RESIDUAL TENSILE PROPERTIES OF CARBON FIBER REINFORCED EPOXY RESIN COMPOSITES AT ELEVATED TEMPERATURES

Huang, G.[1], Lu, Q.J.[1], Li, Q.N.[1], Gu, C.H.[1] and Zheng, J.Y.[1,2,3]

[1] Institute of Process Equipment, Zhejiang University, Hangzhou 310027, China
[2] State Key Laboratory of Fluid Power and Mechatronic Systems, Zhejiang University, Hangzhou 310027, China
[3] Engineering Research Center for High Pressure Process Equipment and Safety, Ministry of Education, Zhejiang University, Hangzhou 310027, China

ABSTRACT

Carbon fiber reinforced epoxy resin composites have attracted great attention in high pressure hydrogen storage for its light weight and excellent mechanical properties. The degradation of residual mechanical properties at elevated temperature from 20 °C to 450 °C were studied experimentally. The effects of temperature on the tensile strength and failure mode of the composite specimens with stacking sequences of 0°, 90° and ±45° (labeled as CF0, CF90 and CF 45) were systematically analyzed followed by the fracture surfaces examination. Results show that the tensile strength residual ratios of the three kinds of specimens decrease significantly with heating temperature increasing. In particular, the decomposing temperature of the resin matrix exerts the largest effects on the degradation of tensile strength of CF0 specimen within 450 °C. While the loss of tensile strength of CF90 and CF45 specimens is dependent on the thermal softening of epoxy resin which has closely related to the glass transition temperature. Furthermore, the debonding and fiber softening appeared in the CF0 specimens when the temperature reached 450 °C. For CF90 specimens, the degradation of bonding strength of epoxy could be found at 150 °C, and regarding CF45 specimens, delamination cracking between plies occurred extensively when the temperature above 125 °C.

Keywords: Mechanical properties, carbon fiber reinforced epoxy resin composite, high temperature

1.0 INTRODUCTION

With the rapid development of hydrogen infrastructures such as hydrogen fuel cell vehicles, the safety of the on-board hydrogen storage systems gradually shades into one of the most crucial issues which has been carefully investigated during recent years [1-5]. Since the type III and type IV (cylinder which contains a metal liner and non-metallic liner reinforced with fully-wrapped composite material, respectively) cylinders are typically accepted as compressed gaseous hydrogen storage for their light weight and high strength characteristics [6, 7]. Generally, for high-pressure hydrogen cylinders, the composite layer is winded by carbon fiber reinforced polymer, and the cylindrical part is made by hoop winding and spiral winding, while the dome part can only be made by spiral winding However, the composite layer tends to degrade under thermal load (heat radiation or fire impingement) and have a high failure risk under accidental fire exposure [8, 9]. The fire might burn thermosetting polymer-like epoxy resin of the composite progressively and cause an increase of the mass loss [10]. Thus, investigating the mechanical properties of fully-wrapped composite material under high temperatures is of significance for evaluating the structural safety of hydrogen cylinders.

The failure modes of hydrogen cylinders exposed to fire have been studied by many researchers due to more flammable and explosive medium of hydrogen and higher storage pressure of cylinders as compared to the CNG cylinders [11]. To eliminate these risks and solve the related fire safety issue, many researchers [3, 12-17] have developed different models and simulation methods to predict the cylinder burst capability and to investigate the damage mechanism. Much of the current literature on the calculation of the time to burst pays particular attention to the criteria [18, 19] which indicates that in order to assess the fire resistance time of the cylinder, one of the most important things is to determine the thermal and mechanical properties of the wound composite material and the cylinder failure criterion. Also, many studies have put insight into the properties of carbon fiber composites under tensile loading during fire or at high temperatures under different factors such as composite material, temperature, and ply orientation. The tensile strengths of CFRP laminates are significantly reduced with increasing temperature, but size dependence is independent of temperature [20]. Besides, the tensile softening rate and failure time of quasi-isotropic laminate also depend on the ply stacking pattern at low applied tensile stresses (less than 50% of the ultimate strength) [21]. However, these studies mainly focused on the residual mechanical properties of the composite after exposure to the heat flux, it is necessary to investigate the failure behavior under a couple of thermomechanical loading.

Furthermore, some studies have attempted to explain the failure mechanism of carbon fiber reinforced epoxy resin composite material under tensile load in high temperatures (between 100 °C and 600 °C) or in the fire [22-24]. Nevertheless, there is hardly any experimental analysis performed on composite under a couple of thermomechanical loading, and the extent of loss on tensile strength in different decomposition stages need to be revealed. Thus, in this work, the authors focus on the tensile properties of composite specimens with stacking sequences of 0°, 90° and ±45° at elevated temperatures. Besides, the fracture characteristics of carbon fiber reinforced epoxy resin composite after tensile test are observed. Based on the results, the evolution of tensile strength with the elevated temperature was discussed quantitatively and the degradation mechanism of tensile strength was investigated.

2.0 MATERIALS AND METHODS

2.1 Materials and experimental parameters

In this study, flat rectangular specimens of the laminate were used to identify the tensile performance of the composite material in high- temperature environment. The laminate was fabricated by unidirectional T700 carbon fiber- epoxy resin prepreg (produced by TORAY and Wuxi Resin Factory), they are usually used to manufacture the high-pressure hydrogen storage cylinders. As the fiber orientation in composite materials has a significant influence on the mechanical stiffness and strength, the effect of high temperature has been studied on composite laminates with different stack patterns: $[0°]_s$, $[90°]_s$ and $[\pm45°]_s$ noted CF0, CF90 and CF45, respectively. In accordance with the requirements of ASTM D3039 and take the situation of the testing machine, such as the height of furnace and loading mode into account, flat rectangular specimens were prepared as shown in Fig.1, the dimensions for the composite laminates are given in Table.1. The aluminum alloy tabs were used for the gripping portions to ensure that failure does not occur at the gripping area, which was bonded by epoxy resin adhesive. Composite laminates were cured in an autoclave at about 130 °C for 2 hours. The cured composite laminate had a fiber volume content of 63%. The glass transition temperature of the cured composites was 120 °C as provided by the manufacturer.

Due to the different degrees of degradation on tensile strength under high temperature, and to figure out the effect of typical temperature on tensile strength, the temperature ranges for the three kinds of specimens are different. To be specific, CF0 composite laminates were tested at 20 °C, 75 °C, 100 °C, 150 °C, 250 °C, 350 °C and 450 °C, the temperatures of CF90 composite laminates were 20 °C, 100 °C, 125 °C and 150 °C, and for CF45 were 20 °C, 75 °C, 125 °C, 150 °C and 200 °C.

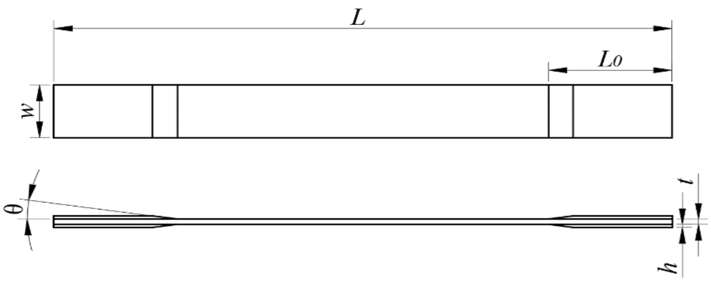


Figure 1. Specimen diagram.

Table 1. Tensile specimen geometry

Specimen	Geometry (Unit: mm)					
	L	w	t	L_0	h	θ
CF0/CF90	330	25	2	60	1.5	20°
CF45	330	25	2.5	60	1.5	20°

2.2 Tensile test

The tensile tests of all the composite laminates were conducted according to the ASTM D 3039 by using an electro-hydraulic servo universal testing system (MTS810-25ton) with an adjustable hydraulic pressure supply for wedge grips. The testing system is equipped with an automatically controlled furnace of which height is 120 mm and ultimate temperature is 1000 °C, as shown in Fig. 2. Prior to the tensile process, specimens were held at the target temperature for at least 20 minutes to ensure that the composite laminates reached a homogenous temperature. Then, the specimens were tested directly under the target temperature until they failed. The tensile load was applied with the displacement rate of 1mm/min for all tests. Four parallel tests were carried out for each temperature condition to determine the tensile properties of the composite laminate, and the average value was adopted as the experimental results.

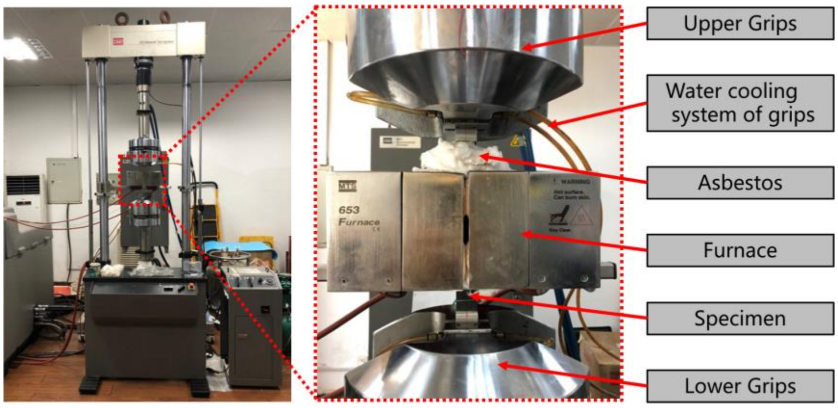


Figure 2. The electro-hydraulic servo universal testing system.

3.0 RESULTS AND DISCUSSION

3.1 Tensile behaviors

Figure. 3 (a), (b) and (c) illustrate the effect of high temperatures on the load-displacement curves for the CF0, CF90 and CF45 specimens. The load-displacement curves of CF0 specimens from 20 °C to 450 °C are similar, showing the characteristic of brittle fracture. At the beginning, the curve is relatively smooth and can be regarded as a linear elastic stage, and then the curve begins to appear "wave", indicating that there is fiber fracture and the load around the fractured fiber is redistributed through the resin. With the increase of applied load, the fiber fracture occurs continuously, and finally the specimen breaks instantaneously. The load-displacement curves of CF90 specimens show different trends at different temperatures (as shown in Fig. 3(b)). It can be seen from Fig. 3 (b) that the load-displacement curves obtained at 20 °C is linear, and finally the tension curve drops sharply with brittle fracture. While for the load-displacement curves at 100 °C, 150 °C and 200 °C, two stages can be observed. Both of them show linear evolution, the slope of the first stage is obviously lower than that of the second stage. The fluctuating range of the curves in the second stage at 150 °C and 200 °C are higher. Fig. 3 (c) represents the load-displacement curves of CF45 specimens, the damage process is quite different from that observed for CF0 and CF90. Here, the curves got at temperatures lower than the glass transition temperature of the epoxy resin including 20 °C and 75 °C show similar trends, and the curves obtained at 125 °C, 150 °C and 200 °C exhibits a similar damage process. Under the temperature of 20 °C to 75 °C, the CF45 specimen behaves like the ductile material, obviously there exist yield points on the curves for 20 °C. However, the tension curves at 125 °C, 150 °C and 200 °C are still linear evolution before the fracture occurred. Meanwhile, in the fracture stage, the load doesn't drop sharply but experiences a series of load drops.

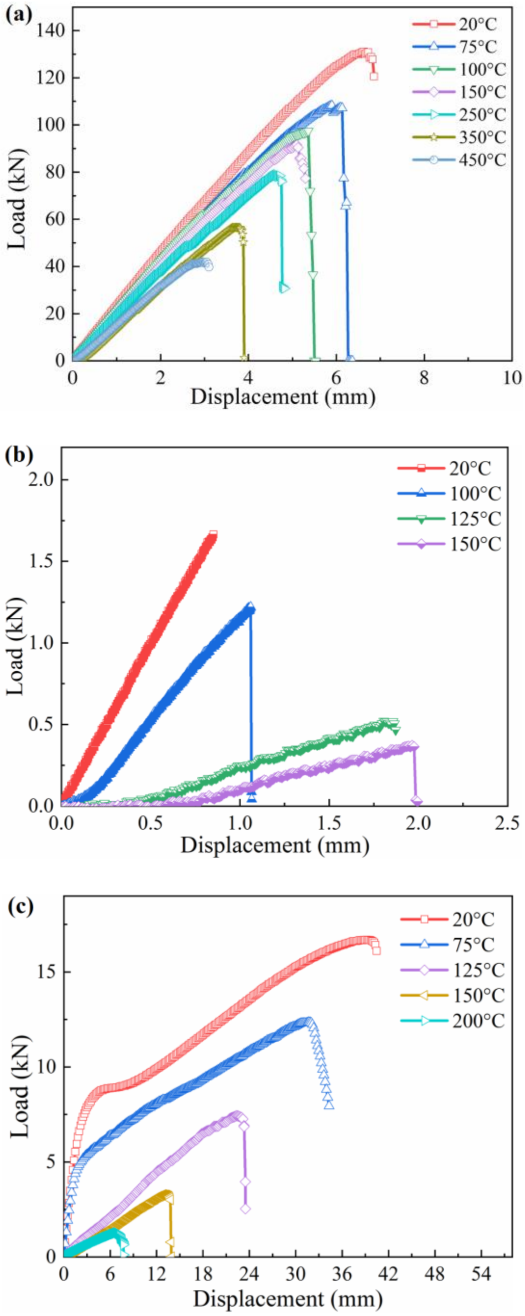


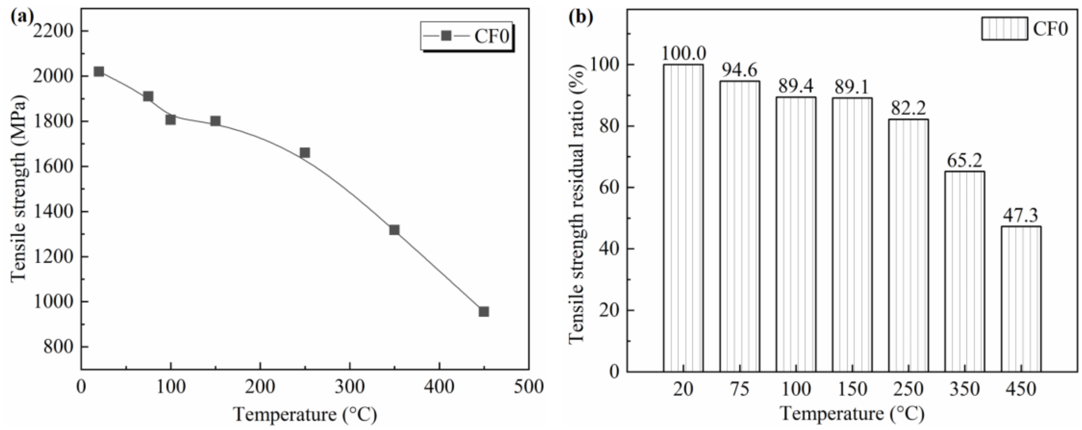
Figure 3. Tensile load-displacement curves at different temperatures for specimens of (a)CF0, (b) CF90 and (c) CF45.

3.2 Mechanical properties

As can be seen from Fig. 4, the temperature clearly has an effect on the tensile strength as well as the stiffness for three kinds of specimens, the average tensile strength of the carbon fiber reinforced epoxy resin composite as a function of elevated temperatures are plotted in Fig. 4 (a), (c) and (e). The tensile strengths are calculated according to the ASTM D3039. Fig. 4 (b) displayed the tensile strength residual ratios of CF0, CF90 and CF45. It is apparent that the tensile strength of specimens at high temperatures deteriorates dramatically with the rising temperature. At room temperature, the tensile strengths for CF0, CF90 and CF45 are 2019.68 MPa, 30.79 MPa and 230.98 MPa, respectively. The tensile strength of CF0 specimen decreases slowly from 20 °C to 150 °C, the tensile strength residual ratio of the CF0 at 150 °C is 89.1%. And between 150 °C and 250 °C, the tensile strength of CF0 varies little. When the temperature reached and exceed 350 °C, a significant strength degradation occurred, and the strength residual ratio of CF0 at 450 is only 47.3%. Similar evolution trends for the tensile strength of CF0 specimen could be observed in the research of Gao et al [25]. However, Cao et al. found that the carbon fiber reinforced resin sheets lost their strength rapidly during the glass transition temperature of epoxy resin (between 40 °C and 60 °C) [23].

As shown in Fig. 4 (c) and (d), below 100 °C, the tensile strength the CF90 specimens decrease slowly, while the decrease of the strength became rapidly in the epoxy resin’s glass transition region between 100 °C and 150 °C. The tensile strength residual ratios of CF90 at 100 °C ,125 °C and 150 °C are 69.6%, 35.1% and 16.5%, which indicates that the strength almost completely lost with the rising temperature.

In Fig. 4 (e), it is noticed that the tensile strength of CF45 specimens began to degrade when the heated to 75 °C, between 75 °C and 200 °C, a rapid reduction in the tensile strength was observed, when the temperature exceeds 125 °C, the strength loss rate increased slightly. The tensile strength residual ratios of CF45 at125 °C ,150 °C and 200 °C are 47.5%, 22.8% and 9.1% as shown in Fig. 4 (f), from this figure, the temperature effect on the strength is clearly evident.



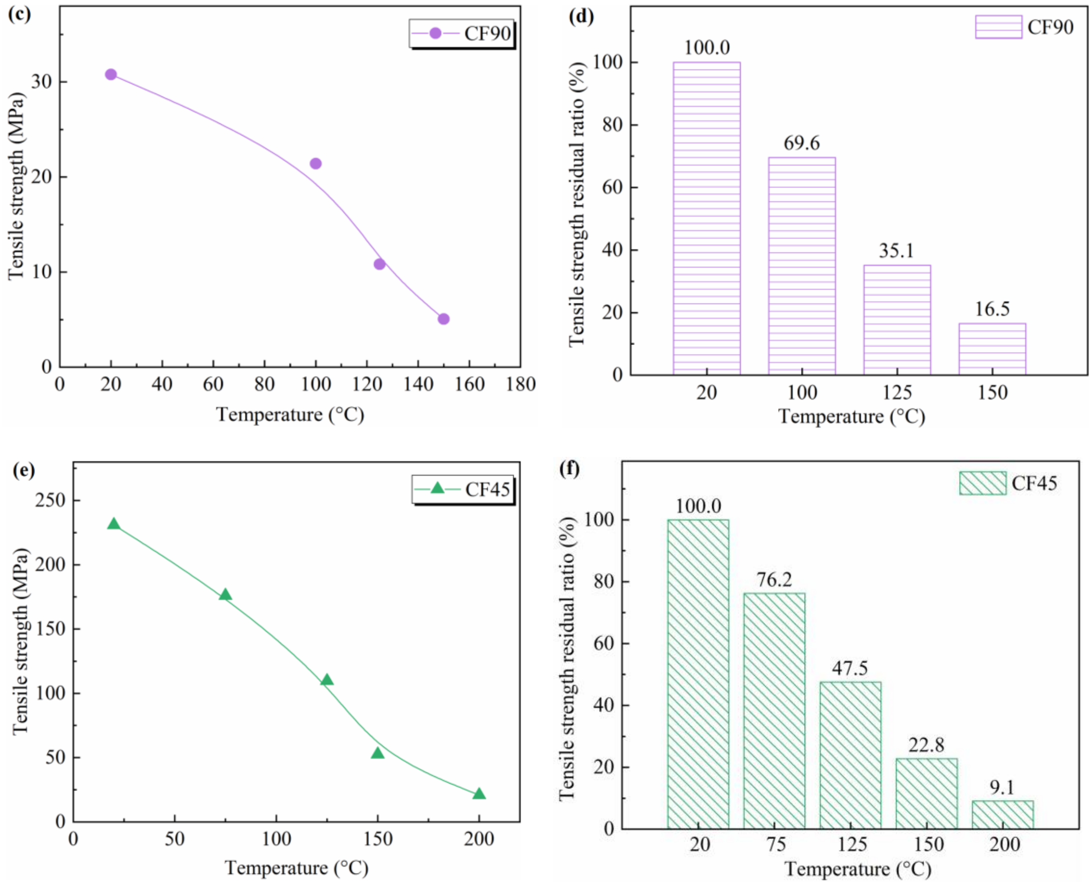


Figure 4. Tensile strength and tensile strength residual ratio at different temperatures: (a) and (b)for CF0, (c) and (d) for CF90, (e) and (f) for CF45.

3.3 Fracture morphology

To study the effects of heated temperature on the fracture modes of CF0, CF90 and CF45, the fracture morphologies of the specimens after tensile testing are observed and compared as shown in Fig.5, Fig. 6 and Fig. 7. As demonstrated in Fig. 5, the CF0 specimen at 20 °C ruptured on multiple areas with fiber breakage, fiber pullout and matrix crack, the fiber bundles are thin. Similar failure modes can also be observed in the specimens at 75 °C and 100 °C. As the temperature rise, the failure area concentrated in the heating part of specimens and located in the middle. Between 150 °C and 350 °C, the fiber bundles became soft and flocculent on the fracture area, this could be attributed to the softening of resin matrix, which leads to the adhesion between matrix and fiber decreased significantly. These findings suggest that the fiber breakage and debonding between plies are the dominant failure modes. Regarding the specimens that failed at temperatures above 350 °C, debonding at the matrix fiber interface was found to be the major reason for failure. Apparently, as the epoxy resin began to decompose, the single fiber exposed whose surface has pieces of resin on it. Without the bonding of the epoxy resin, the carbon fibers became loose and expanded, the higher the temperature is, the larger the expansion area is.

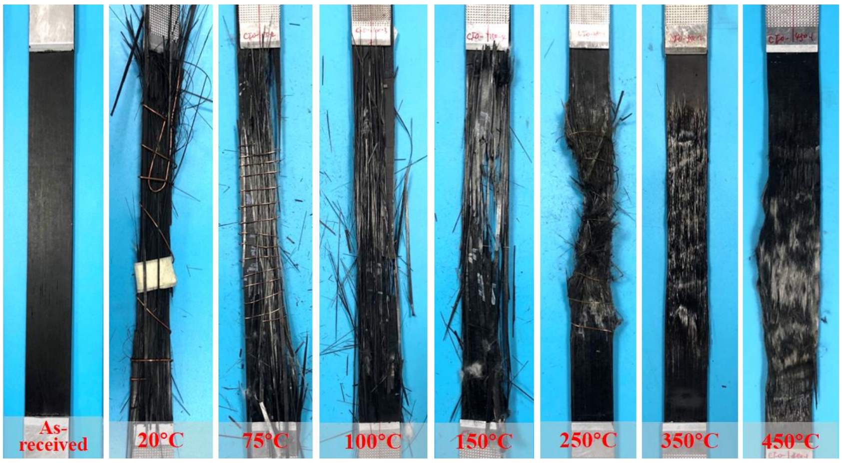


Figure 5. Fracture morphology of CF0 specimen at different heating temperatures.

Figure. 6 represents the fracture mode of the CF90 specimens at different heating temperatures. The fracture mode of the CF90 specimens is brittle fiber matrix debonding. The debonding initiates at the interface fiber/matrix where microdefects laid, then propagate along with the fiber, which leads to failure [26]. While with the rising of heated temperature, the fracture surfaces are not flat as tested in 20 °C, there appeared more fractured fiber bundle at the surface due to the degradation of bonding strength of epoxy, and the specimens are not completely disconnected at 125 °C and 150 °C.

Figure 6. Fracture morphology of CF90 specimen at different heating temperatures.

Figure. 7 shows the failure morphology for the CF45 specimens at elevated heating temperatures. Generally, delamination and debonding at the matrix fiber interface were identified to be the major reason for the shear failure. It can be seen from Fig. 7, the specimen was elongated visibly at 20 °C, and the failure displacement decreased greatly with the rise of temperature. In addition, the "necking" was observed at the failure area at 20 °C and 75 °C, the most obvious one is at 75 °C, along with resin matrix accumulation and sliding between plies. However, the situation is different at 125 °C, 150 °C and 200 °C, the ply of the specimen was debonding and peeling, delamination cracking occurred extensively between many of the plies within the specimen [21].

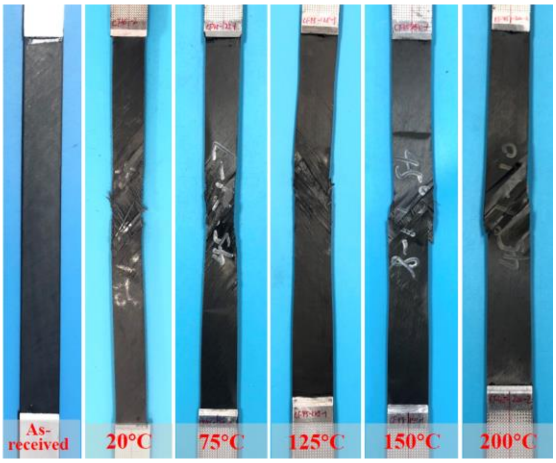


Figure 7. Fracture morphology of CF45 specimen at different heating temperatures.

4.0 CONCLUSION

In this work, the effects of heating temperature on the tensile properties of carbon fiber reinforced epoxy resin composite was investigated. The evolution of tensile properties of CF0, CF90 and CF45 at elevated temperatures were characterized. The following conclusions can be drawn:

(1) The heating temperature has a great impact on the tensile behaviors of CF0, CF90 and CF45 specimens. With the increase of heating temperature, the tensile strength decreases significantly and softening characteristics were found by load-displacement curves. In addition, the loss of tensile strength of CF90 and CF45 specimens is dependent on the thermal softening of epoxy resin which has closely related to the glass transition temperature. While the decomposing temperature of the resin matrix exerts the largest effects on the degradation of tensile strength of CF0 specimen within 450 °C.

(2) Fracture surfaces showed debonding and fiber softening appeared in the CF0 specimens when the temperature reached 450 °C. As for CF90 specimens, the degradation of bonding strength of epoxy could be found at 150 °C. Regarding CF45 specimens, delamination cracking between plies occurred extensively when temperature above 125 °C.

(3) For the secure application of the CFRP composite into cylinders, it is necessary to utilize heat retardant coat to provide thermal resistance, especially for the dome part. It should be better to ensure that the temperature rise of the composite layer does not exceed the glass transition temperature.

ACKNOWLEDGMENTS

This research was supported by the Key Research and Development Program of Zhejiang Province of China (grant numbers 2020C01118).

REFERENCES

1. Berro Ramirez, J.P., Halm, D., Grandidier, J., Villalonga, S. & Nony, F., 700 Bar Type IV High Pressure Hydrogen Storage Vessel Burst – Simulation and Experimental Validation, *International Journal of Hydrogen Energy*, **40**, No. 38,2015, pp. 13183-13192.
2. Tomioka, J., Kiguchi, K., Tamura, Y. & Mitsuishi, H., Influence of Pressure and Temperature On the Fatigue Strength of Type-3 Compressed-Hydrogen Tanks, *International Journal of Hydrogen Energy*, **37**, No. 22,2012, pp. 17639-17644.

3. Zheng, J., Guo, J., Yang, J., Zhao, Y., Zhao, L., Pan, X., Ma, J. & Zhang, L., Experimental and Numerical Study On Temperature Rise within a 70 MPa Type III Cylinder During Fast Refueling, *International Journal of Hydrogen Energy,* **38**, No. 25,2013, pp. 10956-10962.
4. HU, J., CHEN, J., SUNDARARAMAN, S., CHANDRASHEKHARA, K. & CHERNICOFF, W., Analysis of Composite Hydrogen Storage Cylinders Subjected to Localized Flame Impingements, *International Journal of Hydrogen Energy,* **33**, No. 11,2008, pp. 2738-2746.
5. Xu, P., Zheng, J.Y. & Liu, P.F., Finite Element Analysis of Burst Pressure of Composite Hydrogen Storage Vessels, *Materials & Design,* **30**, No. 7,2009, pp. 2295-2301.
6. Liu, P.F., Chu, J.K., Hou, S.J., Xu, P. & Zheng, J.Y., Numerical Simulation and Optimal Design for Composite High-Pressure Hydrogen Storage Vessel: A Review, *Renewable and Sustainable Energy Reviews,* **16**, No. 4,2012, pp. 1817-1827.
7. Roh, H.S., Hua, T.Q. & Ahluwalia, R.K., Optimization of Carbon Fiber Usage in Type 4 Hydrogen Storage Tanks for Fuel Cell Automobiles, *International Journal of Hydrogen Energy,* **38**, No. 29,2013, pp. 12795-12802.
8. Stephenson. Fire Safety of Hydrogen-Fueled Vehicles:System-Level Bonfire Test. In *the first International Conference on Hydrogen Safety.* 2005.Pisa.
9. Zheng, J., Bie, H., Xu, P., Chen, H., Liu, P., Li, X. & Liu, Y., Experimental and Numerical Studies On the Bonfire Test of High-Pressure Hydrogen Storage Vessels, *International Journal of Hydrogen Energy,* **35**, No. 15,2010, pp. 8191-8198.
10. Quang Dao, D., Luche, J., Richard, F., Rogaume, T., Bourhy-Weber, C. & Ruban, S., Determination of Characteristic Parameters for the Thermal Decomposition of Epoxy Resin/Carbon Fibre Composites in Cone Calorimeter, *International Journal of Hydrogen Energy,* **38**, No. 19,2013, pp. 8167-8178.
11. Robert, Z. CNG and Hydrogen Vehicle Fuel Tank Failure Incidents, Testing, and Preventive Measures.2008.
12. Halm, D., Fouillen, F., Lainé, E., Gueguen, M., Bertheau, D. & van Eekelen, T., Composite Pressure Vessels for Hydrogen Storage in Fire Conditions: Fire Tests and Burst Simulation, *International Journal of Hydrogen Energy,* **42**, No. 31,2017, pp. 20056-20070.
13. Kim, Y.M.D.K., Modelling Heat Transfer in an Intumenscent Paint and its Effect On Fire Resistance of On-Board Hydrogen Storage, *International Journal of Hydrogen Energy,* No. 42,2017, pp. 7297-7303.
14. Saldi, Z.S. & Wen, J.X., Modeling Thermal Response of Polymer Composite Hydrogen Cylinders Subjected to External Fires, *International Journal of Hydrogen Energy,* **42**, No. 11,2017, pp. 7513-7520.
15. Magneville, B., Gentilleau, B., Villalonga, S., Nony, F. & Galiano, H., Modeling, Parameters Identification and Experimental Validation of Composite Materials Behavior Law Used in 700 Bar Type IV Hydrogen High Pressure Storage Vessel, *International Journal of Hydrogen Energy,* **40**, No. 38,2015, pp. 13193-13205.
16. Zheng, J., Ou, K., Hua, Z., Zhao, Y., Xu, P., Hu, J. & Han, B., Experimental and Numerical Investigation of Localized Fire Test for High-Pressure Hydrogen Storage Tanks, *International Journal of Hydrogen Energy,* **38**, No. 25,2013, pp. 10963-10970.
17. Benelfellah, A., Halm, D., Bertheau, D., Boulet, P., Acem, Z., Brissinger, D. & Rogaume, T., Effect of a Coupled Thermomechanical Loading On the Residual Mechanical Strength and On the Surface Temperature of Wound Carbon/Epoxy Composite, *Journal of Composite Materials,* **51**, No. 22,2017, pp. 3137-3147.
18. Kashkarov, S.M.D.M. Model of 3D Comjugate Transfer and Mechanism of Compressed Gas Storage Failure in a Fire. In *International conference on hydrogen safety.* 2017. Hamburg,Germany.
19. Bustamante Valencia, L., Blanc-Vannet, P., Domergue, D., Heudier, L. & Jamois, D., Thermal History Resulting in the Failure of Lightweight Fully-Wrapped Composite Pressure Vessel for Hydrogen in a Fire Experimental Facility, *Fire Technology,* **52**, No. 2,2016, pp. 421-442.

20. Cao, S., WU, Z. & Wang, X., Tensile Properties of CFRP and Hybrid FRP Composites at Elevated Temperatures, *Journal of composite materials*, **43**, No. 4,2009, pp. 315-330.
21. Grigoriou, K. & Mouritz, A.P., Influence of Ply Stacking Pattern On the Structural Properties of Quasi-Isotropic Carbon-Epoxy Laminates in Fire, *Composites Part A: Applied Science and Manufacturing*, **99**,2017, pp. 113-120.
22. Feih, S. & Mouritz, A.P., Tensile Properties of Carbon Fibres and Carbon Fibre – Polymer Composites in Fire, *Composites Part A: Applied Science and Manufacturing*, **43**, No. 5,2012, pp. 765-772.
23. Cao, S.H., Wu, Z.S. & Li, F., Effects of Temperature on Tensile Strength of Carbon Fiber and Carbon/Epoxy Composite Sheets, *Advanced Materials Research*, **476-478**,2012, pp. 778-784.
24. Duncan, C., Taras, G. & Marc, L.L., Tensile and Lap-Splice Shear Strength Properties of CFRP Composites at High Temperatures, *Journal of Composites for Construction*, **19**, No. 2,2015.
25. Gao, X. & Zhang, H., The Comparasion of Tensile Strength After High Temperature of BFRP Sheets and CFRP Sheets, *Journal of Disaster Prevention and Mitigation Engineering*, **32**, No. 01,2012, pp. 60-65.
26. Quach, T.H.Y., Benelfellah, A., Batiot, B., Halm, D., Rogaume, T., Luche, J. & Bertheau, D., Determination of the Tensile Residual Properties of a Wound Carbon/Epoxy Composite First Exposed to Fire, *Journal of Composite Materials*, **51**, No. 1,2017, pp. 17-29.