

CARBON FIBER TEXTILE COMPOSITES USING HIGHLY-POLYMERIZED THERMOPLASTIC EPOXY: EFFECT OF MOLECULAR WEIGHT OF EPOXY ON THE MECHANICAL PERFORMANCE OF COMPOSITES

Hironori Nishida¹ *, Keisuke Nagai¹, Souichirou Imagawa¹,
Kazuya Okubo², Toru Fujii², Valter Carvelli³

¹ Graduate School of Doshisha University, Tatara Kyotanabe, Kyoto Japan

² Department of Mechanical Engineering, Doshisha University,
Tatara Kyotanabe, Kyoto, Japan

³ Department of A.B.C., Politecnico di Milano, Milan, Italy

* Corresponding Author: eup1504@mail4.doshisha.ac.jp

Keywords: Thermoplastic epoxy; Weight-average molecular weight; Carbon plain weave composite; Mechanical properties.

ABSTRACT

The purpose of this study is to reveal the effect of resin molecular weight on the mechanical properties of carbon fabric reinforced thermoplastic epoxy composites (CFRTP). An extensive experimental campaign allowed understanding the influence of the thermoplastic resin with weight-average molecular weight (Mw) ranging from 14,000 to 117,000. Different loading conditions were applied, including quasi-static and cyclic three point bending and tensile loadings. Moreover, fiber-matrix adhesion and interlaminar fracture toughness were measured by micro-droplet and End Notched Flexure (ENF) mode II fracture tests. The mechanical responses highlighted the considerable improvements of the composite performances for thermoplastic epoxy with high polymerization (high molecular weight). It is also shown that an excessive polymerization, greater than 60,000 Mw, is not necessary for composite performance.

1. INTRODUCTION

Recent developments have increased the interest of aerospace and automotive industries in carbon fabric reinforced thermoplastic resins (CFRTP) [1]-[7]. They show benefits over their thermoset counterpart, such as an increased toughness, a better recyclability, and shorter production cycle times. In an effort to reduce costs and to bring CFRTPs to their full potential, many developments were made. However, common thermoplastic resins have a higher melt viscosity than the thermosetting ones. This does not allow an easy infusion process and good impregnation of fibers. Therefore, various impregnation methods were studied. In [8], a method was proposed for reducing the viscosity of the resin with a solvent. However, the solvent must be removed during the manufacturing of the composite. Powdered and commingled methods were studied to reduce the impregnation length, which is the path of the matrix to complete the impregnation process [9]. A fine matrix powder was combined with reinforcing fibers in [10, 11], but the powder can be easily dislodged from the filaments. Commingled fabrics were proposed in [12, 13]. Recently, CFRTPs using in-situ resin received a lot of attentions [14, 15], for the development of thermoplastic epoxy resin (TP-epoxy) with linear crosslinked structure. The weight-average molecular weight (Mw) of TP-epoxy depends on the polymerization temperature and the polymerization time [16]. It is also known that the mechanical properties of TP-epoxy depend on the Mw of resin, see e.g. [17]. However, the effect of Mw on the mechanical performance of CFRTP was not well clarified.

The purpose of this study is to give a contribution in understanding the effect of Mw of TP-epoxy matrix on the mechanical properties of CFRTP. Quasi-static and fatigue performances of CFRTP were investigated based on the three-point bending and tensile tests. Moreover, fiber-matrix adhesion and interlaminar fracture toughness were measured by micro-droplet and End Notched Flexure (ENF)

mode II fracture tests. The imparted damage was observation by Scanning Electron Microscopy (SEM) and X-ray Computed Tomography to highlight the considerable effects of the molecular weight of thermoplastic epoxy matrix.

2. MATERIALS

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 inch, areal weight 200 g/m²). Thermoplastic epoxy resin (DENATITE XNR 6850A, ACCELERATOR XNH 6850B; supplied by Nagase ChemteX Corporation, Japan) was used as matrix (T_g was approximately 100 °C).

2.1. Fabrication of CFRTP prepreg

Plain weave CFRTP prepreg was made by the following procedure. The resin, 'XNR6850A', was heated by using an electric oven at 120 °C. Next, when the temperature of the resin reached 105 °C, the accelerator 'XNH6850B' was added to the resin with stirring. After that, 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.

2.2. Fabrication of CFRTP laminates

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 cut into 245x245 mm and dried at 50 °C for 12 hours. CFRTP laminates were prepared by press molding with 10 layers (for quasi-static and cyclic three point bending and tensile tests) and 20 layers (for mode II tests) of dry prepreg at 175~195 °C and 6~12 MPa on a heat-press device. The carbon fiber volume fraction of the CFRTP laminates was approximately 45 %.

In the present experimental investigation, the adopted weight-average molecular weights of the thermoplastic epoxy matrix are listed in Table 1.

Tensile test	37k	63k	84k		
Bending test	36k	63k	100k		
Micro-droplet test	26k	34k	53k	70k	90k
End Notched Flexure test	14k	54k	63k	108k	

Table 1: Weight-average molecular weight (M_w) of specimens used for each test (k means thousand).

3. EXPERIMENTAL PROGRAM

3.1. Measurement of weight-average molecular weight

The weight-average molecular weight of the thermoplastic epoxy matrix was measured 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 molecular weight 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 condition. Equation (1) was used to derive the interfacial shear strength (τ).

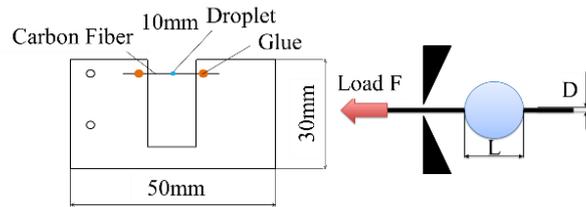


Figure 1: Specimen for micro-droplet test.

$$\tau = \frac{F}{\pi DL} \quad (1)$$

where τ is the interfacial shear strength; F is the pullout 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 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 200 (length) x 25 (width) x 2 (thickness) mm. The surface strain distribution of the specimen was analysed by the DIC (Digital Image Correlation) method. The surface was speckled with black and white acrylic paints for a length of about 4 cm (see Figure 2). During loading, digital images were taken by using a camera (24.16 M pixels) with a frequency of 1 Hz. Post processing of images by the software VIC-2DTM allowed measurements of full-field displacement and strain distribution up to the complete failure, separation in two parts, of the specimen.

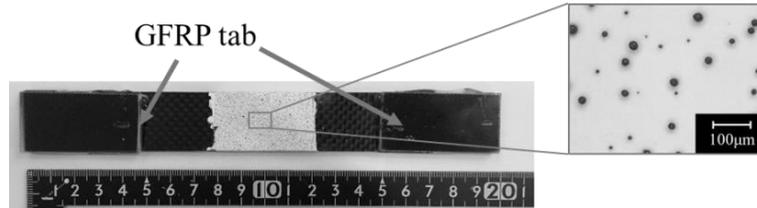


Figure 2: Specimen for quasi-static and fatigue tensile tests.

3.4. Fatigue tension-tension tests

The fatigue life of CFRTP under cyclic tension-tension loading in the warp direction was measured using specimens (Figure 2) whose dimensions were the same as those of quasi-static tensile test. The cyclic stress ratio and frequency were $R=0.1$ and $f=5$ Hz at room temperature. The maximum cyclic stress was 80%, 75% and 70% of the tensile strength. At least 3 specimens were tested for each load level and each M_w .

3.5. Quasi-static bending tests

The quasi-static three-point bending tests of CFRTP were conducted according to the standard JIS K7074 at 1 mm/min (cross head speed) by using a universal material testing machine. Dimensions of parallel sided specimens were 100 (length) x 15 (width) x 2 (thickness) mm. An X-ray CT scanner was used for observing the imparted internal damage.

3.6. Fatigue bending tests

The fatigue life of CFRTP under cyclic three-point bending load was measured with same shape of specimen as quasi-static bending test. The cyclic stress-ratio and frequency were $R=0.1$ and $f=2$ Hz at

room temperature. The maximum cyclic stress was 80%, 70% and 60% of the three-point bending strength. At least 3 specimens for each load condition and each Mw.

3.7. End Notched Flexure (ENF) test

Figure 3 shows geometry of specimen for ENF test. The CFRTP laminate, prepared for ENF test, had 20 layers of plain weave carbon fabric. Specimen with the size of 140 (length) x 20 (width) x 3 (thickness) mm were subjected to quasi-static three-point bending load. The Mode II inter-lamina fracture toughness of CFRTP was determined at 0.5 mm/min of cross-head speed. The length of pre-crack was 50 mm. Kapton film of approximately 30 μ 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.

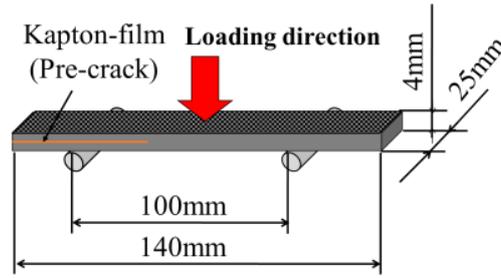


Figure 3: Specimen for ENF test.

$$G_{IIc} = \frac{9a_1^2 P_c^2 C_1}{2B(2L^3 + 3a_1^3)} \quad (2)$$

where

$$a_1 = \left[\frac{C_1}{C_0} a_0^3 + \frac{2}{3} \left(\frac{C_1}{C_0} - 1 \right) L^3 \right]^{\frac{1}{3}} \quad (3)$$

Symbols in Eqns. (2, 3) have the meaning: G_{IIc} is mode II inter-lamina fracture toughness; a_0 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

4. RESULTS AND DAMAGE OBSERVATIONS

4.1. Micro-droplet test

Figure 4 shows the relationship between the weight-average molecular weight of matrix and the interfacial shear strength as obtained by micro-droplet tests. The interfacial shear strengths between the carbon fiber and matrix were improved about 30% when the molecular weight increase from Mw=25k to Mw=54k. The improvement is not significant when the molecular weight is higher than the latter value. Highly polymerization of the matrix was effective for increasing the interfacial shear strength between the carbon fiber and matrix. This allows a better load transfer between carbon fiber and matrix. Figure 5 shows the surface of carbon fiber after micro-droplet tests by SEM. The smooth surface of carbon fiber was observed with resin of Mw=25k (Figure 5a), while considering Mw=90k, the better adhesion is confirmed by some residual matrix still bounded to the fiber (Figure 5b).

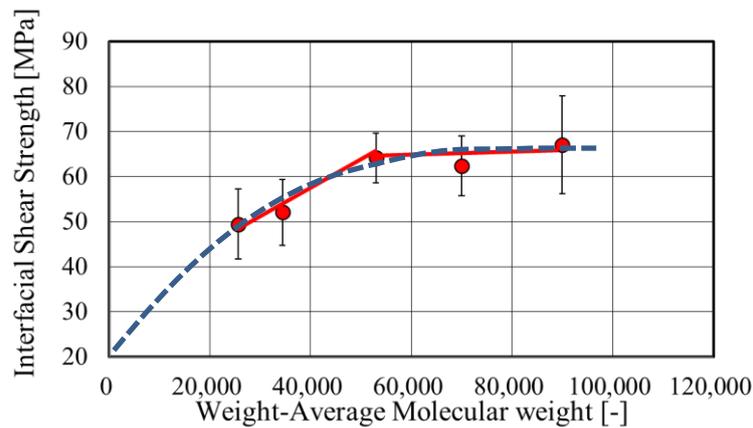


Figure 4: Micro-droplet test: interfacial shear strength vs. Mw.

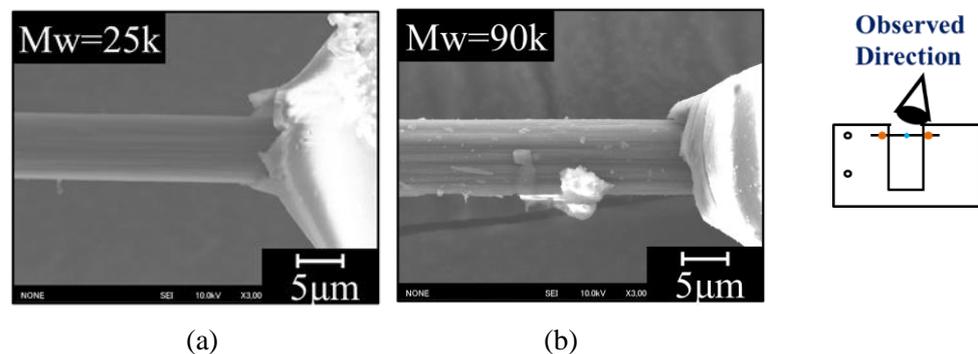


Figure 5: Micro-droplet test: carbon fiber at the adhesion failure for Mw: (a) 25k and (b) 90k.

4.2. Quasi-static tensile tests

Figure 6 presents the relationship between the weight-average molecular weight of the matrix and the quasi-static tensile strength and elastic modulus of CFRTP. The tensile strength of CFRTP was improved by highly polymerization of matrix. Figure 7 shows the results of the DIC measurements. Some differences are clear for the strain distribution on the surface of specimens with lower and higher molecular weight. When the molecular weight of matrix is higher than 63k, the strain attains lower value for the same stress level than for lower molecular weight Mw=37k. Furthermore, in the case of Mw=37k, the strain has local concentrations for tensile stress of 400 MPa. While, in the case of Mw=63k and Mw = 84k, the strain was almost uniform even when the tensile stress reached 600 MPa. The fracture surface after quasi-static tensile tests was observed by SEM (Figure 8). The smooth surface of carbon fibers was observed with matrix of Mw=37k (Figure 8a). In the case of Mw=84k, matrix was still bounded to the surface of carbon fibers (Figure 8b), as observed on the surface of specimens for micro-droplet. Therefore, the better adhesion of fiber and higher molecular weight matrices allows a uniform distribution of the deformation even up to load level close to the failure. This results in the improvement of tensile mechanical properties.

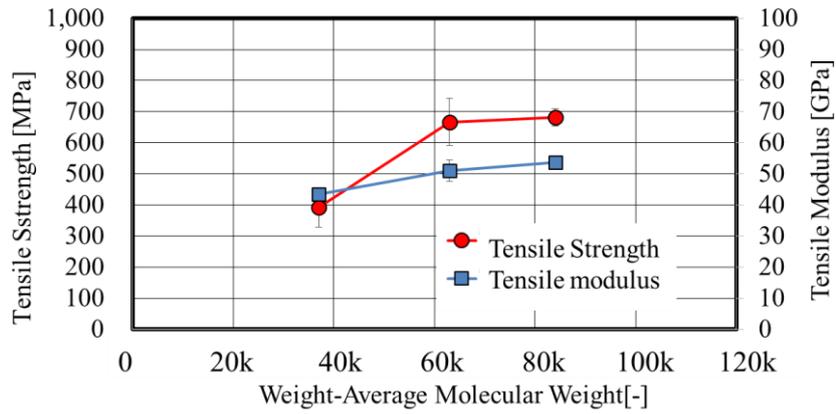


Figure 6: Tensile strength and elastic modulus vs. Mw.

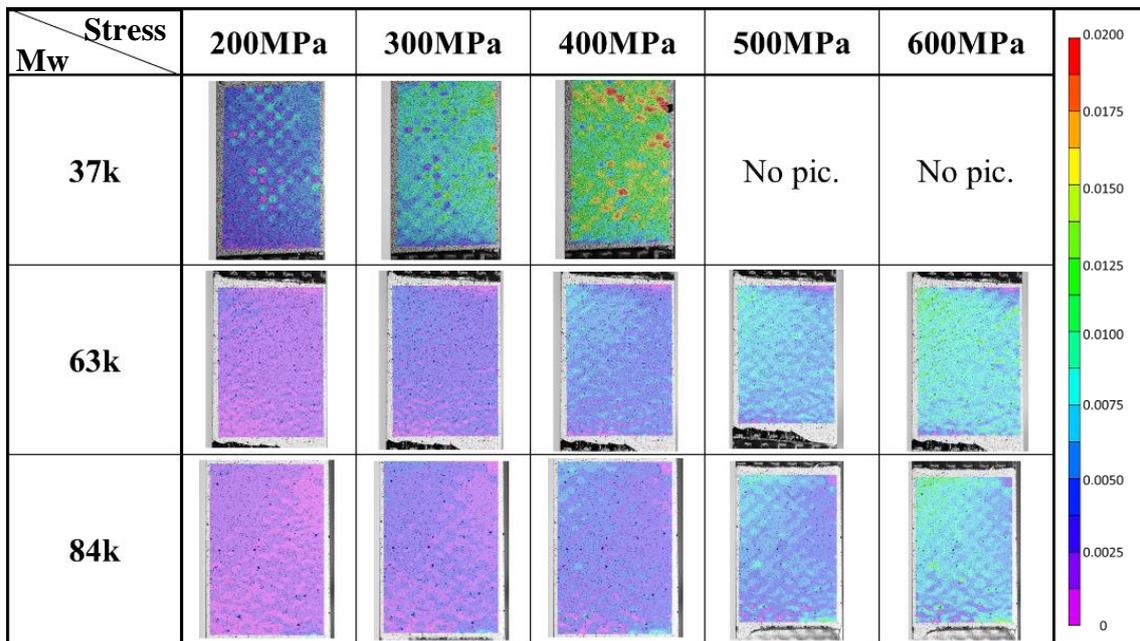


Figure 7: Maximum principal strain component distribution by DIC on the specimen surface for different tensile load levels.

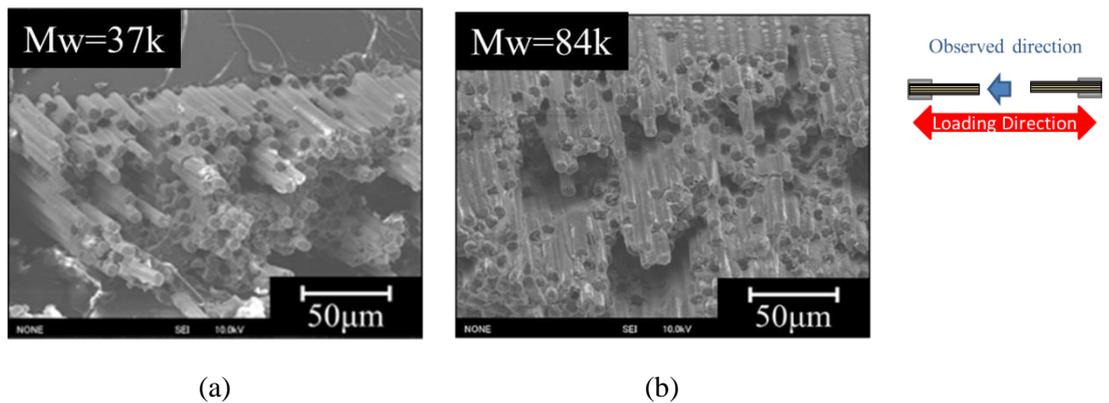


Figure 8: Fracture surface after quasi-static tensile failure for Mw: (a) 37k and (b) 84k.

4.3. Fatigue tension-tension tests

The fatigue life diagram S-N as obtained by tension-tension cyclic tests, is depicted in Figure 9. The tensile fatigue life of CFRTP were improved by approximately 100 times when the Mw was higher than 100k, compared to composite with Mw=32k. Figure 10 shows the fracture surface after cyclic loading of level 75% by SEM. In the case of Mw=100k, as for quasi-static loading, matrix has still good adhesion to carbon fibers (see Figure 10b), while the composite with lower Mw did not have residual resin on fibers (Figure 10a). Therefore, the fatigue life extension is consequence of the better mechanical interaction between the thermoplastic epoxy and the carbon fiber with an enhanced adhesion, as mentioned above.

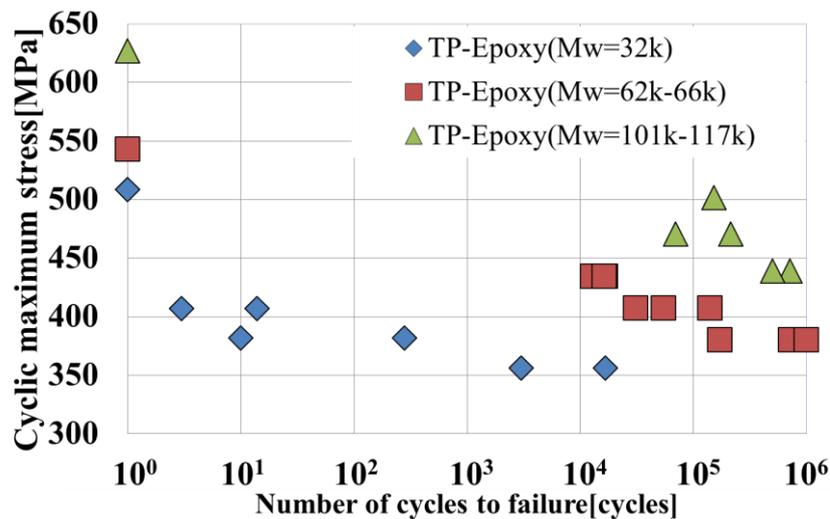


Figure 9: Tensile-tensile fatigue life S-N diagram.

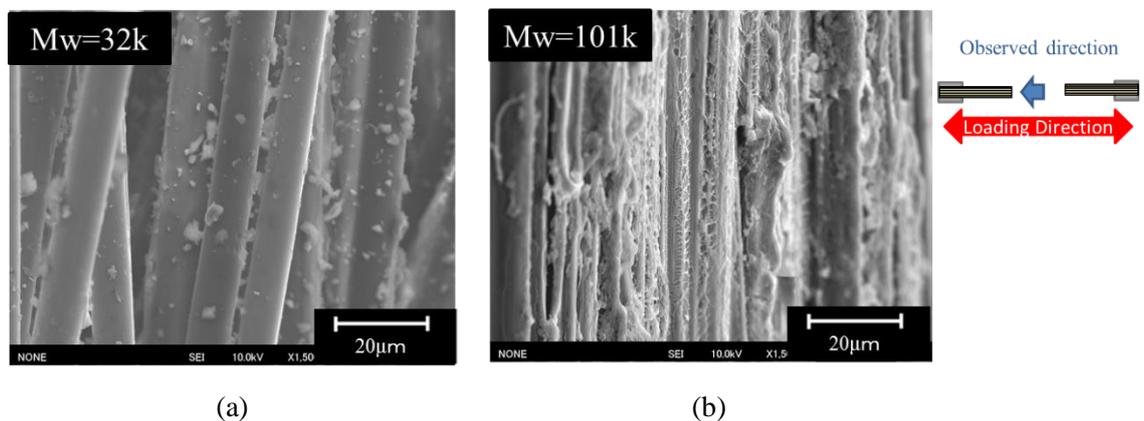


Figure 10: Fracture surfaces after tension-tension fatigue tests: load level 75%.

4.4. Bending tests

Figure 11 shows the relationship between the weight-average molecular weight of the matrix and the quasi-static bending strength and elastic modulus of CFRTP. The bending strength was improved about 60% with the Mw=100k compared to Mw=36k. The quasi-static three-point bending strength highlights the same tendency of tensile strength (Figure 6).

The fracture surface after quasi-static three-point bending test as observed by SEM is detailed in

Figure 12. The smooth surface of carbon fibers was observed with matrix of Mw=36k (Figure 12a). In the case of Mw=100k, matrix was still bounded to the surface of carbon fibers (Figure 12b).

Observations by X-ray CT of the failure mode after quasi-static three-point bending test provide more insight of the Mw effect. In the case of Mw=36k, some cracks propagate at interlaminar and interface between CF and matrix (Figure 13a). In the composite with matrix of Mw=100k only few interlaminar cracks were detected of limited length (Figure 13b) and fibers failure was the main failure mode. The higher Mw matrix delayed the initiation of cracks at the fiber/matrix interface and at the inter-laminae level.

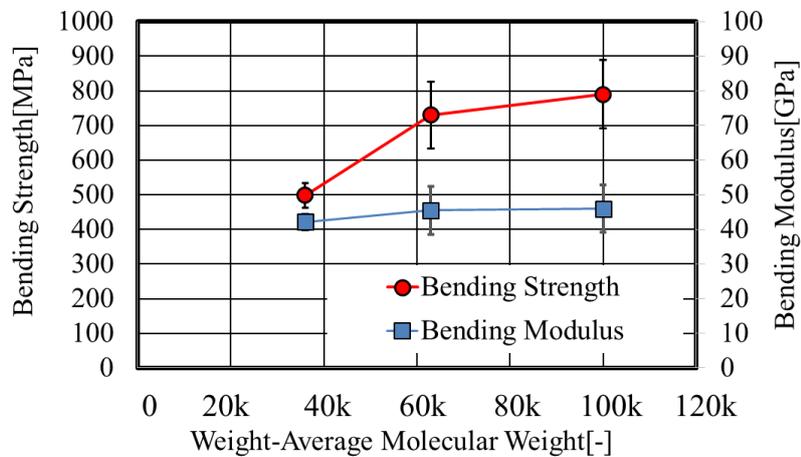


Figure 11: Bending strength and elastic modulus vs. Mw.

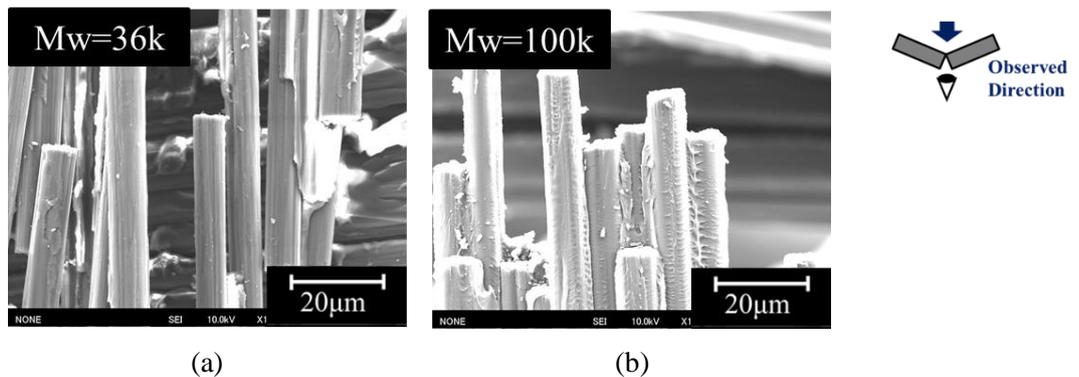


Figure 12: Fracture surface after static three-point bending test for Mw: (a) 36k and (b) 100k.

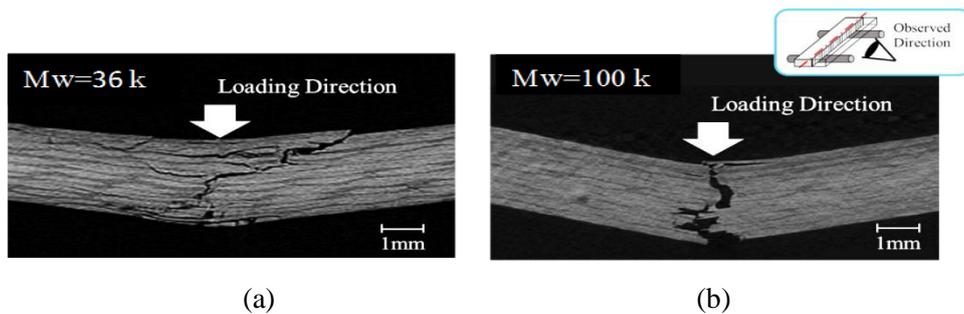


Figure 13: Three-point bending failure mode by X-ray CT, inside view of specimens with Mw: (a) 36k and (b) 100k.

4.5. Fatigue bending tests

The fatigue life S-N diagram of three-point cyclic bending tests is in Figure 14. The bending fatigue life of CFRTP were improved by approximately 10 times when the TP-epoxy of Mw=100k is adopted, compared to composite with Mw=36k. The fracture surface after three-point bending cyclic loading of level 80%, observed by SEM, reveals for Mw=100k matrix still with good adhesion to carbon fibers (Figure 15b). Decreasing the MW creates a weaker adhesion, and, at the bending failure, fibers show almost clean surface (Figure 15a).

Figure 16 and Figure 17 present the failure mode observed from the side and the inside of specimen after three-point bending fatigue test load level 80%, by microscope (Figure 16) and X-ray CT (Figure 17). The delamination was extremely reduced when the TP-epoxy with high weight-average molecular weight was selected (Figure 16b and 17b). While extensive delamination was observed at different layer levels in the thickness when the lower Mw matrix is considered (Figure 16a and 17a). The latter created a more complex interaction of damage mechanisms including fiber-matrix debonding, delamination and fibers breakage.

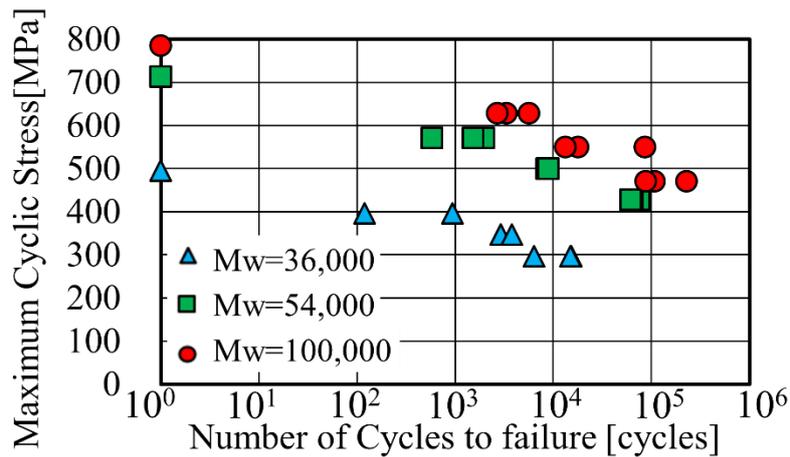


Figure 14: Bending S-N diagram of CFRTP.

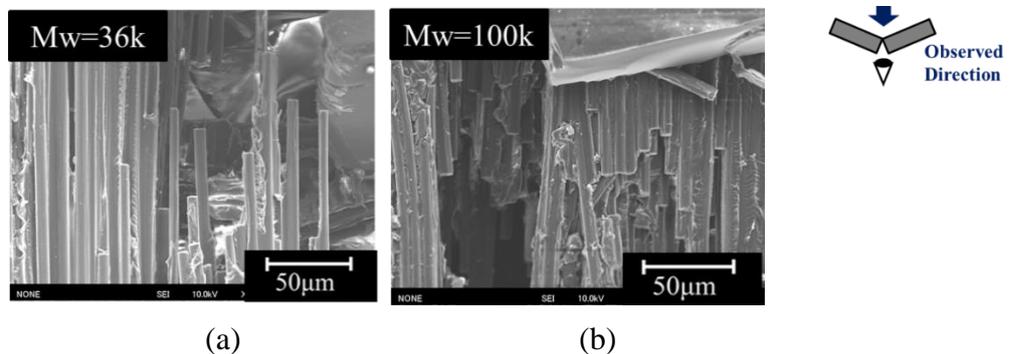


Figure 15: Fracture surfaces after three-point bending fatigue tests, load level 80%, for Mw: (a) 36k and (b) 100k.

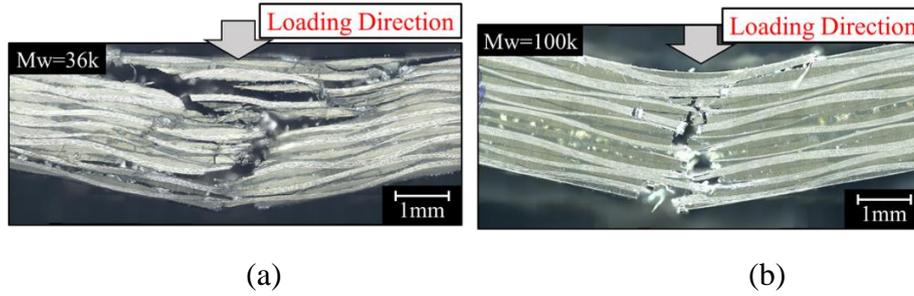


Figure 16: Microscope observation of the three-point bending fatigue failure mode, side surface, for Mw: (a) 36k and (b) 100k.

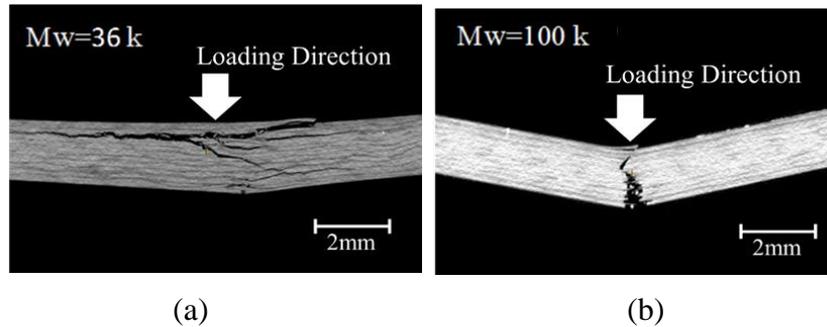


Figure 17: Three-point bending fatigue failure mode by X-ray CT, inside view of specimens with Mw: (a) 36k and (b) 100k.

4.6. Mode II inter-lamina fracture toughness

The Mode II inter-lamina fracture toughness modification with increasing weight-average molecular weight of matrix is detailed in Figure 18. The Mode II fracture toughness increases of almost 9 times from the lower to the higher considered Mw. This improvement can be connected to the SEM observations of the crack propagation surface close to the pre-crack tips after ENF tests (Figure 19). Brittle fracture with glassy matrix and carbon fiber/matrix debonding was observed for TP-epoxy of Mw=14k (Figure 19a). The “plastic” deformation of the matrix with good adhesion to carbon fiber was recorded for TP-epoxy of Mw=108k (Figure 19b). The ‘ductile’ behavior of the high Mw matrix allowed a relaxation of the stress concentration due to the increase of the radius at the crack tip, and, as consequence, the propagation of crack was delayed.

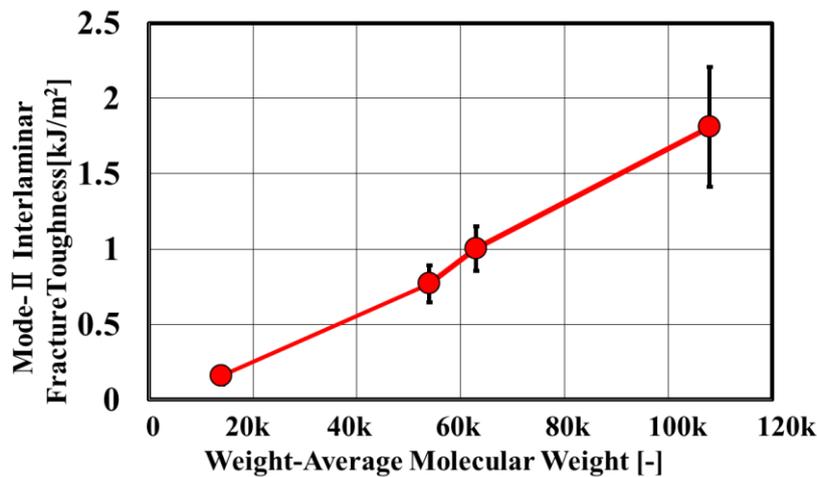


Figure 18: Mode II inter-lamina fracture toughness vs. Mw.

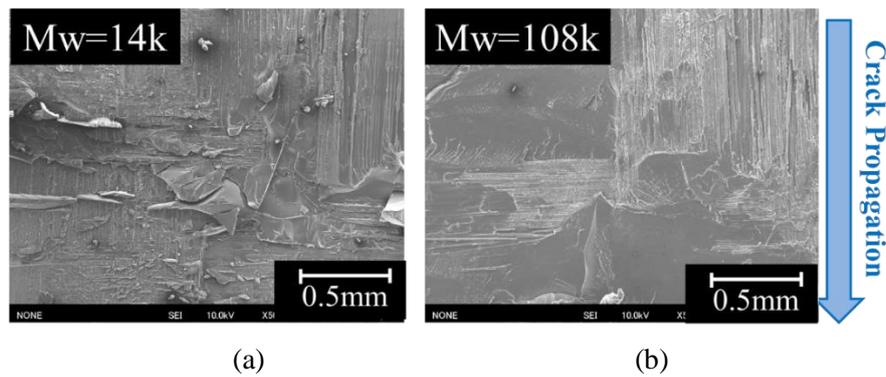


Figure 19: Fracture surfaces after ENF tests for Mw: (a) 14k and (b) 108k.

5. CONCLUSIONS

The influence of the weight-average molecular weight of thermoplastic epoxy resin (TP-epoxy) was experimentally investigated considering the mechanical response of a carbon textile reinforced composite. The mechanical performance was measured for different loading conditions. Quasi-static and cyclic bending and tensile behavior of different Mw thermoplastic epoxy carbon reinforced composites were considered. Moreover, micro-droplet tests were performed to preliminarily measure the effect at the level of the fiber and matrix adhesion. Finally, the Mode II inter-lamina fracture toughness was also measured.

The main results of the present investigation are:

- TP-epoxy matrix with Mw higher than 54k had an improvement of the adhesion to carbon fiber of about 30% compared to the lower considered Mw.
- Both quasi-static tensile and bending strength were notably improved with Mw higher than 60k. This is related to the better fiber and matrix adhesion leading to the modification of the failure mode involving mainly higher energy mechanisms (e.g. fibers breakage).
- The fatigue life of the textile composite with the higher Mw was considerably extended for both bending and tensile cyclic loading.
- The improvement of the fiber and matrix adhesion strength was, moreover, confirmed with the enhancement of the mode II fracture toughness, mainly motivated with the ‘ductile’ behavior of the high Mw TP-epoxy matrix leading to stress redistribution at the crack tip.

In conclusion, the present investigation demonstrates the capacity of the thermoplastic epoxy matrix with high level of polymerization to effectively improve the fiber and matrix adhesion, to delay the initiation and propagation of the damage and to considerably enhance the mechanical performance of the considered carbon textile reinforced composite.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the support of Doshisha University Reserch & Development Center for Advanced Composite Materials and Nagase ChemteX Corporation, Japan.

REFERENCES

- [1] A. Erber, S. Spitko, Expanded role for thermoplastic composites, *Reinforced Plastics*, **58**, 2014, pp. 29-33
- [2] M. Pam Brady, Automotive composites: which way are we going?, *Reinforced Plastics*, **51**, 2007, pp. 32-35
- [3] M. Pam Brady, Automotive composites –the search for efficiency, value and performance, *Reinforced Plastics*, **51**, 2007, pp. 26-29
- [4] R. Stewart, Automotive composites offer lighter solutions, *Reinforced Plastics*, **54**, 2010, pp. 22-28

- [5] G. Marsh, Composites poised to transform airline economics, *Reinforced Plastics*, **57**, 2013, pp. 18-24
- [6] J. Klimke, D. Rothmann, Carbon composite materials in modern yacht building, *Reinforced Plastics*, **54**, 2010, pp. 24-27
- [7] M. Pam Brady, Technology developments in automotive composites, *Reinforced Plastics*, **54**, 2010, pp. 25-29
- [8] B. Liu, A. Xu, L. Bao, Preparation of carbon fiber-reinforced thermoplastics with high fiber volume fraction and high heat-resistant properties, *Journal of Thermoplastic Composite Materials*, 2015, DOI: 10.1177/0892705715610408
- [9] A. Xu, L. Bao, M. Nishida, A. Yamanaka, Molding of PBO Fabric Reinforced Thermoplastic Composite to Achieve High Fiber Volume Fraction, *Polymer Composites*, **34**, 2013, pp. 953-958.
- [10] J.H. Chen, E. Schulz, J. Bohse, G. Hinrichsen, Effect of fibre content on the interlaminar fracture toughness of unidirectional glass/fibre polyamide composite, *Composites: Part A*, **30**, 1999, pp. 747-755
- [11] A. K. Mohanty, L. T. Drzal & M. Misra, Engineered natural fiber reinforced polypropylene composites influence of surface modifications and novel powder impregnation processing, *Journal of Adhesion Science and Technology*, **16**, 2002, pp. 999-1015
- [12] A.C. Long, C.E. Wilks, C.D. Rudd, Experimental characterization of the consolidation of a commingled glass/polypropylene composite, *Composites Science and Technology*, **61**, 2001, pp. 1591-1603
- [13] L. Ye, K. Friedrich, J. Kästel, Y. Mai, Consolidation of unidirectional CF/PEEK composites from commingled yarn prepreg, *Composites Science and Technology*, **54**, 1995, pp. 349-358
- [14] G. Ben, K. Sakata, Fast fabrication method and evaluation of performance of hybrid FRTPs for applying them to automotive structural members, *Composite Structures*, **133**, 2015, pp. 1160-1167
- [15] A. Hirabayashi, G. Ben, H. Ozeki, Heat resistance properties of FRTP composed of in-situ polymerization PA6 and CF and GF fabrics, *Proceedings of 19TH International conference on composite materials*, Montreal, Canada, 2013.
- [16] H. Nishida, The development of thermoplastic epoxy resin and continuous fiber reinforced thermoplastics using it, *Journal of the Adhesion Society of Japan*, **51**, 2015, pp. 516-523.
- [17] T. Imanishi, H. Nishida, N. Hirayama, N. Tomomitsu, In situ polymerizable thermoplastic epoxy resin and high performance FRTP using it and fiber fabrics, *Proceedings of 16TH International conference on composite materials*, Kyoto, Japan, 2007.