by three tests: ENF, DCB and ILSS.

4.3.1. End Notched Flexure (ENF) test. Figure 10 shows the results of the Mode II inter-lamina fracture toughness. The Mode II fracture toughness of CFRTP depends on the weight-average molecular weight (Mw) of the matrix [13]. The better properties is for Mw>60,000. Here, for comparison, the TP-EP with Mw=108,000 was considered. The comparison shows a considerable higher, almost double, Mode II inter-lamina fracture toughness of CFRTP than CFRTS.
4.3.2. **Double Cantilever Beam (DCB) test.** Figure 11 shows the results of the Mode I inter-lamina fracture toughness. For comparison, the TP-EP with Mw=70,000 was adopted. As for Mode II, the Mode I inter-lamina fracture toughness of CFRTP is almost double than the CFRTS counterpart.

4.3.3. **Inter-laminar shear strength (ILSS) test.** The inter-laminar shear strength of CFRTP was ~20% higher than that of CFRTS laminate (Figure 12). Figure 13 shows the load - mid span displacement curves, which had similar maximum load but different evolution. CFRTP curve had bi-linear shape with ‘hardening’ behaviour, while CFRTS curve had a sudden drop after the maximum load, meaning a fast inter-laminar crack development. The difference is visible observing the damage imparted after the ILSS tests. Figure 14 shows the failure modes. The CFRTS specimen had several and longer inter-laminar clacks than the CFRTP counterpart.
4.4. **Izod impact strength test**

The Izod impact strength of CFRTP was ~10% higher than CFRTS (Figure 15). Figure 16 shows the SEM observation of the fracture surface of CFRTP and CFRTS, respectively. The ‘plastic’ deformation of the matrix with good energy absorption was recorded for the TP-EP matrix of CFRTP (Figure 16 left). The ‘brittle’ behavior of the TS-EP matrix allowed lower energy absorption. Consequently, the impact strength was improved due to the energy dissipated for ‘plastic’ deformation of the matrix.
5. Conclusion
A summary and comparison of the complete set of experimental results is shown in Figure 17. As main outcome, the composite with highly polymerized thermoplastic epoxy has better mechanical performance than the conventional thermoset epoxy textile composite.

![Figure 17. Comparison of CFRTP and CFRTS mechanical properties.](image)
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