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Experimental characterization of tensile properties of epoxy resin by using micro-fiber specimens

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Abstract

In unidirectional carbon fiber reinforced plastic (CFRP) laminates, the distance between fibers can vary from submicron to micron length scales. The mechanical properties of the matrix at this length scale are not well understood. In this study, processing methods have been developed to produce high quality epoxy micro-fibers with diameters ranging from 100 to 150 um that are used for tensile testing. Five types of epoxy resin systems ranging from standard DGEBA to high-crosslink TGDDM and TGMAP epoxy systems have been characterized. Epoxy macroscopic specimens with film thickness of 3300 um exhibited brittle behavior (1.7 to 4.9% average failure strain) with DGEBA resin having the highest failure strain level. The epoxy micro-fiber specimens exhibited significant ductile behavior (20 to 42% average failure strain) with a distinct yield point being observed in all five resin systems. In addition, the ultimate stress of the highly cross-linked TGDDM epoxy fiber exceeded the bulk film properties by a factor of two and the energy absorption was over 50 times greater on average. The mechanism explaining the dramatic difference in properties are discussed and is based on size effects (the film volume is about 2000 times greater than the fiber volume within the gage sections) and surface defects. Based on the findings

presented in this paper, the microscale fiber test specimens are recommended and provide more realistic stress-strain response for describing the role of the matrix in composites at smaller length scales.

Keywords

Carbon fiber reinforced composites, epoxy resin, mechanical properties, size effect

Introduction

CFRPs are widely used in aerospace, automotive, sporting goods, marine and infrastructure applications because of their high strength, stiffness and light weight. Tensile strength of CFRP is an important property in these applications and its improvement can lead to lighter weight and wider usage of CFRPs.

The failure mechanism of unidirectional CFRP during tensile loading has been studied extensively in a number of previous studies.[1-3] In CFRP, where the matrix has a higher strain to failure than the carbon fiber, first damage is fiber breakage and the role of the resin is to transfer load to the adjacent fibers. Load transfer occurs through the interphase and

the matrix to the adjacent fibers through shear in a characteristic distance typically referred to as the ineffective length (i.e. distance along the broken fiber length to recover 90% of the far-field stress in the fiber). Within the ineffective length in the vicinity of the fiber break, a shear stress concentration in the matrix and an axial stress concentration in the adjacent fibers develop. Further loading creates additional fiber breaks leading to ultimate composite failure. In addition to the fiber strength distribution, the matrix resin properties play an important role on load transfer and stress concentration at lower length scales.

Several studies have been conducted to gain an understanding of the role of the matrix resin properties on axial tensile strength of unidirectional CFRP.[3-6] Behzadi, Foreman et. al. have reported that yielding behavior (elasto-plasticity) of matrix resin strongly affects the tensile strength of unidirectional CFRP. They observed resin yielding behavior during compression test and this yielding behavior was introduced in their finite element (FE) model of UD-composite. They mentioned that the shear yielding of the matrix reduced the stress concentration factor in the fiber at the vicinity of a fiber break and hence increased the composite failure strain compared to an elastic matrix.

However, the properties of the matrix at lower length scales may differ from the bulk properties. The width of the matrix resin region that exists between fibers in CFRP can vary from submicron to micrometer scales (The closest distance between fibers is 1.6 μm for hexagonal packing of 7 μm diameter fibers with 60% fiber volume fraction). Matrix resin properties are generally evaluated using macroscopic specimens. This length scale is on the order of millimeters and can be orders of magnitude greater than that found in CFRP (microns).

Several studies have reported the presence of size effect during mechanical testing of various materials. Several extensive reviews have been published on the general issue of size effects.[7,8]

However, fewer studies have been reported on size effect of thermosetting resin on their properties.[9-12] Odom et al. studied size effects of Hercules 3501-6 epoxy, a highly cross-linked resin commonly used as the matrix material in a number of composite materials. They manufactured dog-bone tensile specimens with gage section volumes between 66~4590 mm^3 (volume ratio of 70) with thicknesses in the range of 0.5-10.2 mm.[9] Their results exhibited an increase in failure stress from 41 to 94 MPa as the specimen size is

reduced. However, the volume of their smallest specimen is still much larger than the volume of the polymer fibers evaluated in this study. Hobbiebrunken et al. developed a manufacturing method for creating epoxy resin fiber specimens for tensile testing.[12] They used RTM6 epoxy resin and obtained fibers with diameters in the range of 22.3-51.4 μm. Their results indicated that the failure stress increased from 87 to 135 MPa as specimen size was reduced from a macroscopic dog–bone shape specimen (gage volume: 75.0 mm^3) to the micro fiber specimen (average gage volume: 0.0063 mm^3). However, the stress-strain curve including yield stress and failure strain was not measured for these epoxy fibers. The authors also reported that voids were observed in their specimens and may have adversely affected the failure stress. Therefore, developing a manufacturing method for making micro-scale specimens with minimal defects is necessary for accurate evaluation of micro-scale mechanical properties of epoxy resin.

In this study, processing methods have been developed to produce high quality micro-scaled epoxy micro-fibers. Tensile tests of these epoxy micro-fibers were carried out to obtain stress-strain behavior of epoxy resin. Tensile tests using dog-bone macroscopic specimens were also carried out as the baseline to determine the size effect of epoxy resin.

Five types of epoxy resin systems composed of epoxy resin monomers used for high performance structural composites were characterized. The fracture surfaces of the failed specimens were inspected under a confocal microscope. In addition, Dynamic Scanning Calorimetry (DSC) was also conducted to confirm that the macroscopic and micro-fiber specimens have the same degree of cure since differences in degree of cure can also affect the mechanical properties.

Experimental

Materials

Figure 1 shows the chemical compounds used for preparation of epoxy resin samples in this study. TGDDM and TGMAP are used in high-performance composite applications and are known to exhibit high modulus and high thermal resistivity thanks to their high crosslink density. DGEBA is known as standard-type epoxy resin and used in a wide range of applications. DETDA was used as curing agent for all these resin systems. All resin systems were formulated with a 1:1 molar ratio of epoxide to active hydrogen of the curing

agent. Details on the epoxy resin systems prepared in this study are listed in Table 1.

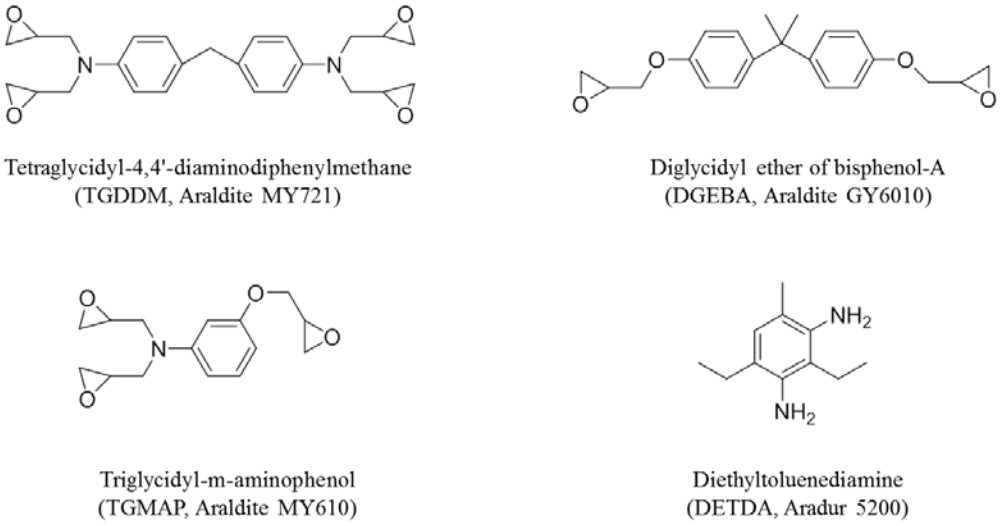

Figure 1. Epoxy compounds and curing agent used in this study

Table 1. Epoxy resin systems

Sample name	Epoxide blend	Curing agent
TGDDM	100% TGDDM	DETDA
DGEBA	100% DGEBA	DETDA
TGMAP	100% TGMAP	DETDA
TGDDM-A1	TGDDM with additive-epoxy compound α	DETDA
TGDDM-A2	TGDDM with additive-epoxy compound β	DETDA

Preparing process of epoxy micro-fiber and macroscopic specimens

Figure 2 shows the preparation process of epoxy micro-fibers. A small amount of formulated epoxy resin was poured into an aluminum cup and it was placed in an oven at 130℃.

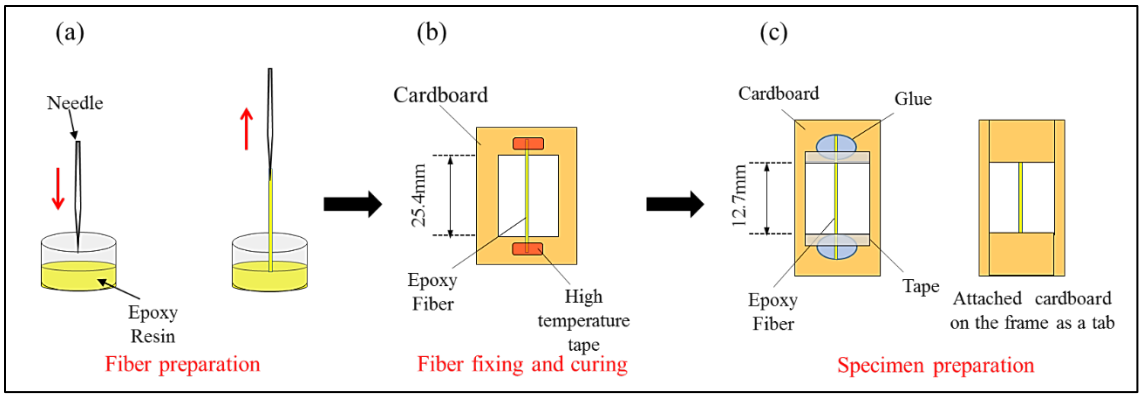

Figure 2. Preparation process of epoxy resin micro-fiber specimens

Figure 3 shows viscosity-time curve for the epoxy resin systems at 130℃. Table 2 shows the time taken for resin viscosity to attain a value of 5 Pa·s at 130℃ and the corresponding degree of cure for this viscosity. After 25-60 minutes, when the resin viscosity increased to approximately 5 Pa·s, a needle of 500 μm or 1000 μm diameter were inserted into the resin

bath and and then extracted out of the bath to form a fiber of approximately 50 mm in length. Fibers with diameters in the range of 5 to 400 μm were created. It is possible to control the fiber diameter by changing the amount of resin poured into the aluminum cup and the diameter of the needle inserted into the resin bath. The resin fibers were cut and attached to a cardboard holder using a high-temperature tape, and cured at 80℃ for 1 hour, 130℃ for 30 minutes, and 180℃ for 2 hours in an oven. The specimens for tensile testing were prepared according to the standard test method for evaluating tensile strength and Young's modulus of fibers (ASTM C1557). Cured epoxy micro-fibers were glued onto a cardboard with a 12.7 mm-by-12.7 mm square open window. The length of this window is defined as the gage length. The fiber ends were covered with additional cardboard on the frame to prevent the mechanical grips from crushing the fibers. Fiber diameters were measured at four equally spaced locations within the gage section using an optical microscope and the average value was used as the diameter of the specimen in the data reduction process. For precise evaluation of micro-scale tensile properties, only specimens with less than 5% variation in diameter with respect to the average value were used for tensile testing.

For manufacturing macroscopic epoxy resin specimens for tensile testing, a mixture of epoxy resin was poured into a mold and cured at 130℃ for 1 hour and 180℃ for 2 hours in an oven to obtain a resin plaque. The plaque was machined using a laser beam machining system to prepare specimens for mechanical testing. The edges of the specimens were polished with sandpaper to minimize edge-scratches. Dog-bone specimens for tensile testing were prepared with a gage length of 50.8 mm and a gage width of 12.7 mm and a thickness of 3.3 mm according to ASTM D638.

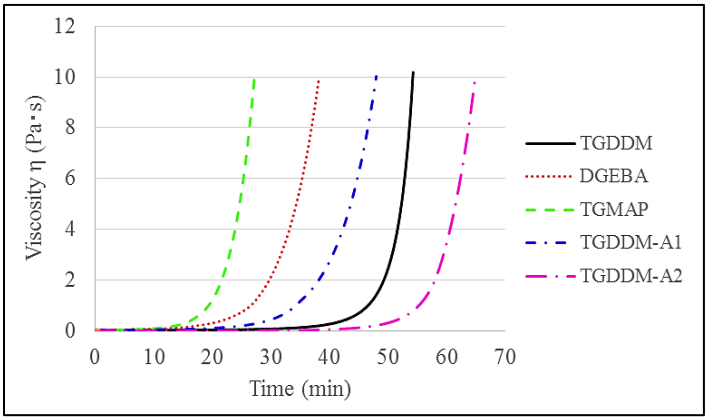

Figure 3. Isothermal viscosity-time curve for epoxy resin systems at 130℃

Table 2. Amount of time and degree of cure when resin viscosity reached 5Pa·s

	Amount of time it takes for resin viscosity to 5Pa·s at 130℃ (min)	Degree of cure when resin viscosity reached 5Pa·s (%)[a]
TGDDM	52	45
DGEBA	34	68
TGMAP	25	40
TGDDM-A1	44	48
TGDDM-A2	62	50

[a] Evaluated by DSC.

Tensile test using micro-scale epoxy fiber

Micro scale epoxy fiber tensile test was carried out in an Instron Micro Tester 5848 with 5N load cell. A 1.27 mm/min (strain rate: 10%/min) crosshead speed was used. The system compliance of the tensile testing equipment was evaluated using a stainless steel wire according to ASTM C1557. The system compliance was linear and the value used to correct displacement measurements was 0.0178 mm/N. Engineering stress and strain was calculated as Equations (1) and (2).

$$\sigma_e = F/A_0 \quad (1)$$

$$\varepsilon_e = (\Delta l - C_s F)/l_0 \quad (2)$$

Where, σ_e is the engineering stress, F is the applied force, A_0 is the original cross-sectional area, ε_e is the engineering strain, Δl is the recorded cross-head displacement, Cs is the system compliance, and l_0 is the gage length, respectively. The Young's Modulus of each specimen was determined from the slope of a secant line between 0.5% and 1.0% strain on a stress-strain curve. Energy absorption was calculated by integrating the stress-strain curve up to the failure strain.

Tensile test using macroscopic epoxy resin specimens

Macroscopic specimen tensile test was carried out according to ASTM D638. A 1.27 mm/min (strain rate: 2.5%/min) crosshead speed was used. A strain gage was used to evaluate engineering strain of the macroscopic specimens. Engineering stress was calculated as per Equation (1) and modulus was determined from the slope of a secant line between 0.5% and 1.0% strain on a stress-strain curve. Energy absorption was calculated by integration of the stress-curve to the failure strain.

Measurement of resin viscosity

The resin viscosity was measured in dynamic shearing mode with a Discovery Hybrid Rheometer-2 (TA Instruments) using parallel-plates at 130℃ (Gap between the plates: 1 mm, Frequency: 1.6 Hz)

Differential Scanning Calorimetry (DSC)

The degree of cure of the cured epoxyspecimens was determined using a Mettler Toledo DSC1. DSC experiments were conducted using an aluminum DSC pan from 50-350 ℃ at rates of 5 ℃/min. The total amount of heat used in the thermal crosslinking reaction can be related to the exothermic peak areas of the DSC curves. The degrees of cure were calculated based on the residual heat from the cured samples. The reference heat value for the completely cross-linked sample was considered as the heat of the thermal crosslinking of the uncured formulation. The degree of cure was calculated from Equation (3).

$$\text{Degree of cure}(\%) = (1 - \Delta H_{residual\ cure}/\Delta H_{total\ cure}) \times 100 \quad (3)$$

Where, $\Delta H_{residual\ cure}$ is the residual exothermic peak area from the cured resin and $\Delta H_{total\ cure}$ is the exothermic peak area from the uncured epoxy resin.

Results and discussion

Tensile properties of micro-scaled epoxy fiber specimen

Tensile properties of micro-scale epoxy fiber and macroscopic specimens are presented in Table 3. The difference of epoxy fiber specimen diameters can affect the tensile properties. Hence, the diameter range of epoxy micro-fibers was limited to 100-150 μm for precise evaluation of the overall stress-strain response.

Table 3. Tensile testing result

	Sample name	Yield Stress (MPa)		Failure Stress (MPa)		Failure Strain (%)		Modulus (GPa)		Energy Absorption (mJ/mm^3)	
		Avg.	SD.	Avg.	SD.	Avg.	SD.	Avg.	SD.	Avg.	SD.
Epoxy fiber specimen	TGDDM	103	6	107	10	25	11	3.1	0.2	2368	1142
	DGEBA	84	6	89	11	42	18	2.9	0.2	3328	1623
	TGMAP	106	5	112	10	22	15	3.4	0.3	2082	1550
	TGDDM-A1	100	6	104	4	21	6	3.0	0.2	1857	582
	TGDDM-A2	114	6	107	5	20	9	3.3	0.2	1981	987
Macroscopic Specimen	TGDDM			51	5	1.7	0.2	3.1	0.0	46	11
	DGEBA			70	4	4.9	0.6	2.3	0.0	215	39
	TGMAP			70	16	2.3	0.8	3.4	0.2	97	55
	TGDDM-A1			63	14	2.6	0.9	2.8	0.1	97	61
	TGDDM-A2			60	19	1.7	0.7	3.6	0.1	62	44

The macroscopic specimens exhibited brittle behavior as shown in Figure 4. The DGEBA specimens showed the highest failure strain of 5% due to their low crosslink density. In contrast, epoxy micro-fibers exhibited ductile behavior with distinct yield point in all resin systems as shown in Figure 5. The failure strains were in excess of 20% in all resin systems, with the highest failure strain being 50% for DGEBA micro-fibers (about 10 times higher than the macroscopic specimen). In addition, the epoxy micro-fiber specimens showed quite a high value of yield stress when compared with ultimate stress of

macroscopic specimens for all of the resin systems considered in this work. As an example, ultimate stress of TGDDM resin system was increased from 51MPa to 103 MPa and the energy absorption was over 50 times greater on average.

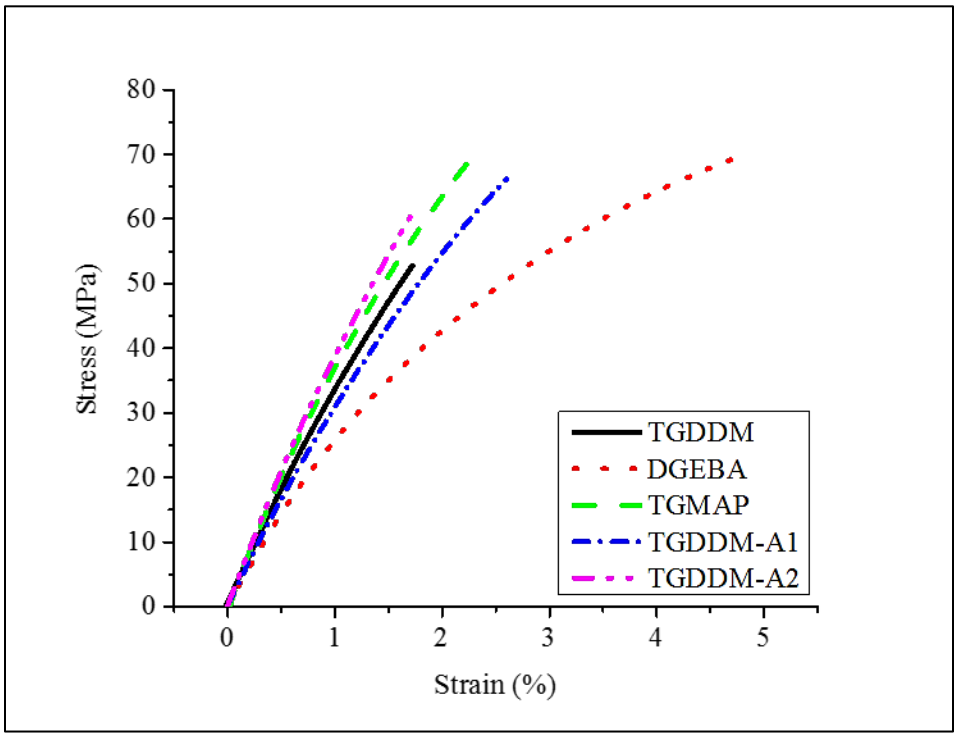

Figure 4. Representative stress – strain curves of tensile tests using macroscopic specimens

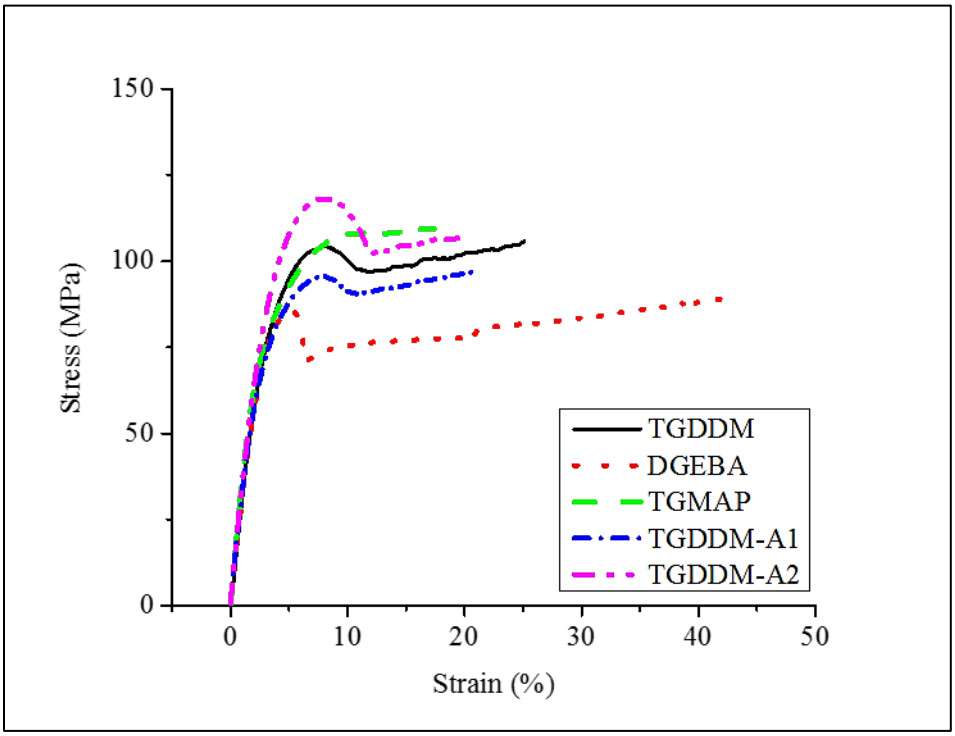

Figure 5. Representative stress – strain curves of tensile tests using epoxy micro-fiber specimens

Odom et al. have reported that the average flaw size in epoxy resin tensile test specimens decrease as the specimen size reduces and this causes an increase in strength.[9] The volume difference of the specimens strongly affected their failure strains and strengths based on the higher probability of the presence of critical defects in larger volumes. Inspection of the

surface of the macroscopic specimens revealed micro-damage caused by machining during specimen preparation even though the surfaces were extensively polished after machining. Figure 6 shows a comparison of the surface quality between micro-fiber specimen and macroscopic specimen observed using a Scanning Electron Microscope (SEM). The remnant surface damage can nucleate cracks leading to a reduction in failure strain in the bulk samples. Since the surface of the micro-fiber samples were not machined, they are less sensitive to surface defects. Inspection of the fiber surfaces shows that our processing method produced very high quality materials. The small diameter fibers also have less volume than the bulk samples, thus resulting in the presence of smaller critical defects within the interior of the specimen. These results indicate that epoxy resins have much higher levels of ductility and strength at lower length scales.

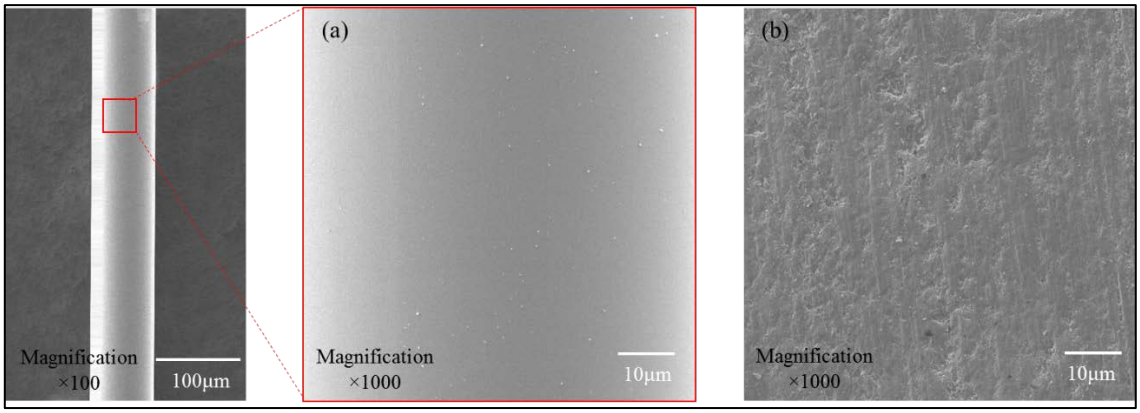

Figure 6. Comparison of surface quality between (a) epoxy micro-fiber specimen and (b) bulk specimen (TGDDM sample)

Size effect on epoxy micro fiber tensile properties

Epoxy micro fiber specimens were processed with a wide range of diameters (70~400μm) to study the volume effects on tensile properties. Volume is defined as stressed volume within the gage section (e.g. product of gage length and cross-sectional area). As a reference, the volume of the bulk epoxy sample is 2130 mm^3 while the micro-fibers are three orders of magnitude smaller (0.05 to 2 mm^3). Figures 7 to 10 show plots of yield stress, failure stress, tensile modulus and failure strain, respectively, versus gage volume. Yield stress (Figure 7) is significantly higher than maximum stress of the bulk specimens but does not show sensitivity to volume in the fiber diameter range tested. One concludes that defects in this size range do not affect yielding of the epoxy fibers.

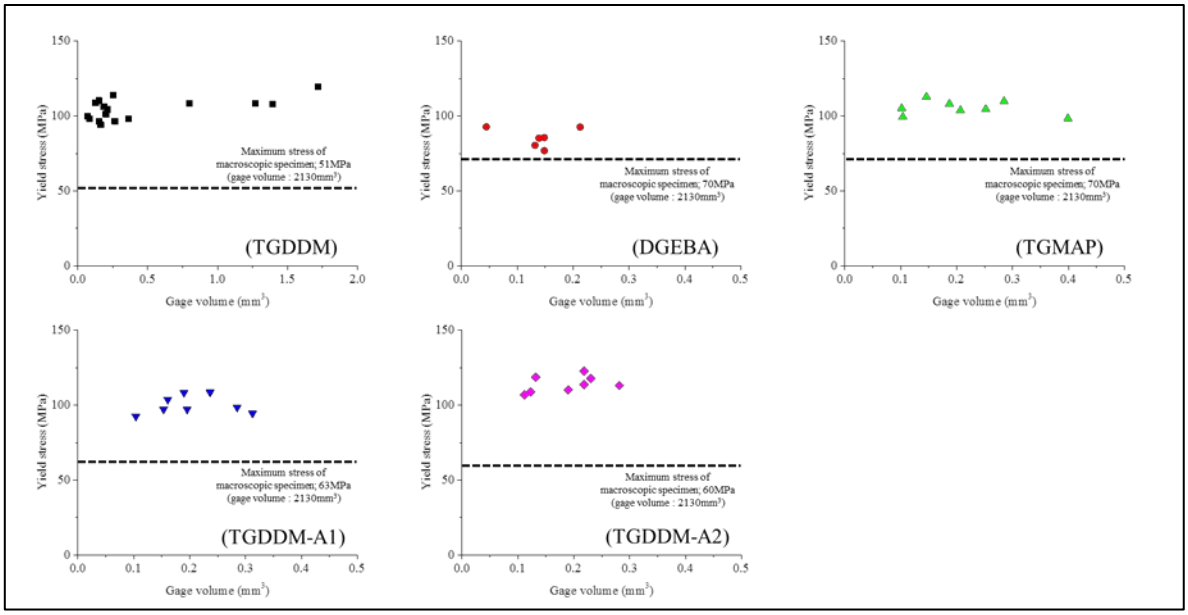

Figure 7. Yield stress against gage volume of specimens for each resin system

Ultimate failure stress (Figure 8) also doesn't show sensitivity to volume in this fiber diameter range. Young's Modulus (Figure 9) is comparable to the bulk properties and shows no dependence on volume. A large concentration of defects would be required to affect specimen stiffness averaged over the gage section and this is not the case in our high quality specimens. Conversely, failure strain (Figure 10) showed the tendency to increase with decreasing volume and exhibit larger variation in results at smaller volumes. This

observation is consistent with the general size effect on materials. These results indicate that for fiber diameters closer to the value of the length scale of the matrix region between reinforcement fibers in a composite, the epoxy resins may exhibit a higher failure strain than the values obtained from the fiber specimens used in this study whereas the yield stress and modulus may remain the same as the values obtained from fiber specimens in this study.

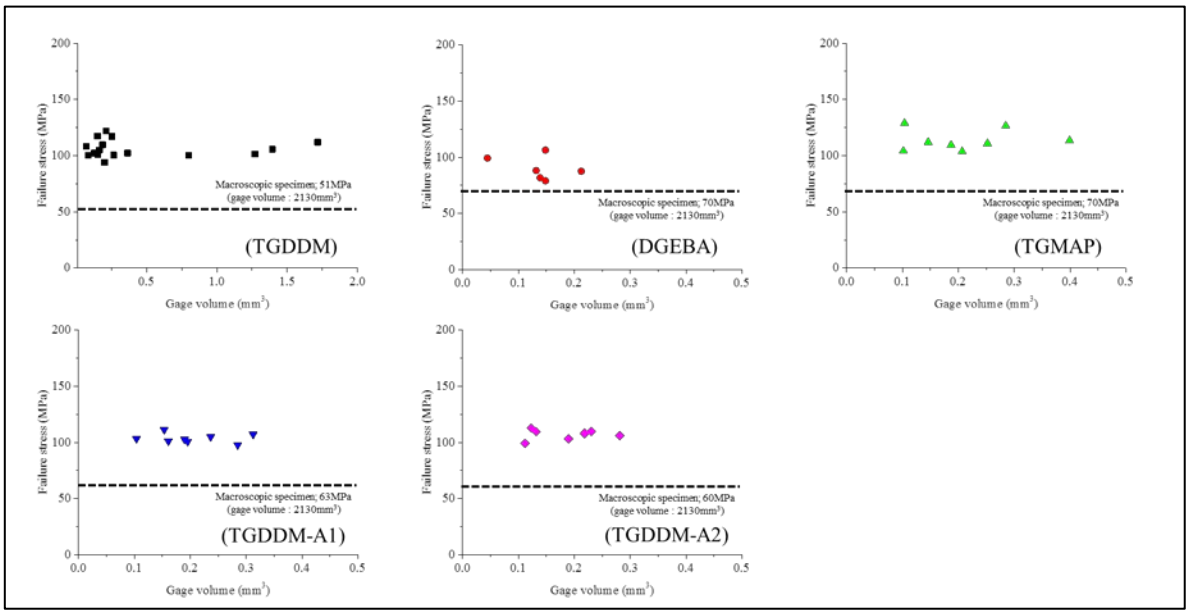

Figure 8. Failure stress against gage volume of specimens for each resin system

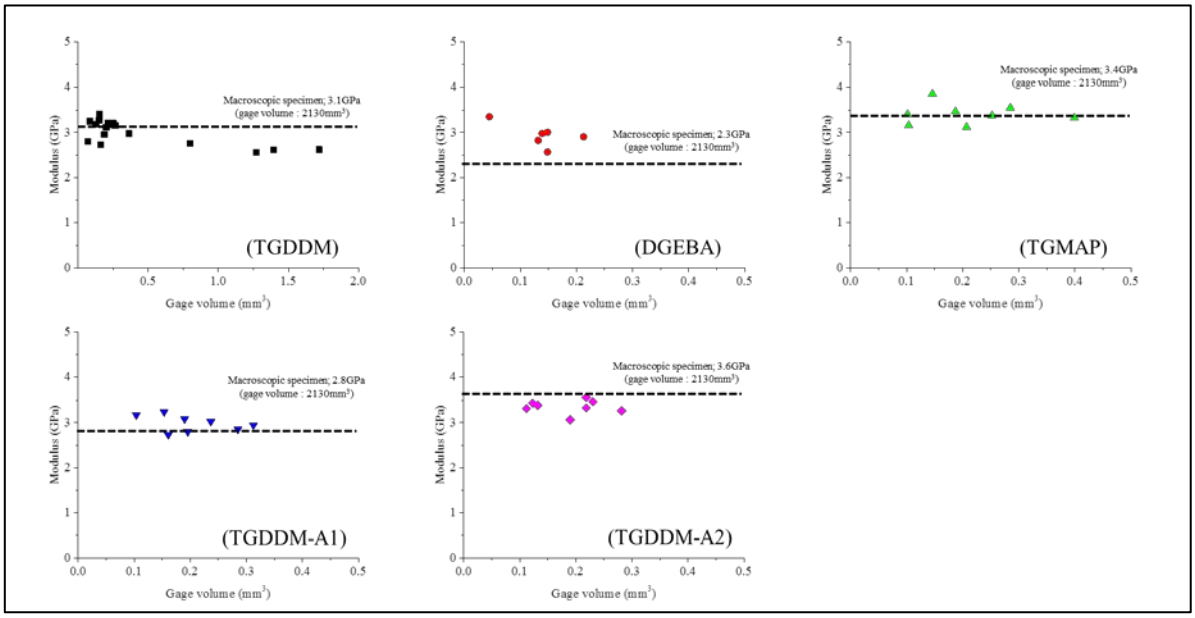

Figure 9. Young's modulus against gage volume of specimens for each resin system

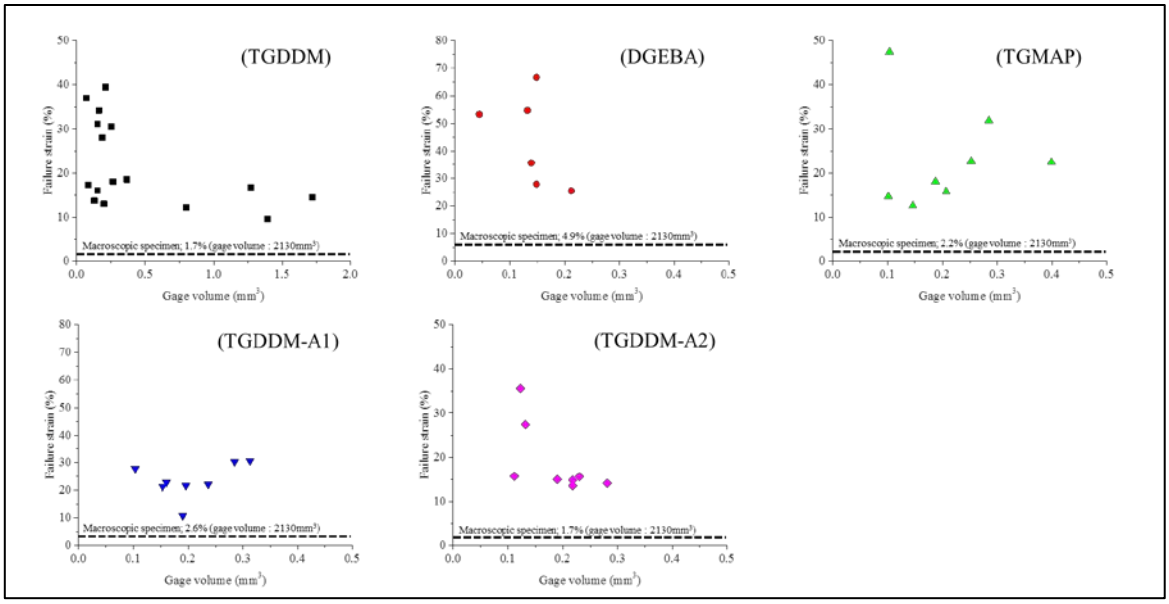

Figure 10. Failure strain against gage volume of specimens for each resin system

Analysis of fracture surface of epoxy micro fiber

Figure 11 shows the observation of the fracture surface of an epoxy micro-fiber specimen (TGDDM) using confocal laser microscopy. In about 80% of the specimens in all resin systems, failure was initiated at the surface as indicated in Figure 11 (a). In the remaining specimens, failure was initiated within the interior as indicated in Figure 11. (b). Some epoxy micro fiber specimens in TGDDM, DGEBA and TGDDM-A2 resin systems showed

necking behavior during tensile test as indicated in Figure 12 (b). In general, macroscopic thermosetting specimens do not exhibit significant necking behavior during tensile testing at room temperature (none of the five bulk epoxies studied exhibited necking). Their large volume and sensitivity to surface and interior defects triggers failure at low strain levels. This result indicates that changing macroscopic specimens to micro scale epoxy fibers significantly improved their plasticity. Our results are consistent with Hobbiebrunken et al. who have also reported some epoxy micro fibers using RTM6 resin that showed necking behavior during tensile test.[12]

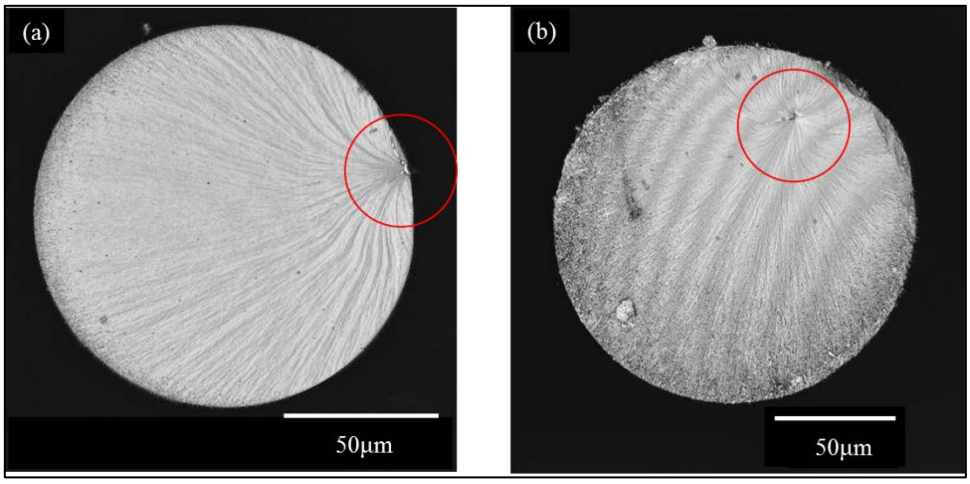

Figure 11. Fracture surfaces of epoxy fiber specimens after tensile test; (a) Surface initiation failure (b) Internal initiation failure

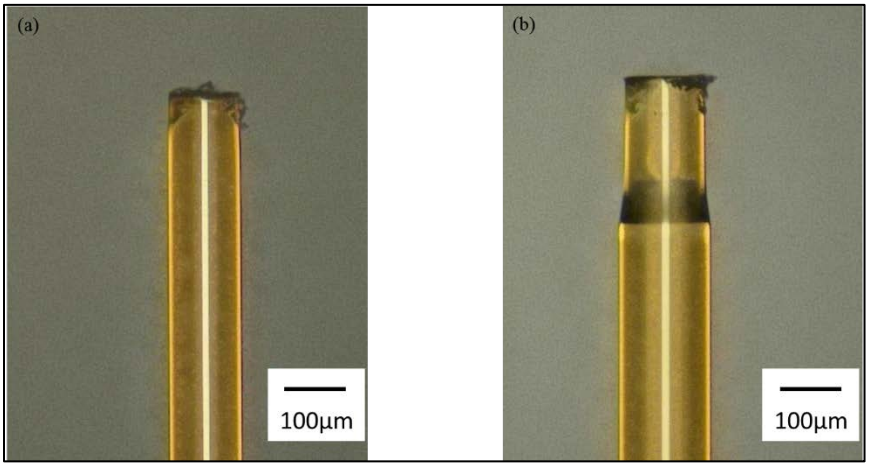

Figure 12. Side view of tensile failure location of epoxy fiber specimens (a)Failure without necking (b) Failure with necking

Thermal analysis of tensile specimens

It is important to prove that the macroscopic and micro-fiber specimens which have significantly different surface area per specimen volume ratios have the same degree of cure since differences in degree of cure can also affect mechanical properties. Thermal analysis using DSC was conducted to measure the degree of cure for the epoxy micro-fiber

and macroscopic specimens. Table 4 presents the DSC results and the degree of cure were quite consistent between micro-fiber and macroscopic specimens in all resin systems. These results indicate that the difference in the mechanical properties between microfiber and macroscopic specimens are mainly caused by the difference in specimen volume and surface roughness, and not due to the degree of cure.

Table 4. Results of DSC analysis

Sample name	DSC	
	Degree of cure (%)	
	Epoxy resin fiber	Macroscopic specimen
TGDDM	93	92
DGEBA	100	100
TGMAP	99	98
TGDDM-A1	95	92
TGDDM-A2	99	99

Conclusion

In this study, preparation method of micro scale epoxy fiber specimen for tensile testing was developed to evaluate epoxy resin mechanical properties at length scales representative

of matrix resin in CFRP. Five types of epoxy resin systems were prepared and epoxy fiber specimens with diameters in the range of 100-150 μm were used for tensile testing. Epoxy micro-fibers showed ductile behavior with distinct yield point in all resin systems, while macroscopic specimens exhibited brittle behavior with no yield point. Failure strain and ultimate stress of epoxy micro-fiber specimens were significantly higher than those of their macroscopic counterparts. These results indicate that epoxy resin potentially has much higher ductility and strength at lower length scales.

Some epoxy micro-fiber specimens showed necking behavior during the tensile test. This indicates that changing macroscopic specimens to micro scale epoxy fibers significantly improved their plasticity. It was proven that macroscopic and micro-fiber specimens have the same degree of cure by using DSC measurements. These results indicate that the difference of the mechanical properties between micro-fiber and macroscopic specimens are mainly caused by the difference of specimen volume and surface roughness. Tensile testing of unidirectional CFRP will be conducted in future studies to understand the effect of matrix resin properties on the tensile strength of CFRP.

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