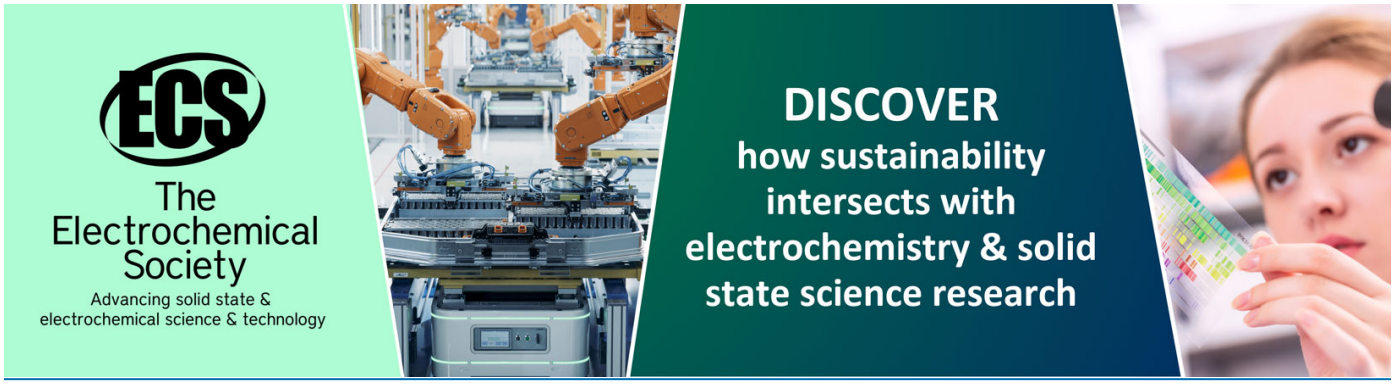
Improvement of mode-II interlaminar fracture toughness of carbon textile composites with modified matrix of thermoplastic and thermoset epoxy-addition of glass fibers



IOP Conf. Series: Materials Science and Engineering **406** (2018) 012045 doi:10.1088/1757-899X/406/1/012045

Improvement of mode-II interlaminar fracture toughness of carbon textile composites with modified matrix of thermoplastic and thermoset epoxy -addition of glass fibers

Soichiro Imagawa[1], Hironori Nishida[2], Kazuya Okubo[2], Toru Fujii[2]

[1] Graduate School of Doshisha University, Kyotanabe, Kyoto 610-0394, Japan
[2] Department of Mechanical Engineering, Doshisha University, Tatara Kyotanabe, Japan

Abstract. Interlaminar fracture toughness of a material with a layered structure such as CFRP is poor and cracks between the layers easily lead to fatal result. Interlaminar fracture toughness still plays an important role in damage propagation of CFRP. In this study, mode II inter-lamina fracture toughness of CFRP was investigated by ENF test for clarifying effect on weight-average molecular weight of matrix and matrix modification with glass fiber. Micro glass fibers whose diameter was 0.5μm with 0.3wt% of weight content were added into thermoplastic epoxy resin and thermoset epoxy resin, respectively, for the matrix of the textile carbon fiber composite prepared by our laboratory. State of the fracture surface was also changed accompanying with the change of the weight-average molecular weight of the matrix. In these results, Mode II interlaminar fracture toughness of the composite was improved by preventing the crack propagation with fiber bridging of added glass fibers on the interface regardless of the types of matrix of thermoplastic and thermoset epoxy resin.

1. Introduction

Carbon fiber reinforced thermal polymer (CFRTP) is one of the most important materials for structural applications, particularly in aviation industries owing to its high strength to weight ratio.[1]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 [2], 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 [3]. A fine matrix powder was combined with reinforcing fibers in [4, 5], but the powder can be easily dislodged from the filaments. Commingled fabrics were proposed in [6, 7]. Recently, CFRTPs using in-situ resin received a lot of attentions [8], 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 [9]. It is also known that the mechanical properties of TP-epoxy depend on the Mw of resin, see e.g. [10]. In previous study, it is also known that mechanical performance of CFRP was improved by addition of glass fiber. However, effect of the addition of glass fibers as extra modification into highly polymerized thermo-plastic epoxy resin on

mechanical properties of the composite has not been experimentally discussed, comparing the effect on that with thermoset-plastic. In this study, mode II inter-lamina fracture toughness of CFRP was investigated by ENF test for clarifying effect on weight-average molecular weight of matrix and matrix modification with glass fiber. Micro glass fibers whose diameter was 0.5 μ m with 0.3wt% of weight content were added into thermoplastic epoxy resin and thermoset epoxy resin, respectively, for the matrix of the textile carbon fiber composite preparedby our laboratory.

2. Materials and testing machine

2.1 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 (Tg was approximately 100 °C). Thermoset epoxy resin (supplied by Mithubishi Chemical Corporation, Japan) was used as matrix. Glass fiber (FM1700) were used as modified matrix. Glass fiber with a diameter of 0.5μm and length of 150μm. Figure 1 shows a scheme of thermoplastic epoxy resin. Figure 2 shows a scheme of glass fiber (Nippon Muki Corporation, Japan).

Figure 1. Thermoplastic epoxy resin.

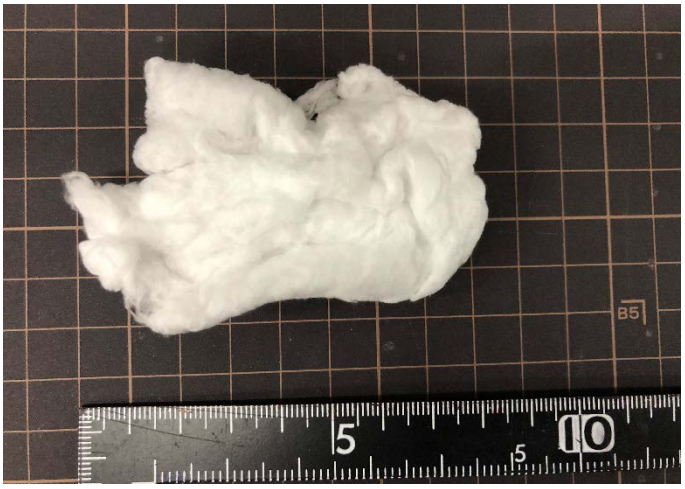


Figure 2. Glass fibers.

2.2 Condition of highly polymerization of thermo-plastic epoxy for matrix and measurement method of weight average molecular weight.

Figure 3 shows example of conditions for increasing the molecular weight Mw vs. Polymerization time of each temperature and Figure 4 shows measurement method of weight average molecular weight. The weight-average molecular weight of the thermoplastic epoxy matrix were measured by the gel permeation chromatography (Gel Permeation Chromatography; GPC) (CLASS-LC10: Shimadzu Corporation) and a column (Styragel HR4E, Styragel HR5E: waters). Tetrahydrofuran (THF) was used as the solvent. The calibration curves were drawn based on the retention time and the molecular weight of standard polystyrene (Polystyrene Polymer Laboratories Ltd.).

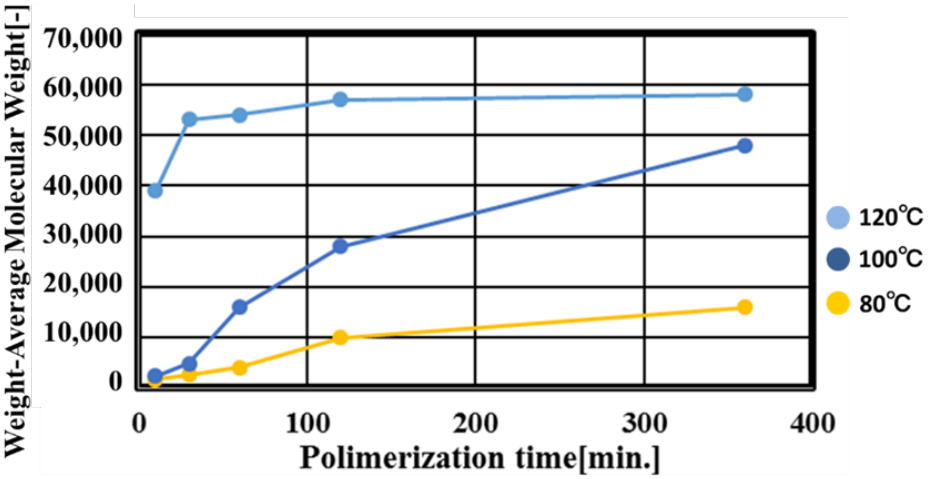


Figure 3. Relationship between Mw and polymerization time on temperature.

Figure 4. Measuring equipment of weight average molecular weight of resin.
(Gel Permeation Chromatography; GPC)

2.3 Fabrication procedure of matrix plate specimen of modified matrix

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 or modified resin with stirring. Viscosity of thermoplastic epoxy resin was reduced using electric furnace. After that, glass fiber was added on thermoplastic and thermoset epoxy resin in according to Figure 5 procedure. Matrix of

resin were prepared in which the weight content of glass fiber were 0.3wt%. Glass fiber was added into thermoplastic and thermoset epoxy resin using process homogenizer under the condition of 5,000 rpm 10min.

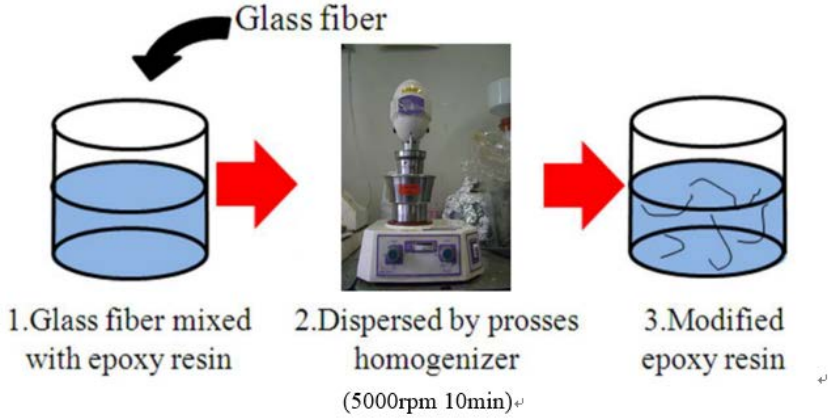


Figure 5. Mixed glass fibers with epoxy resin.

2.4 Fabrication of plain-woven CFRTP and CFRTS laminate

Plain weave CFRTP prepreg was made by the following procedure. 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 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 three point bending test) 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 case of CFRTP which added glass fiber on thermoplastic epoxy resin was the same of proceduer.

2.5 Fabrication of plain-woven CFRTS laminate

Plain weave CFRTS prepreg was made by the following procedure. The plain weave carbon fabric was impregnated with the thermoplastic epoxy resin by hand lay-up. The CFRP plates were cured at 80 degree-C for 1 hour and then at 150 degree-C for 3 hours. After curing, the plain-woven CFRP plates were cut into the dimension of specimen in orthotropic direction of fiber cloths. In the case of CFRTS which added glass fiber on thermoplastic epoxy resin was the same of proceduer.

3. Test procedure

3.1 Three point bending test

The resin which wrote Section 2/3 was poured into a glass plate and they were insert in electric oven. After that, modification of epoxy resin were polymerized and use it for three point bending test.
Dimensions of the specimen were 80 (length) x 10 (width) x 4 (thickness) mm. Three point bending test were conducted by using machine shown in Figure 6.

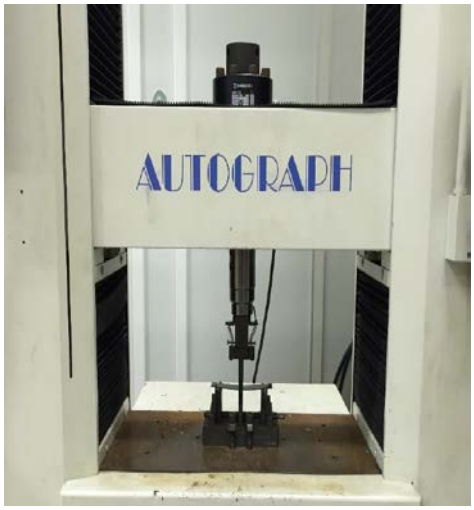


Figure 6. Test device for bending test.

3.2 ENF test

The CFRTP laminate, prepared for ENF test, had 20 layers of plain weave carbon fabric. Five specimen, for each considered Mw (see Table 2), 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. The Mode II inter-lamina fracture toughness was calculate by (1)

$$G_{IIC} = \frac{9a_1^2 F_c^2 C_1}{2B(2L^3 + 3a_1^3)} \tag{1}$$

where

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

Variables of GIIC, a0, Fc, C0, C1, a1, L, B denote the mode II interlaminar fracture toughness, initial crack length, critical load, compliance of the initial elastic region at loading point, compliance at critical load, estimated crack growth length at critical load, supports span, specimen width, respectively. Figure 7 shows a scheme of specimen of ENF. ENF test were conducted by using machine shown in Figure 6.

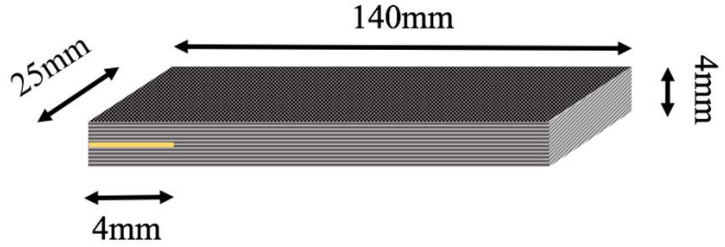


Figure 7. Geometry of ENF specimen.

4. Result and discussion

4.1 Monolithic matrix strength

Figure 8 shows the monolithic resin strength with respect to the weight average molecular weight. For comparison, the strength of TS-Epoxy and TSGF0.3wt% were also plotted. Test results showed that the monolithic resin strength of TP-Epoxy was improved with increase of its molecular weight. Moreover, when the molecular weight of TP-Epoxy exceeded about Mw=60,000, its monolithic strength was greater than that of TS-Epoxy. Test results also showed that the addition of glass fibers was effective to improve the monolithic resin strength regardless the type of epoxy. However, the degree of improvement in monolithic resin strength was significant when glass fibers were added into TS-Epoxy compared to that of TPGF0.3wt%.

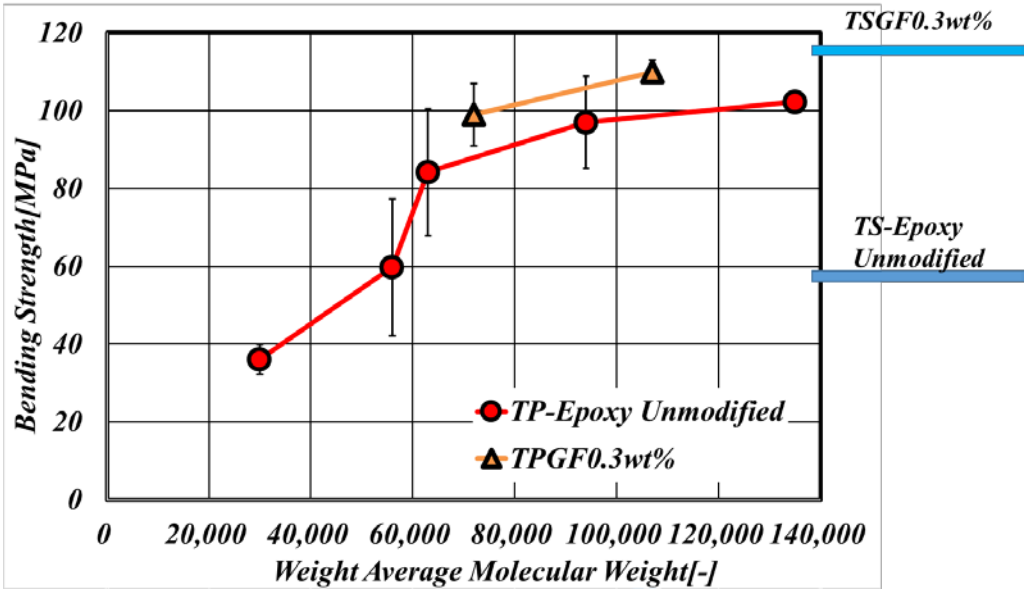


Figure 8. Relationship between bending strength and weight-average molecular weight on epoxy resin plate.

4.2 Mode II inter-laminar fracture toughness

Figure 9 shows the Mode-II interlaminar fracture toughness with respect to the weight average molecular weight. For comparison, the fracture toughness of TS-Epoxy and TSGF0.3wt% were also plotted. Test results showed that the Mode-II interlaminar fracture toughness was improved with almost linearly along its molecular weight increases. When the molecular weight of TP-Epoxy exceeded about Mw=60,000, the fracture toughness of CF/TP-Epoxy composites was greater than that of CF/TS-Epoxy composites. Figure 10 shows the fractured surfaces of ENF specimen observed by SEM. The observation of fractured surfaces revealed that the manner of fractured surface was changed with change of molecular weight of TP-Epoxy. At low molecular weight condition (Figure 10-a), the rough fractured surface was observed, while high molecular weight condition (Figure 10-b) showed smooth fractured surface. The addition of glass fibres was effective to improve the fracture toughness regardless the type of matrix. However, when TS-Epoxy was used as matrix, the degree of improvement in fracture toughness by adding the glass fibres was depend on its molecular weight. At low molecular weight TP-Epoxy (MW=45,000) was used, the improvement in fracture toughness by adding the glass fibres was about 25%, while high molecular weight condition (MW=60,000), its improvement in fracture toughness was about 140%. Figure 11 shows the magnified observation of fractured surface of TPGF0.3wt%. The existence of added glass fibres at its fractured surface was confirmed and residual resin on fibre surface was also confirmed. These results suggested that the Mode-II interlaminar fracture toughness of the composites was improved by fibres bridging of added glass fibres to preventing the

crack propagation.

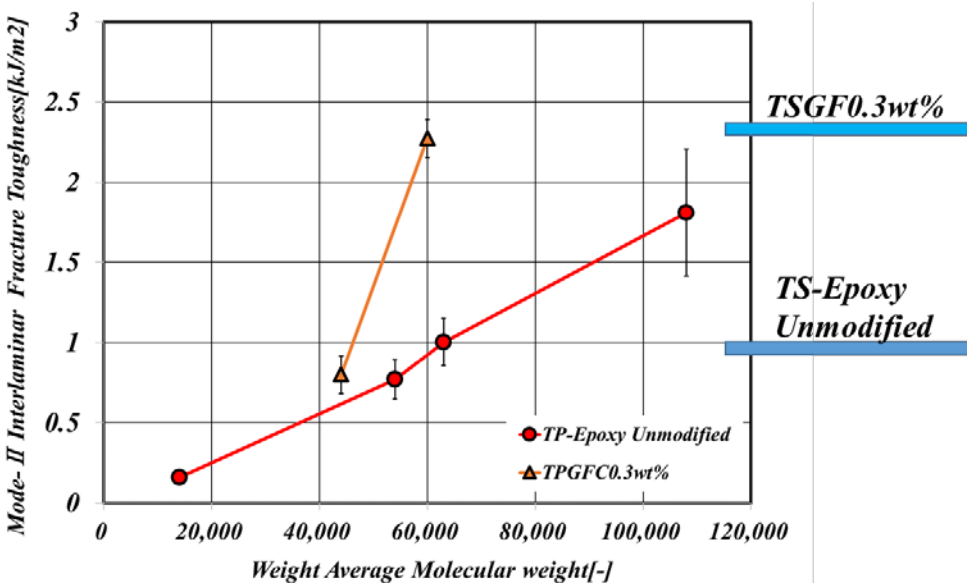
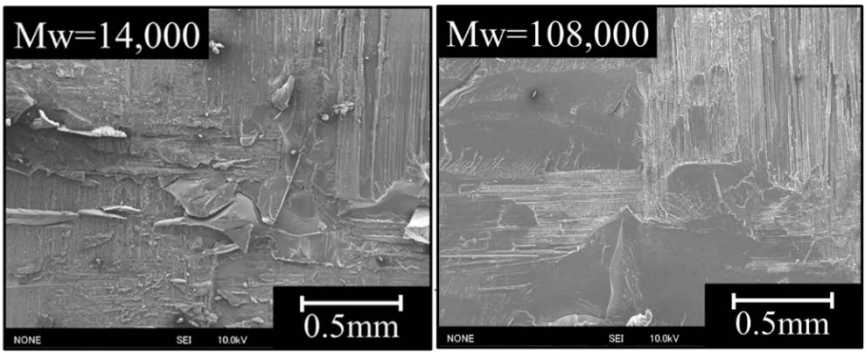


Figure 9. Relationship between Mode- II interlaminar fracture toughness and weight-average molecular weight and addition of glass fiber.



(a) (b)

Figure 10. State of the fracture surface for Mw: (a) 14,000 and (b) 108,000.

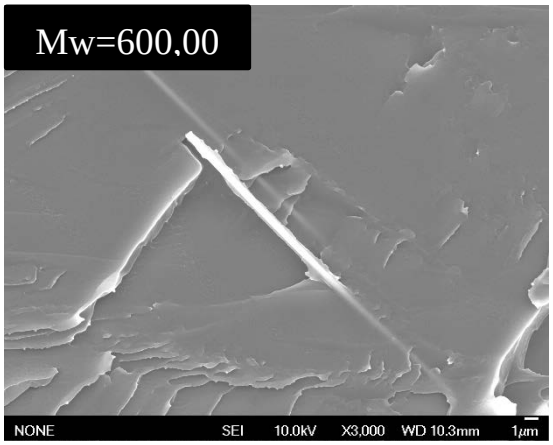


Figure 11. State of the fracture surface on addition of glass fiber on thermoplastic epoxy.

5. Conclusions

5.1 Monolithic resin strength was improved with increase of weight average molecular weight of thermo-plastic epoxy and also improved by addition of glass fibers to the thermoplastic and thermoset epoxy resin.

5.2 When addition of glass fiber on thermoplastic epoxy resin, fiber bridging was caused on CFRTP. Mode II interlaminar fracture toughness of the composite was improved by preventing the crack propagation with fiber bridging of added glass fibers on the interface regardless of the types of matrix of thermoplastic and thermoset epoxy resin.

Acknowledgements

The authors gratefully acknowledge the support of Doshisha University Reserch & Development Center for Advanced Composite Materials and Nagase ChemteX Corporation, Japan. And also, this work was financially supported by a (advanced technological) research project on “Research and Development Center for Advanced Composite Materials” of Doshisha University and MEXT (the Ministry of Education, Culture, Sports, Science and Technology, Japan) -Supported Program for the Strategic Research Foundation at Private Universities, 2013-2017,

References

[1] CFRTP and stainless steel laser joining: Thermal defects analysis and joining parameters optimization Junke Jiao Zifa Xu Qiang Wang Liyuan Sheng Wenwu Zhang doi: org/10.1016/j.optlastec.2018.01.023

[2] 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. doi: org/10.1177/0892705715610408

[3] 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. doi: org/abs/10.1002/pc.22501

[4] 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 doi: org/10.1016/S1359-835X(98)00188-2

[5] 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 doi: org/10.1163/156856102760146129

[6] 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. doi: org/10.1016/S0266-3538(01)00059-8

[7] Phong, N.T, Mohamed H. G., Okubo K., Chuong B., Fujii T. (2013) “Improvement in the mechanical performances of carbon fiber/epoxy composite with addition of nano-(Polyvinyl alcohol) fibers”, *Composite Structures*, Elsevier Limited, 99, pp.380-387. doi: org/10.1016/j.compstruct.2012.12.018.

[8] 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 doi: org/10.1016/j.compstruct.2015.07.093

[9] 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. doi: org 10.11618/adhesion.51.516

[10] 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.

[11] Hironori Nishida, Kazuya Okubo, Toru Fujii, Valter Carvelli, Improvement of bending strength of carbon fiber/ ther-moplastic epoxy composites- Effects of molecular weight of epoxy on carbon

fiber/matrix interfacial strength and connection of cracks in matrix -,Kyoto, Japan,2017 doi: 10.4236/ojcm.2017.74014.

[12] Nishida, H., .Carvelli, V., Fujii, T., and Okubo, K. (2018) 'Quasi-static and fatigue performance of carbon fibre reinforced highly polymerized thermoplastic epoxy', Composites Part B: Engineering, 144, pp. 163–170. doi: 10.1016/j.compositesb.2018.03.002. doi: 10.1016/j.compositesb.2018.03.002.

[13] Nishida, H., Okubo, K., Fujii, T., and Carvelli, V. (2017) 'Improvement of Bending Strength of Carbon Fiber/Thermoplastic Epoxy Composites-Effects of Molecular Weight of Epoxy on Carbon Fiber/Matrix Interfacial Strength and Connection of Cracks in Matrix', Open Journal of Composite Materials, 7(4), pp. 207–217. doi: 10.4236/ojcm.2017.74014. doi: 10.4236/ojcm.2017.74014.