Heterogeneous thermoset/thermoplastic recycled carbon fiber composite materials for second-generation composites

*Seyed Hossein Mamanpush[a], Hui Li[a], Azadeh Tavousi Tabatabaei[a] and Karl Englund[a]

[a]Composite Materials and Engineering Center, Washington State University, Pullman, WA 99164-1806, USA

Abstract

With an increase in the use of carbon fiber composites in the aerospace and automobile industry a collateral issue of what to do with end-of-life carbon fiber composites has risen. In this study, we successfully developed a second-generation composite using a heterogenous mixture of thermoset and thermoplastic recycled carbon fiber composites (CFCs). The recovered vinyl ester and epoxy CFCs were characterized using thermogravimetric analysis. Adhesive performance was evaluated through double lap shear tests by melt-bonding a thermoplastic polyether ether ketone (PEEK) CFC to either the thermoset epoxy or vinyl ester CFC. The waste carbon fiber composites were also mechanically milled and classified through screening techniques. The resulting milled materials were used to form and produce composite panels through high temperature compression molding. The influence of particle size and platen temperature were evalauted through mechanical testing. Results indicate that melt-bonding with the vinyl ester/CFC exhibited significantly higher lap shear strength values than that between epoxy/CFC and PEEK. Findings also show that adding thermoset CFCs to the thermoplastic system (PEEK) enhanced the flexural properties of composites.

Keywords: Recycling, Carbon fiber composite, Thermoset composite

* Corresponding Author
Email: s.mamanpush@wsu.edu

1. **Introduction**

Carbon fiber composites (CFCs) are commonly used in aerospace applications and high-technology products due to their unique mechanical properties and light weight [1-2]. However, unlike metal wastes that are easily recyclable, end-of-life products of carbon and other synthetic fiber composites have limited option for reuse [3-4]

Estimations predict that carbon fiber composite demand is increasing at a rate of 15% per year [5]. However, reuse or recycling of this ever-increasing amount of processing scrap and end-of-life CFCs is complex and is compounded by the use of non-reversible thermoset resins used for most CFCs [6]. Sending CFCs to the landfill has negative environmental effects and disregards their potential use as a viable feedstock for second-generation products. Finding an economical solution for end-of-life CFCs is critical [6].

It is possible to recycle fiber from the thermoset matrix via chemical or thermal treatments [7-8]. However, the resulting fiber often has inferior mechanical properties to virgin material and becomes very difficult to disperse into second-generation products. In addition, the amount of energy and chemicals required to obtain these products is considerable [9-10]. Mechanical techniques that employ shredders, hammer-mills, knife-mills and the like provide a low-cost option to create a reliable, recycled carbon fiber composite as a feedstock for next generation composites [11]. However, appropriate methods and classification procedures are needed in order for the mechanical refining process to develop low-cost, energy-efficient recycled carbon fiber composite (rCFC) materials.

Traditionally, CFCs utilize thermoset resins for stress transfer between carbon fibers and matrices. Recycling these CFCs are difficult, due to the thermoset binder used in the synthetic fiber (carbon fiber) composite [12-13]. In a more recent trend, manufacturers are increasing their use of thermoplastic binders such as polyether ether ketone (PEEK) in certain applications. An important characteristics of thermoplastics CFCs is their storage flexibility, recyclability, and their potential for reforming into many composite shapes [6].

In this study, we developed a recycling process to create composites derived from carbon fiber/epoxy composite (epoxy/CFC) and carbon fiber/vinyl ester composite (VE/CFC) blended with a PEEK/CFC that not only acted as a reinforcement, but also the PEEK functioned as a binder for the heterogeneous composite system. We characterized the influence of adding recycled thermoset CFCs to the thermoplastic CFC system. In detail, we evaluated the adhesive performance between thermoset and thermoplastic CFCs using melt-bonding. We also mechanically refined the recovered CFC scraps into usable fractions and used compression molding techniques to fabricate the recycled composites. Since the melting/processing temperature of PEEK is quite high (around 321°C) [6] and the potential for thermoset based CFCs to thermally degrade and cause issues during processing, a thermal analysis was employed to determine a processing range for manufacturing recycled composite.

2. Materials and methods

2.1.Materials

Waste scraps of epoxy/CFC and VE/CFC were donated by Zoltek Corporation (Bridgeton, MO, USA) the PEEK/CFC were donated by Triumph Composites (Spokane, WA) and were shipped to the Composite Materials and Engineering Center (CMEC) at Washington State University.

2.2.Characterization of original CFCs

2.2.1. Thermal analysis

Thermal gravimetric analysis (TGA) was carried out to determine the thermal stability of the

CFC material and to determine a processing range for manufacturing recycled composite. Specimens were heated from ambient to 800 ℃ under a nitrogen atmosphere at a heating rate of 20 ℃ min^{-1}.

2.2.2. Double lap shear test

A melt-bonding double lap shear test (DLS) was performed based on ASTM D3528 to evaluate the adhesive bonding between the CFCs and PEEK/CFCs. To carry out DLS, CFC scraps were cut into samples (25.4 mm in width and by 114.3 mm in length) and heat-treated for 10 min at 360 ℃. This temperature was chosen based on the degradation temperature of CFCs from TGA. We considered a melt bonding time of 10 min and a temperature starting at 320 ℃ (based on the T_m of PEEK) [6]. Control specimens without the heat treatment were also evaluated for DLS performance. Test specimens were assembled under minimum pressure (110 KPa [14]) to optimize test conditions. Samples were tested under standard conditions at a room temperature of 23 ℃ and a relative humidity of 50%. A minimum of three replicated samples were tested. Apparent lap shear strength (σ_{LS}) was calculated using equation (1).

$$\sigma_{LS} = \frac{P_{max}}{2A} \qquad (1)$$

where P_{max} is the maximum load recorded during the test and *A* is the overlap bond area (25.4 ×12.7 mm^2). Six temperatures (320 ^oC-380^oC) were selected for melt-bonding with the existing PEEK in the composite.

2.3. Milling and classifying recycled carbon fiber composites

Initially, the waste CFC scraps were mechanically refined by a shredder with 19 mm wide teeth. Further reduction of the CFC material was then carried out with a hammer mill using a

25.4 mm mill screen size (MSS). Particle size distribution of the hammer milled recycled carbon fiber composite (rCFC) was performed [15-18]. During a sieve analysis, the sample is shaken or agitated through a series of varying size sieves and the weight retained on each level measured. The percentage of the total mass represents the mass fraction within that specific particle size distribution range as shown in Figure 1.

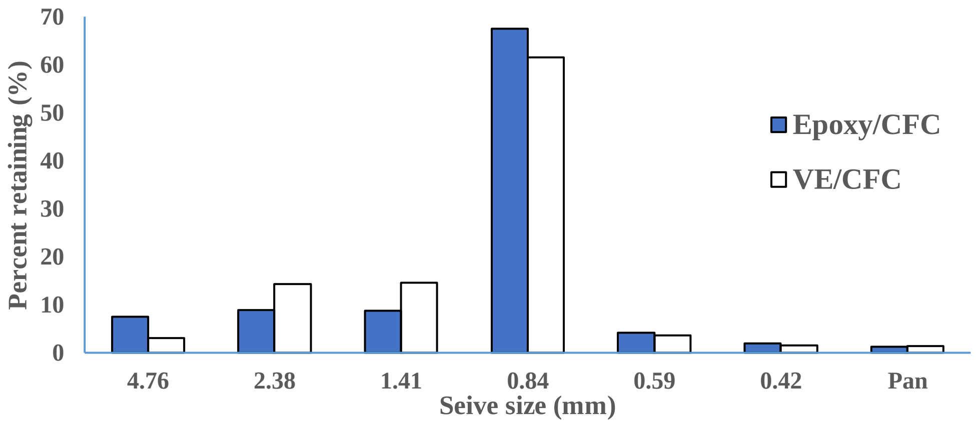


Figure 1. Particle size distribution of rCFC from 25.4 mm mill screen sizes (MSS).

The hammer-milled material was then screened and classified into two categories, material that was passed through a 3.4 mm (<3.4) and those that passed through a 1.2 mm (<1.2) screen. All material that did not pass through the 3.4 mm screen was removed from the study. Particle size distribution of the two classified rCFC was performed on each fraction, as shown in Figure 2.

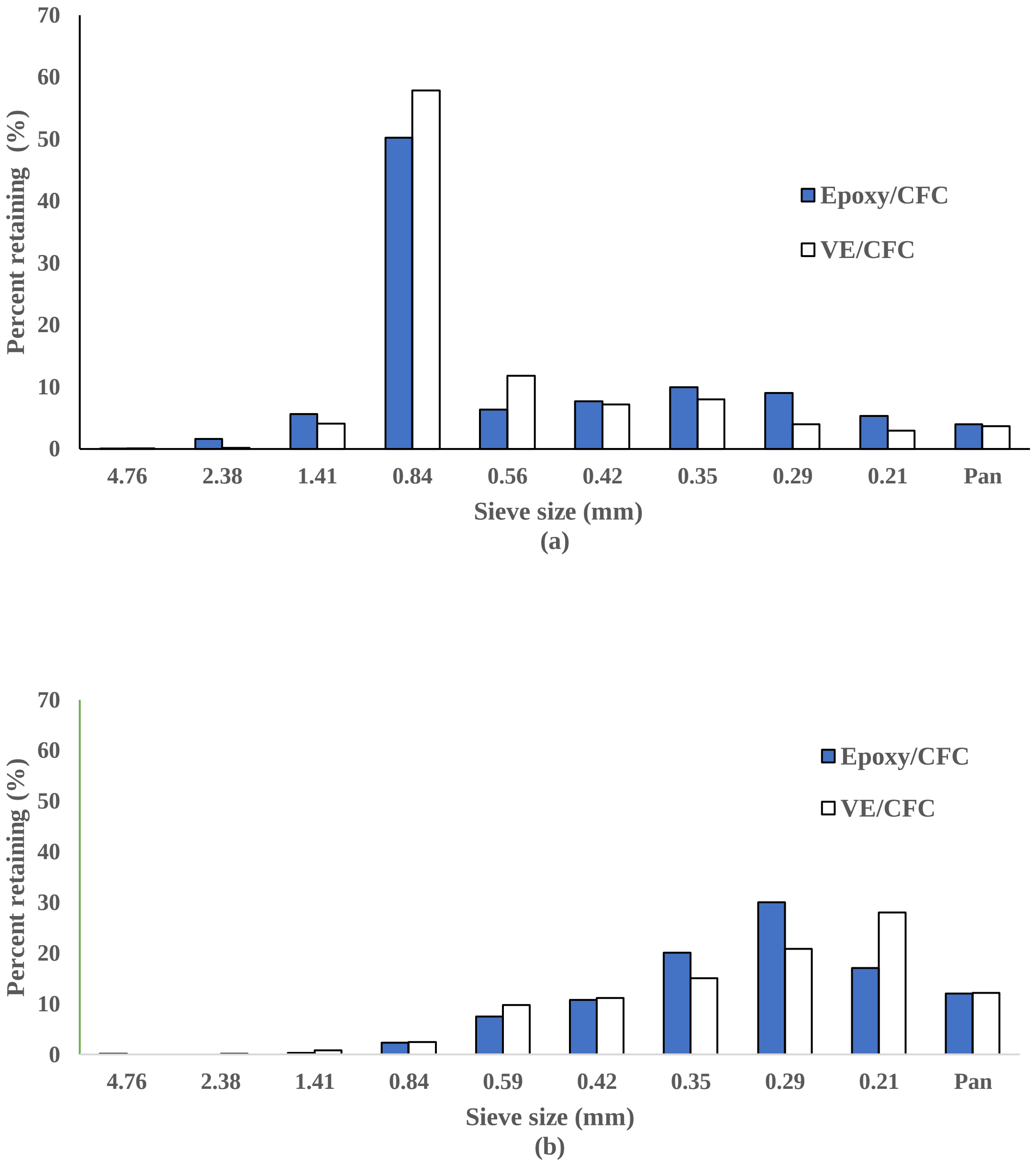


Figure 2. Particle size distribution of rCFC from the two separated fractions (a) 3.4 mm (b) 1.2 mm.

2.4.*Second-generation composite panel fabrication*

After the rCFC materials were classified, they were compression molded into flat panels by using a hydraulic ram press equipped with high temperature platens [6]. The processing parameters of platen temperature (360$_o$C- 400$_o$C) and particle size distribution (3.4 and 1.2mm) were evaluated to determine their influence on the mechanical properties of the second-generation composites.

Mechanical tests (flexural and tensile) were performed based on ASTM D790 and ASTM D3039, respectively. The flexural samples were cut as 127 mm by 12.7 mm and the tensile samples were 254 mm by 25.4 mm. In addition, the testing rate and the flexural span were determined via the methods outlined in the standards. All samples were conditioned for 24h at a temperature of 23 °C and a relative humidity of 50%. Five replicates were performed for each treatment.

3. Results and discussion

3.1.Thermal properties of the CFC

The thermal degradation profiles of epoxy-based CFC and vinyl ester-based CFC by TGA reveal that most of the degradation events occur between 300°C and 460°C for both specimen types. (Figure 3). At 450°C, both of the specimens lost 21.5 % of their weight and then remained stable up to 800°C in a nitrogen purge environment.

The thermal decomposition of the CFCs was caused primarily by the scission and cleavage reactions of polymer chains, such as epoxy and vinyl ester chains, at an elevated temperature [19-20]. TGA result indicates that VE/CFC had two degradation events. When looking at the derivative thermogravimetry (DTG) curve of weight loss to temperature (dW/dT) the first event reached a peak derivative at approximately 318°C and the second one around 414°C. The mechanisms behind the first degradation is still not clear, and further studies are needed to give a proper explanation. The second degradation event is in good agreement with the literature. Chatterjee [21] reported that around 420°C, significant weight loss was observed for VE resin.

Li et al. [6] reported an onset of T_m of PEEK of approximately 321°C. Therefore, based on T_m of the PEEK and degradation temperature of CFCs, processing temperatures for melt-bonding or manufacturing a second-generation composite panel ideally should be above the T_m and below the onset of thermal degradation when melt-bonding is the primary adhesion mechanism (Figure 3).

However, Stokes-Griffin et al. [22] reported that bonding between carbon fiber and PEEK can accrue at temperature below the melting point called sub-melting temperature. To assess the possible bonding below the melting point of PEEK and the potential interactions of the decomposition gases with the melt bond, the DLS test was performed from 320 to 380°C.

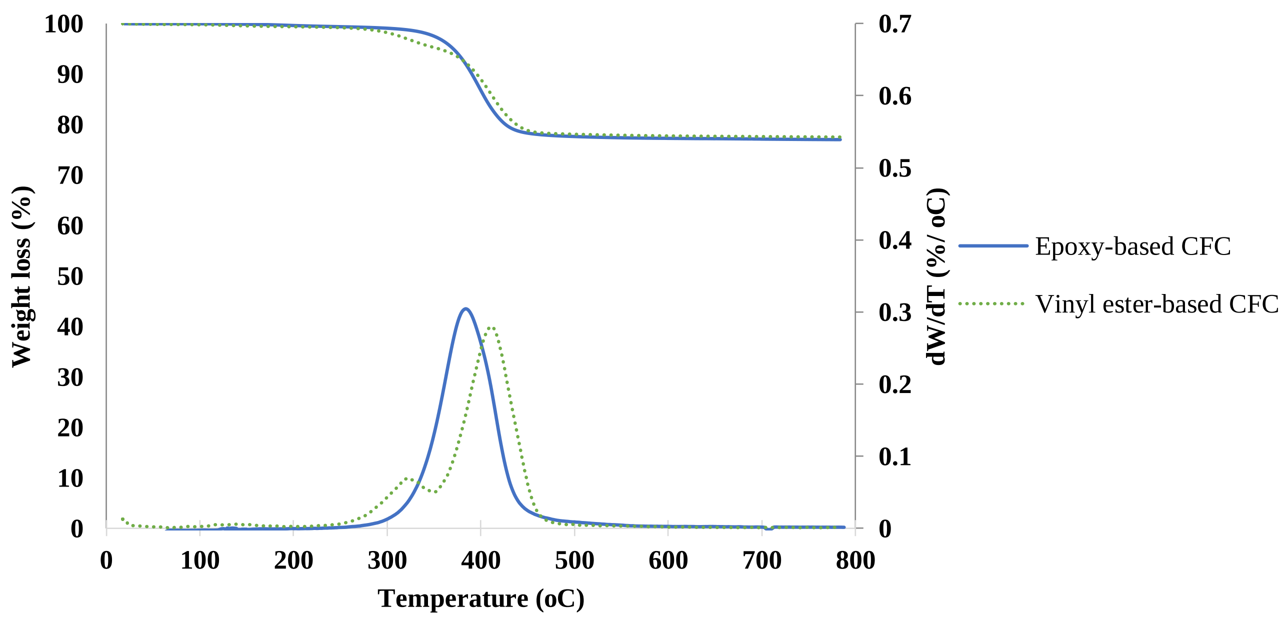


Figure 3. TGA curve of CFCs recorded in nitrogen at heating rate of 20 oC min -1.

3.2.Double lap shear test

To better understand the influence of exceeding the decomposition temperature range of the thermosets, we evaluated a pre-heating step for our DLS tests. Specimens were heat-treated at 360 °C for 10 min to remove and volatile compounds that may interfere by off gassing during composite pressing. Results of heat-treated epoxy/CFC (HT epoxy/CFC) and heat-treated VE/CFC (HT VE/CFC) show that heat treatment has no considerable influence on the σ_{LS} results of CFCs. Because heat treatment lacked any change in performance, it was not used at manufacturing second generation composites.

Within the temperature range utilized, 360 °C and 370 °C had the highest double lap shear strength results (Figure 4). Lap shear strength (σ_{ls}) results indicate that melt-bonding between the VE/CFC and PEEK is significantly higher than that between epoxy/CFC and PEEK and are positively influenced with an increase in melt-bonding temperature up to 370°C, as shown in Figure 4. For temperatures ranging from 350°C to 380°C, the σ_{LS} value of epoxy/CFC and PEEK is between 4.77 MPa – 5.24 MPa. For VE/CFC and PEEK, it is between 9.99 MPa-13MPa for temperatures ranging from 360 °C to 370 °C. The epoxy/CFC bonding did not show much improvement with increasing bonding temperatures. However, as the temperature increased over 370°C, there was a decrease in σ_{LS} results, especially in the VE/CFC specimens.

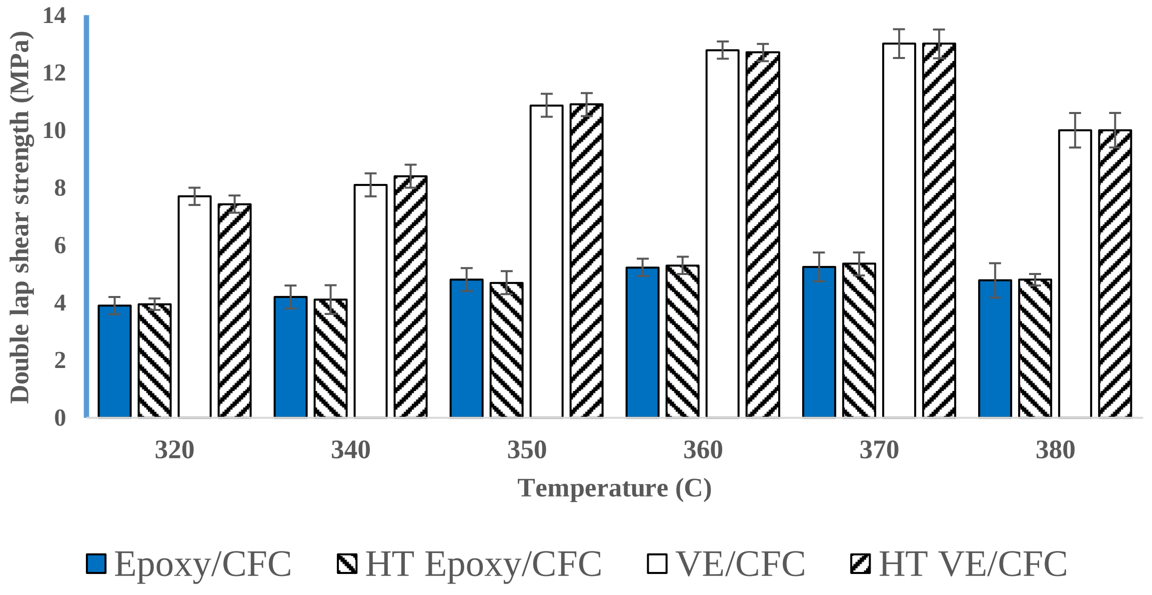
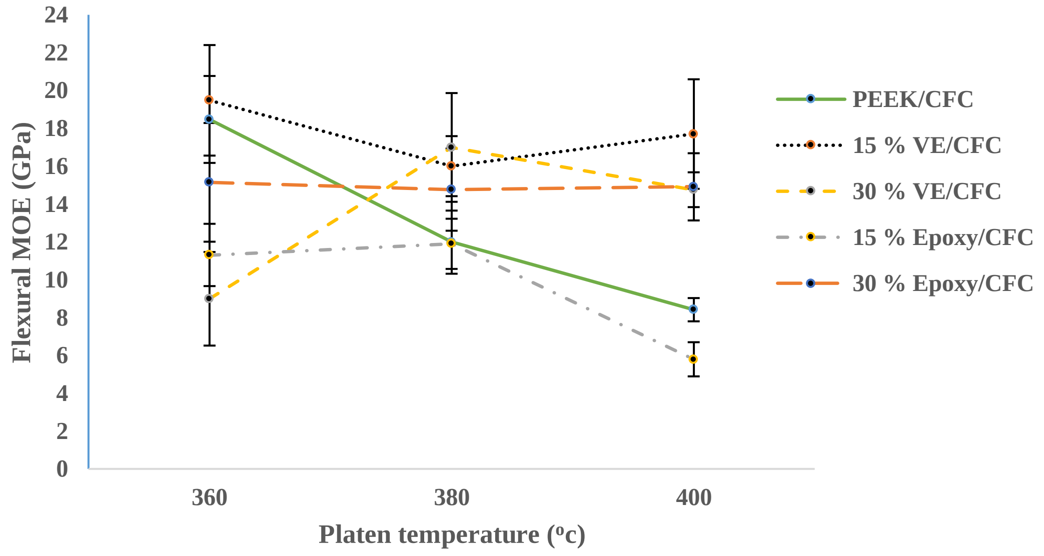


Figure 4. Apparent lap shear strength of melt-bonding between the CFCs and PEEK/CFCs.

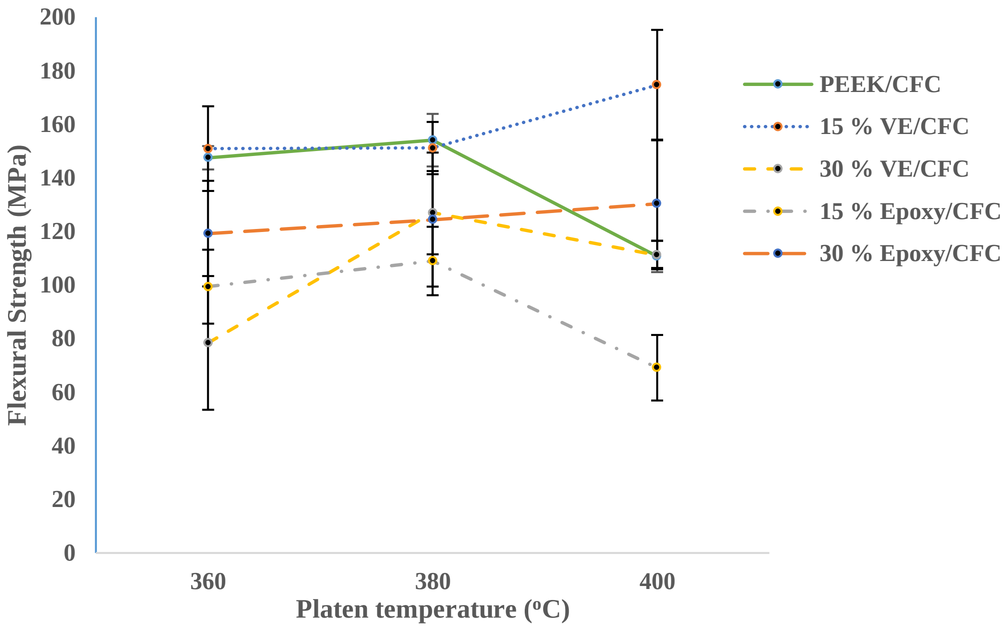
Note: HT indicates heat-treated specimens

3.3.Mechanical properties of second-generation composites

The flexural and tensile properties of composite panels from rCFC are shown in Figures 5-6. As the platen temperature increased, the flexural properties of homogenous PEEK/CFC decreased. Adding VE/CFC to the PEEK/CFC improved the flexural modulus of elasticity (MOE) of the heterogenous composite notably at hot press temperatures of 380 ° C and 400 °C. Results shown in Figure 5 indicate that adding 15% VE/CFC to the homogenous PEEK/CFC enhanced the flexural MOE of the heterogenous composite observably (almost twice) at 400 °C platen temperature. At 360 °C, results show that by increasing the amount of VE/CFC from 15% to 30%, the flexural MOE decreased. Increasing the amount of VE/CFC enhances the flexural strength of heterogenous composite at 400 °C.



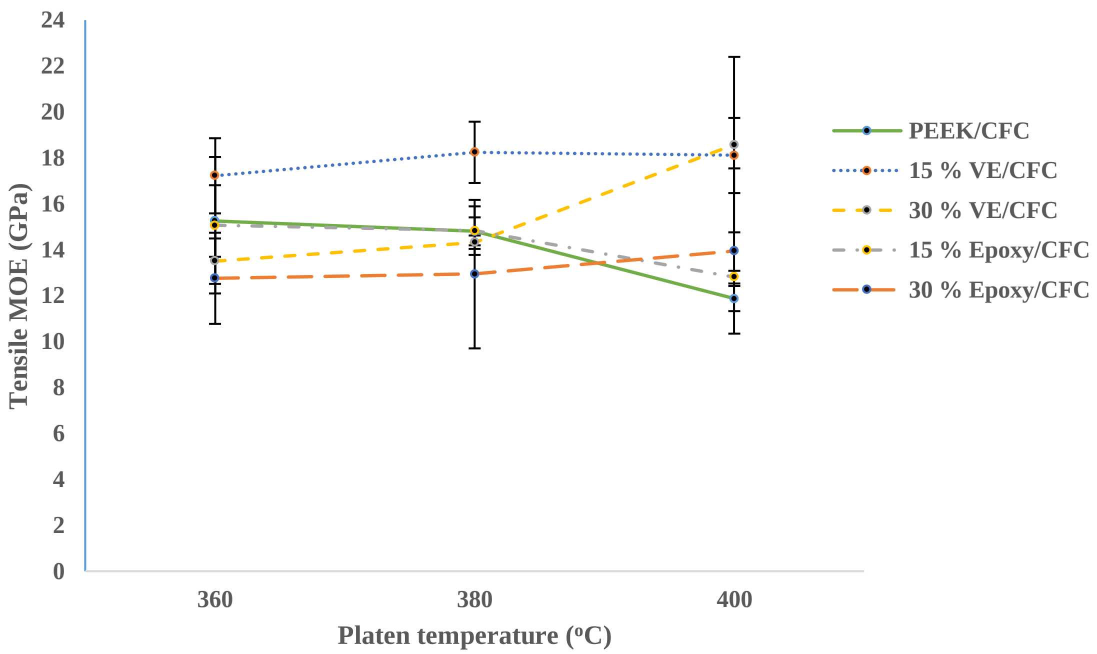
(a)



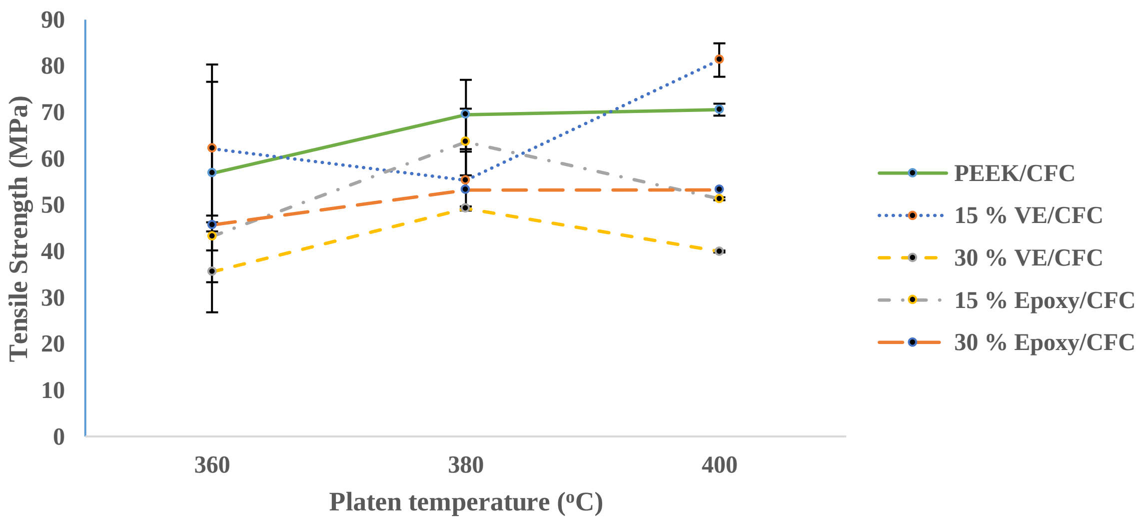
(b)

Figure 5. Flexural properties of rCFC panels that were pressed at varying platen temperature. (a) Flexural MOE (b) Flexural strength. (Sieve screen size =3.4 mm)

Results on the flexural MOE of heterogenous composite indicate that at 360 °C, the mixture of epoxy/CFCs caused a reduction in stiffness compared to the homogenous PEEK/CFC. At 400°C, epoxy/CFC has a notable influence on flexural MOE of the heterogenous composite. At this temperature, adding 15% and 30% epoxy/CFC to the homogenous mixture of PEEK/CFC enhanced the flexural MOE of heterogonous composite by 20% and 100%, respectively. (Figure 5).



(a)



(b)

Figure 6. Tensile properties of rCFC panels that were pressed at varying platen temperatures (a) Tensile MOE (b) Tensile strength. (Sieve screen size=3.4 mm)

By increasing the platen temperature, the tensile MOE and tensile strength of homogenous PEEK/CFC composite decreased and increased, respectively. Adding 15 % VE/CFC enhanced the tensile MOE of the heterogenous composite. Adding 30% VE/CFC had no observable influence on tensile MOE at 360 °C and 380 °C, yet enhanced the tensile MOE at 400 $_o$C. However, it reduced the tensile strength of the heterogonous composite at nearly every temperature (Figure 6).

Results also show that epoxy/CFC improved the tensile MOE only at 400 °C and had no influence on tensile properties at 360°C and 380°C. In addition, results show that epoxy/CFC reduced tensile strength at every temperature tested.

Overall the composite panel properties correlate well with the lap shear results. The VE/CFC 15% has the best performance overall and compared to the control. This is in agreement with VE being more compatible with PEEK and having higher shear values. At 30% there is likely not enough PEEK resin to sufficiently provide stress transfer to the added VE/CFC material. In all cases the Epoxy based composites showed generally lower properties, similar to the lap shear data.

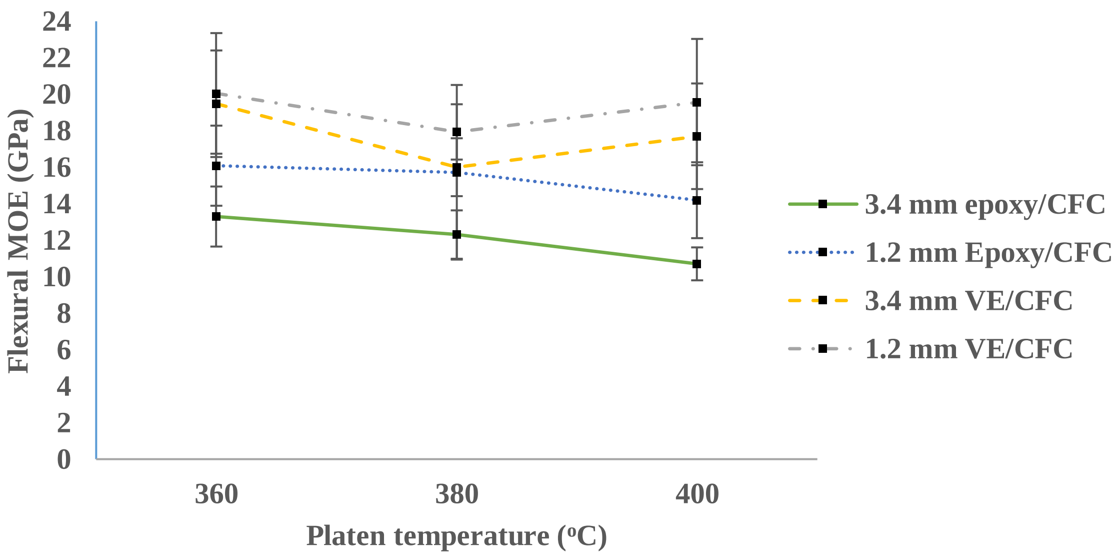
3.4.Particle size effect

To evaluate the influence of rCFC particle size on the mechanical properties of second-generation heterogenous composite, we considered two particle size distributions of rCFCs (3.4 mm and 1.2 mm sieve screen size) as the reinforcement in manufactored recycled heterogenous composite. Because rCFCs are almost a needle shape, 1.2 mm particles are actually shorter in length (Figure 7). Comparing the flexural properties of composites reinnforced with short and long epoxy/CFC indicates that using shorter epoxy/CFC improves the flexural properties of the composite (Figure 8). The flexural MOE of this composite increased by around 30% for all temperatures tested. Using the shorter epoxy/CFC enhanced the flexural strength of the composite at 380 °C and 400 °C platen temperatures (Figure 8). Two possible reasons for the improvement in flexural properties are that the better distribution of shorter epoxy/CFC in the heterogenous composite or that the better penetration of the binder in the reinforcement enhanced the bending properties of the heterogenous composite.

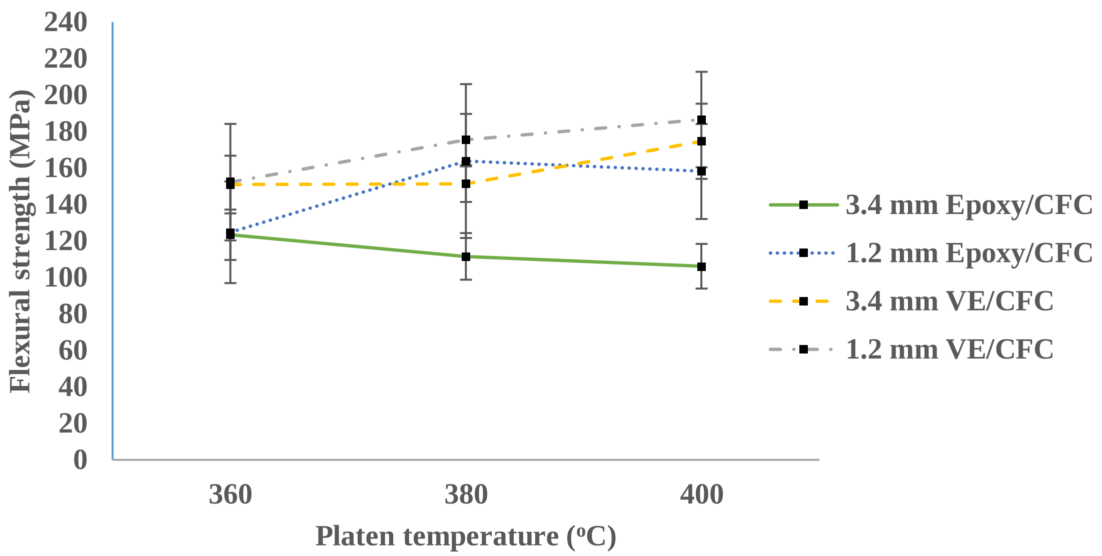
(a)

(b)

Figure 7. (a) recycled CFCs passed from 3.4 mm seive screen size (b) recycled PEEK/CFCs passed from 3.4 mm sieve screen size. (Note: it is visable that recycled CFCs are needle shape)



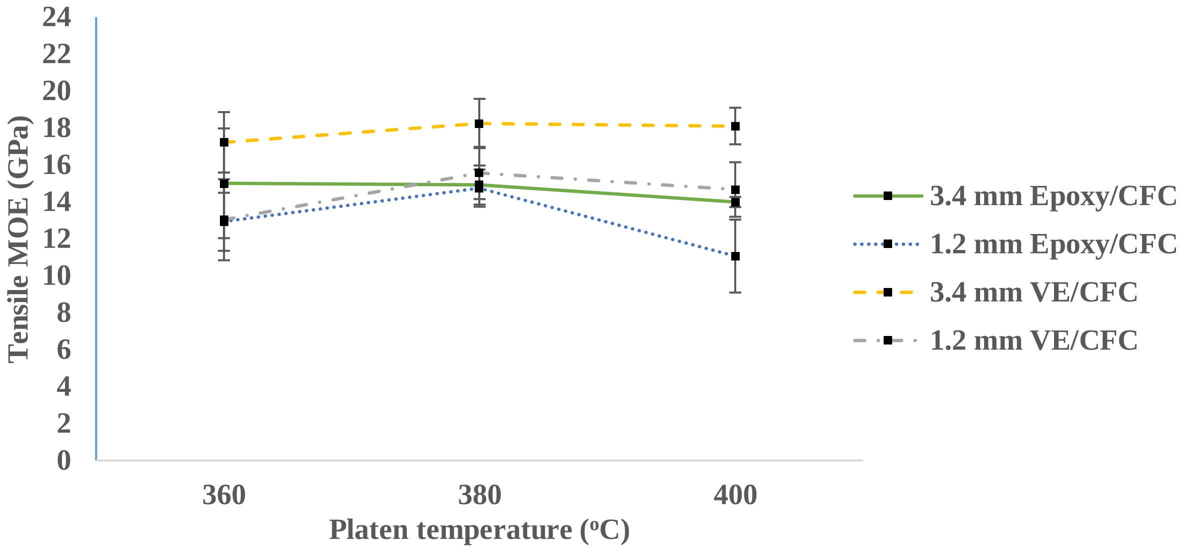
(a)



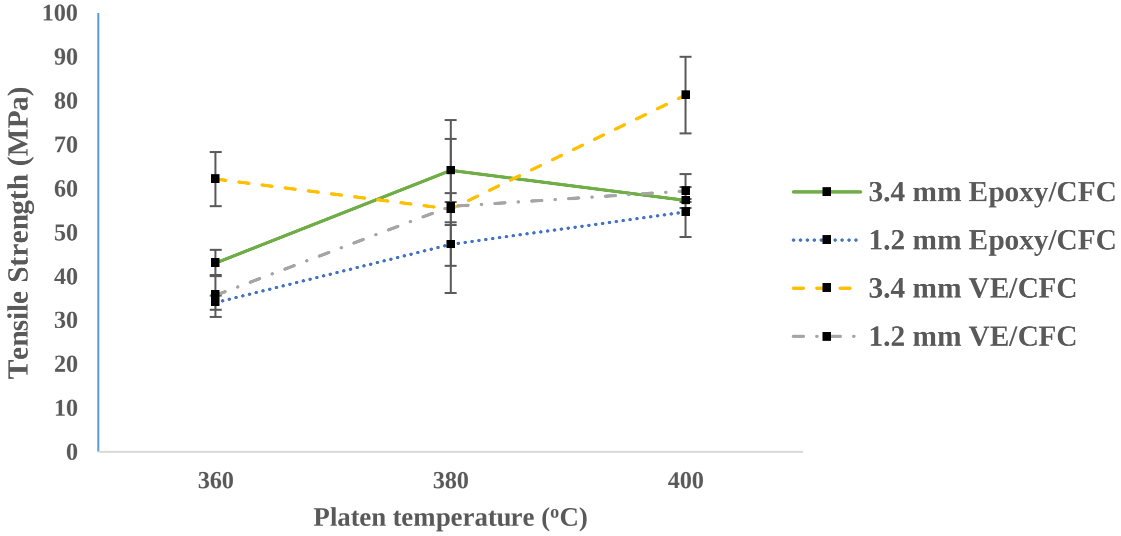
(b)

Figure 8. Effects of particle size on mechanical properties of second-generation composite. (a) Flexural MOE (b) Flexural strength.

The mechanical properties of VE/CFC reinforced composite show similar results to those of epoxy/CFC reinforced composite (Figures 8-9). Smaller particle sizes enhanced the flexural properties and reduced the tensile properties. Results show more enhancement in flexural properties of epoxy/CFC composite than for VE/CFC composite which is likely due to the epoxy/CFC material is smaller than the VE/CFC.



(a)



(b)

Figure 9. Effects of particle size on mechanical properties of second-generation composite (a) Tensile MOE (b) Tensile strength.

Conclusion

The waste scraps of thermoset CFCs were characterized using thermogravimetric analysis. Adhesive performance was evaluated through double lap shear tests by melt-bonding a PEEK/CFC to either the thermoset epoxy or vinyl ester CFC. The waste carbon fiber composites were also mechanically milled and classified. The resulting milled materials were used to form and produce heterogenous composite panels through high temperature compression molding. The effects of different particle sizes, different processing temperature on the mechanical properties were carried out. The results show that melt-bonding between the VE/CFC and PEEK is significantly higher than that between epoxy/CFC and PEEK and are positively influenced with an increase in melt-bonding temperature up to 370°C.

Adding VE/CFC to the PEEK/CFC improved the flexural modulus of elasticity of the heterogenous composite notably. Just adding 15% VE/CFC to the homogenous PEEK/CFC enhanced the flexural MOE of the heterogenous composite observably (almost twice) at 400 °C platen temperature. At 400°C, the mixture of epoxy/CFC has a notable influence on flexural MOE of the heterogenous composite. At this temperature, adding 15% and 30% epoxy/CFC to the homogenous mixture of PEEK/CFC enhanced the flexural MOE of heterogonous composite by 20% and 100%, respectively. Results indicate that rCFCs with smaller particle size enhanced the flexural properties and reduced the tensile properties of heterogenous composites.

Declaration of Conflicting Interests

The author(s) declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

Funding

The author(s) disclosed receipt of the following financial support for the research, authorship, and/or publication of this article: The authors gratefully appreciate the financial support by the Joint Center for Aerospace Technology Innovation, Triumph Group and Zoltek Corporation. Thermoset CFCs were obtained from Zoltek Corporation (Bridgeton, MO, USA) and the PEEK/CFC were donated by Triumph Composites (Spokane, WA).

References

[1] E. Fitzer, Carbon 27 (1989) 62.

[2] M. Jarrah, et al., The effect of elevated temperatures on the tensile performance of GFRP and CFRP sheets., Construction and Building Materials 190 (2018) 38–52.

[3] SH. Mamanpush, et al., Recycled wind turbine blades as a feedstock for second generation composites., Waste Management 76 (2018) 708-714.

[4] SH. Mamanpush, et al., Extruded fiber-reinforced composites manufactured from recycled wind turbine lade material., Waste and Biomass Valorization, April (2019). Springer Nature. doi:10.1007/s12649-019-00659-0.

[5] PMA. Sherwood, Surface analysis of carbon and carbon fibers for composites, Journal of Electron Spectroscopy and Related Phenomena, 81 (1996) 319-342.

[6] H. Li and K. Englund, Recycling of carbon fiber-reinforced thermoplastic composite wastes from the aerospace industry, Journal of Composite Materials, 51(9) (2017) 1265-1273.

[7] J. Li, PL. Xu, et al., A promising strategy for chemical recycling of carbon fiber/thermoset composites: self-accelerating decomposition in a mild oxidative system. Green Chem 14 (2012) 3260–3263.

[8] Y. Liu, J. Liu, et al., Chemical recycling of carbon fiber reinforced epoxy resin composites in subcritical water: synergistic effect of phenol and KOH on the decomposition efficiency. Polymer Degrad Stabil, 97 (2012) 214–220.

[9] JA. Onwudili, N Insura and PT. Williams PT. Autoclave pyrolysis of carbon reinforced composite plastic waste for carbon fiber and chemicals recovery. J Energy Inst 86 (2013) : 227–232.

[10] S. Ramakrishna, WK. Tan, et al. Recycling of carbon fiber/PEEK composites. Key Eng. Mater 137 (1997) 1–8.

[11] Phoenix Fiberglass Inc. Fiberglass composite recycling: report. Ontario: Ministry of Environment and Energy, 1994.

[12] The European Commission for the Environment. The European Commission for the Environment Website (accessed 26 January 2016)

[13] H. Rodin, et al. Recycled glass fiber reinforced polymer composites incorporated in mortar for improved mechanical performance, Construction and Building Materials 187 (2018) 738–751

[14] D. Martine, AL. Chazerain, et al. Characterization of resistance-welded thermoplastic composite double-lap joints under static and fatigue loading, Journal of Thermoplastic Composite Materials 28(6) (2015) 762–776

[15] Method of Determining and Expressing Fineness of Feed Materials by Sieving. ANSI/ASAE S319.3 FEB03

[16] SH. Mamanpush, et al., Data on the mechanical properties of recycled wind turbine blade composites. *Data in brief* 19 (2018): 230-235.

[17] SH. Mamanpush, et al., Dataset demonstrating physical properties of recycled wind turbine blade composites. *Data in brief* 20 (2018): 658-661.

[18] SH. Mamanpush, et al., Physical properties data of extruded composites from recycled wind turbine blade material. *Data in brief* 25 (2019): 104030.

[19] Z. Hong-Gang, et al. Thermal performance and flame retardancy studies of vinyl ester and glass fiber reinforced plastic composites containing nanoclay. Journal of Composite Materials 48(2) (2014) 165–177

[20] SH. Mamanpush, et al., Experimental data on the mechanical and thermal properties of extruded composites from recycled wind turbine blade material. *Data in brief* 25 (2019): 104253.

[21] A. Chatterjee. Thermal Degradation Analysis of Thermoset Resins. Published online 23 June 2009 in Wiley Inter Science (www.interscience.wiley.com).

[22] CM. Stokes-Griffin and P. Compston. Investigation of sub-melt temperature bonding of carbon-fiber/PEEK in an automated laser tape placement process. Composites: Part A. 84 (2016) 17-25.