ENERGY EFFICIENT MANUFACTURING OF HIGH PERFORMANCE COMPOSITES BASED ON RECYCLED CARBON FIBRE

S. Huo[1], Y. Wang[1], X. Yao[1], Y. Liu[2], E. Bilotti[3] and H. Zhang[1]

[1] School of Engineering and Materials Science, Queen Mary, University of London, Mile End Road, London E1 4NS
[2] Department of Material, University of Loughborough, Loughborough, LE11 3TU
[3] Imperial College of London, London, SW7 2BX

Keywords: Recycled carbon fibre, Positive temperature coefficient, Out-of-oven curing

ABSTRACT

This study provides a value-added solution for short recycled carbon fibre (rCF) with an average length of microns as conductive fillers in conductive polymer composites (CPCs). Making use of the pyroresistive behaviour of CPCs paves an efficient path for the out-of-oven (OoO) curing of carbon fibre reinforced polymers (CFRPs). rCF filled PVDF, HDPE and HDPE/PVDF binary polymer were fabricated through melt pressing to achieve both single and double positive temperature coefficient (PTC) effects. For both rCF/PVDF and rCF/HDPE composites, single PTC as well as self-regulating heating behaviour, were achieved with the switching temperature at around 150 ℃ and 112 ℃, respectively. For the rCF/HDPE/PVDF hybrid system, double PTC behaviour was achieved at around 120 ℃ and 139 ℃, owing to the thermal expansion of HDPE and PVDF. This work provides selections for both single and double PTC systems, which can be tuned and used to safely cure CFRP composites OoO through self-regulating Joule heating.

1 INTRODUCTION

Over the last few decades, the demand of light weight materials have been increased significantly to reduce the energy consumption and greenhouse gas emission in many sectors. Carbon fibre reinforced polymers (CFRPs) have been extensively used in aerospace, automotive, sports, wind energy and defense, due to its superior strength to weight ratio. The global carbon fibre market size is projected to grow from $3.7 billion in 2020 to $8.9 billion by 2031, at a CAGR of 8.6% in the forecast period [1]. However, with the ever increasing demand for zero-impact and sustainable development, the environmental impact of each stage from composite production to their end-of-life options should be considered to take the advantage of this high growth rate in the composite sector.

In general, the average lifetime of CFRPs is between 25 to 30 years. Taking a windmill as an example, the utilization of CFRPs in wind turbine has been leading the demand [2]. The service life of a windmill is around 25 years. At the end of the lifetime, the wind blades are disassembled, sectioned and recycled in the form of composite boards (glass fibre composites), grinder fillers (mixture of cut-offs) and fibres (high value fibres) for secondary use. As carbon fibres possess higher embodied energies than other synthetic fibres, CFRPs in wind blades have been through either thermal, chemical, or combination of both recycle processes to recover carbon fibres. Although intensive studies have been carried out to utilise the recycled carbon fibres in the form of continuous and/or long fibres for mechanical reinforcement, how to upcycle these end of life reclaimed carbon fibres (rCF) for value added applications remain a challenge, especially for short rCF with an average length of micrometer only.

Conductive polymer composites (CPCs) consisting conductive fillers, such as carbon black, carbon nanotubes/fibres (CNTs/CNFs), graphene nanoplatelets (GNPs), as multifunctional materials have exhibited a temperature dependent electrical resistivity, namely pyroresistive properties. Our group has performed diverse study in pyroresistive performance of CPCs and achieved reliable self-regulating heating performance based on nanocomposites [3-6]. With the self-regulating heating function, CPCs with recycled carbon fibres/fillers can be used for sustainable out-of-oven (OoO) curing for high performance composites. Comparing with the composites cured by traditional methods, OoO curing needs only 1% of energy consumption which significantly contributes to the sustainable manufacturing, especially considering the growing demand of advanced composites need to be manufactured in next decades. Moreover, the integrated CPC layer could also be used for structural health monitoring, anti-/de-icing, etc., to achieve advanced multifunctional lightweight composites structures.

Positive temperature coefficient (PTC) effect was employed to control the heating procedure, in which the electrical resistance of the CPC increased dramatically at a desired curing temperature and protect the system from over-heating. In the case of high performance CFRP composites, the curing cycle commonly consists of two stages of curing and post-curing at elevated temperatures. In this work, a two-step PTC effect is developed to fulfill this requirement in manufacturing high performance composites.

In this work, CPC layers with both single and double PTC effects were fabricated, in which a selection of different polymers with distinct melting points were combined to fulfill the cure cycle at desired temperatures. In addition, different loadings of rCF fillers were incorporated to provide the conductive and heating paths. Melt-mixing and compression were applied to fabricate the CPC composites.

2 EXPERIMENTAL

2.1 Materials

Short rCF CF-MLD$_{100}$ with average length of 100 µm from Apply Carbon S.A. was used as the conductive fillers in this work. RIGIDEX HD5218EA HDPE (density of 0.952 g/cm^3) and Solef 1015 PVDF (particle size < 300 µm, density of 1.78 g/cm^3) were used as polymer matrices, owing to their PTC switching temperatures of ~120 °C and ~150 °C respectively, which fit well with curing cycle of the epoxy resin system. Polymers were dried at 80 °C in the oven overnight before processing. Copper wires and meshes were used as the electrical buses to connect the CPC composite sheets to a power supply.

2.2 CPC composite preparation

Xplore MC 15 HT Micro Compounder was used to melt mix rCF with PVDF and HDPE. Sample weight was calculated based on the equation:

$$m = \rho \bullet V_n \bullet 0.7 \qquad (1)$$

where ρ is the melt density, V_n represents net chamber volume (15 ml) and 0.7 is the filling percentage. As both PVDF and HDPE are simi-crystalline polymer, 80% of their solid densities were used as melt densities.

rCFs were mixed into PVDF with the loading of 40 wt% under 250 °C, torque of 40 Nm for 5 min. Afterwards, the 40 wt.% rCF/PVDF compound was further diluted with specific amount of HDPE for 5 min (HDPE/PVDF volume ratio of 1/4), to achieve 30 wt.% rCF/HDPE/PVDF. Both 40 wt.% rCF/PVDF and 30 wt.% rCF/HDPE/PVDF compounds were compressed into sheets (~1 mm thick for pyroresistive behaviour testing, and ~ 2 mm thick for Joule heating) using Dr. Collin P300E at 200 °C under 100 bar. Copper meshes were hot pressed on both surfaces of the 2 mm CPC sheets at 200 °C under 50 bar.

2.3 Characterisation

A FEI Inspect F Field emission Scanning electron microscopy (SEM) was used to observe the morphology of rCF and polymers, as well as brittle fractured cross section surfaces of the CPC composites.

The pyroresistive behaviour test was achieved by measuring the resistance of the sample under various temperatures. Samples were placed in a temperature-controlled oven and connected an Agilent 34410A 6½ Digit Multimeter to measure the real time electrical resistance using thee two-wire method. A K type thermocouple was attached to the surface of the sample for the temperature recording. The resistance and temperature were recorded simultaneously.

A GE EPS 301 power supply was used for Joule heating, with different voltages applied. K type thermocouples accompanied with a TC-08 thermocouple data logger from Pico Technology were used to record the temperature of various positions on thee sample surface during the tests.

3 RESULTS AND DISCUSSION

3.1 Morphology

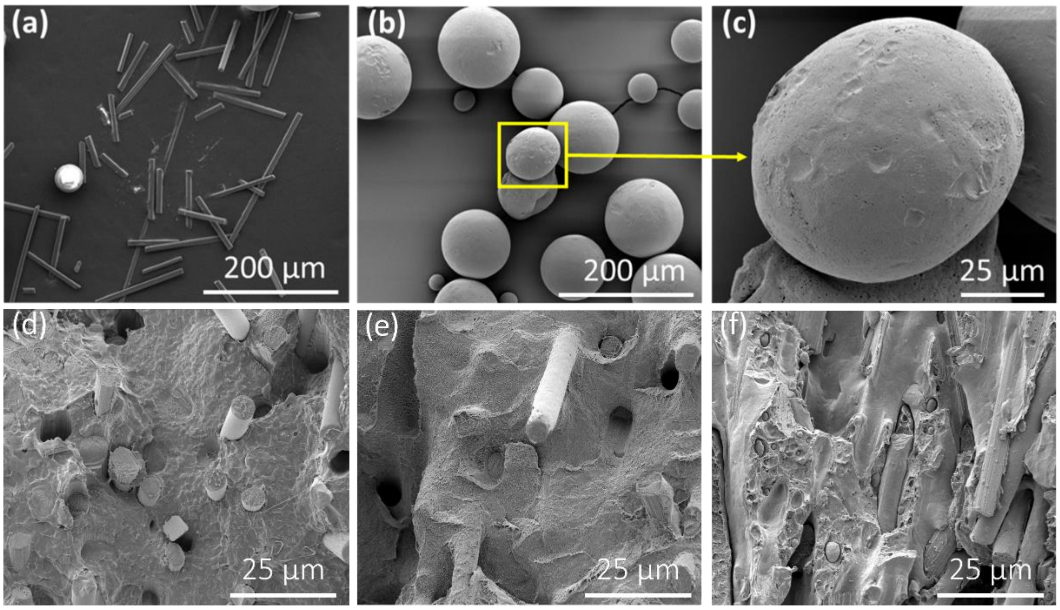

Figure 1: SEM images of as-received (a) rCF CF-MLD$_{100}$, (b) and (c) PVDF powder; brittle fractured cross-section of (d) 30 wt.% rCF/PVDF, (e) 30 wt.% rCF/HDPE, and (f) 30 wt.% rCF/HDPE/PVDF hot pressed under 240 bar.

The as-received rCF, PVDF, cross section of 30 wt.% rCF/PVDF, 30 wt.% rCF/HDPE and 30 wt.% rCF/HDPE/PVDF were characterised by SEM for their morphology, as shown in Figure 1. It shows that HDPE forms small sphere structure in PVDF after mixing HDPE with rCF/PVDF (HDPE/PVDF volume ratio of 1/4). As the diameters of majority HDPE spheres are from 1 μm to 4 μm, which is smaller than the diameter of rCF (5~6 μm), rCFs maintain in PVDF region.

3.2 rCF/PVDF composite

Hot pressed (under 100 bar) rectangular samples (15 mm × 6 mm × 1 mm) were used for pyroresistive behaviour tests. As shown in Figure 2 (a), 30 wt.% rCF/PVDF sample shows the single-step PTC effect, owing to the thermal expansion of PVDF, with the PTC intensity (peak resistivity/room temperature resisitivity) of 3.96 and switching temperature at around 150 ℃.

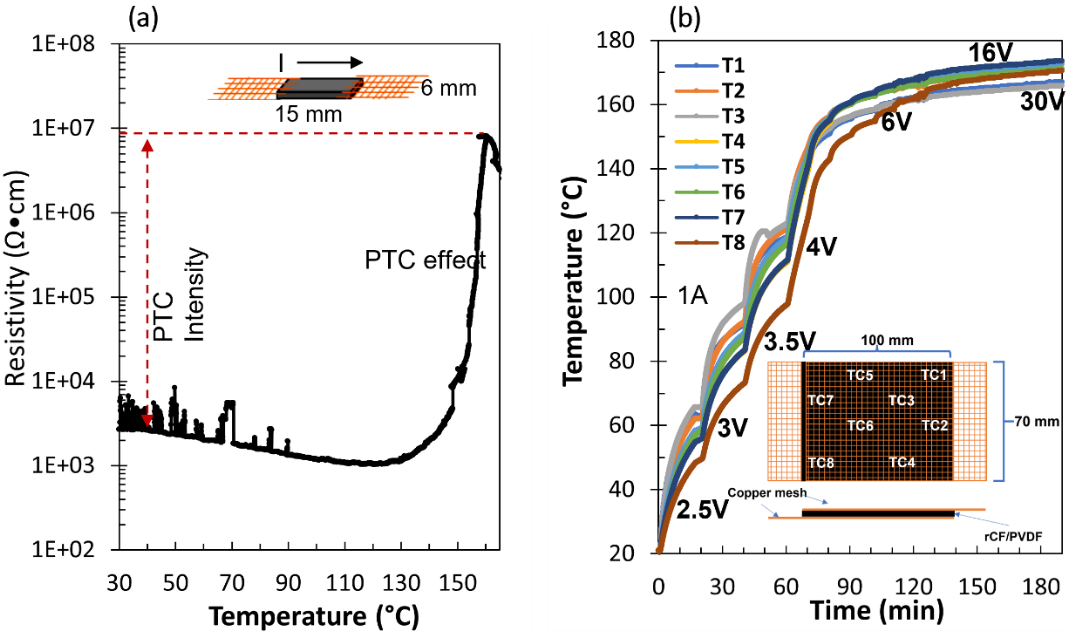

Figure 2: Pyroresistive behaviour (a) of 30 wt.% rCF/PVDF and Joule heating behaviour (b) of 40 wt.% rCF/PVDF samples, embedded with the sample dimensions and set up, including power supply connection, copper meshes and thermocouples (TCs).

In order to check the capability of the compounded CPC composites for OoO curing CFRP composites, Joule heating behaviour of the samples were tested. 40 wt% rCF/PVDF sheet was hot pressed into a rectangular shape (10 cm × 7 cm), with the thickness of 0.1 cm, resistance of 2.8 Ω and copper meshes applied as the electrodes, as shown in Figure 2 (b).

During the Joule heating test, thermal insulating materials (polyester fabric) were used to cover the samples to prevent the major heat loss, convention [7]. In this case, energy generated by resistive heating contributes to heat up the composite accompanied with heat loss via heat conduction and radiation, following the below equation:

$$q_{in} = \frac{U^2}{R} \tag{2}$$

$$q_{out} = c \cdot m \cdot \frac{dT(t)}{dt} + q_{cond} + q_{rad} \tag{3}$$

According to the law of conservation of energy:

$$\frac{U^2}{R} = c \cdot m \cdot \frac{dT(t)}{dt} + kA\frac{T_S - T_\infty}{\Delta x} + \varepsilon\sigma A(T_S^4 - T_\infty^4) \tag{4}$$

where U is the applied voltage; t is the time; R, T, c and m are the resistance, temperature, specific heat capacity and mass of the samples; A is the heating area; T_s and T_∞ are the sample surface and environmental temperature respectively; Δx is the distance between sample surface and environment; k, ε and σ are the thermal conductivity of the insulating material, emissivity and Stefan-Boltzmann constant.

Due to its PTC effect, resistance of the 40 wt.% rCF/PVDF film increased with increasing temperature, particularly around and after the switching temperature (~150 ℃). As a result, further increased voltage (16V, 20V, 24V to 30 V) only contributed to limited extra input power ($\frac{U^2}{R}$), as well as a limited temperature increase, thus reaching a self-regulating state.

3.3 rCF/HDPE composite

30 wt.% rCF/HDPE sample (15 mm × 6 mm × 1mm, hot pressed under 100 bar) were used for pyroresistive behaviour tests and 20 wt.% rCF/HDPE sheets (10 cm × 7 cm × 0.1 cm, hot pressed under 100 bar, resistance of 3.1 Ω) were used for Joule heating tests, as shown in Figure 3. Owing to the

thermal expansion of HDPE 30 wt.% rCF/HDPE shows the single-step PTC effect. At the switching temperature around 112 °C, the PTC intensity reaches to the maximum and the sample become non-conductive. As the sample cools down naturally, the sample become conductive and recovers to the original resistance while the temperature reaches to room temperature.

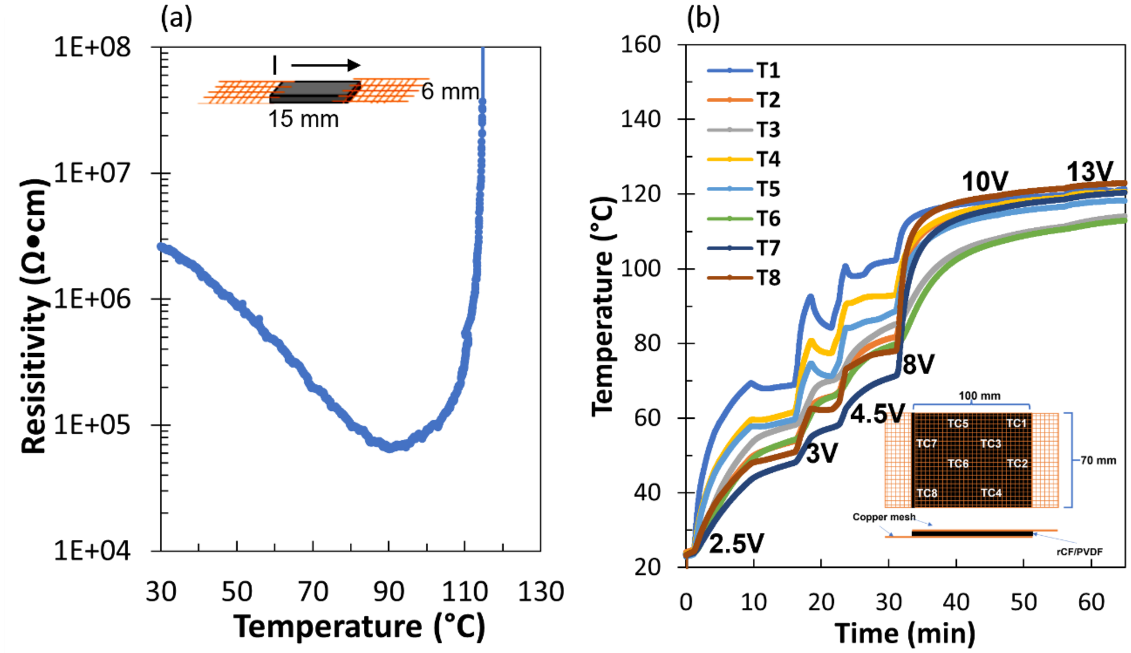

Figure 3: Pyroresistive behaviour of 30 wt.% rCF/HDPE (a) and Joule heating behaviour of 20 wt.% rCF/HDPE (b), embedded with the sample dimensions and set up, including power supply connection, copper meshes and thermalcouples (TCs).

Similar Joule heating behaviour as rCF/PVDF was observed in 20 wt.% rCF/HDPE composites. Resistance of the 20 wt.% rCF/HDPE sheet increased with increasing temperature , particularly around and after the switching temperature (~112 °C). As a result, further increased voltage (10 V to 13 V) only contributed to limited extra input power as well as a limited temperature increase. Thus, the rCF/HDPE sheet reached a self-regulating state.

3.4 rCF/HDPE/PVDF composite

While using HDPE to dilute rCF/PVDF and forming a binary polymer system, a double or two-step PTC effect was observed in 30 wt.% rCF/HDPE/PP, as shown in Figure 3. The PTC intensities of first and second step achieved at 0.74/∞, with two switching temperature sit at ~120 °C and ~139 °C contributed by the thermal expansion of HDPE and PVDF respectively. The Joule heating behaviour of rCF/HDPE/PVDF will be analysed in the near future for OoO composite curing.

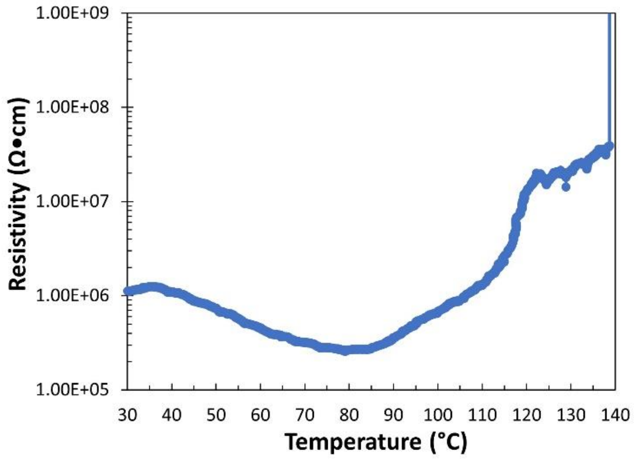

Figure 4: Pyroresistive behaviour of 30 wt.% rCF/HDPE/PVDF samples.

4 CONCLUSIONS

rCF filled polymer composites with both single and double polymer matrices were manufactured through melt mixing and compression mold. For the single polymer system, single step PTC behaviour was observed due to the thermal expansion of PVDF and HDPE. Meanwhile, self-regulating heating behaviour of the both single polymer systems was also observed (PVDF at around 150 ℃, HDPE at around 112 ℃), which is the switching temperature of PTC effect. For the binary polymer system, double PTC behaviour was achieved via the thermal expansion of both HDPE and PVDF at different temperature. Two stage self-regulating heating behaviour will be assessed in the next step. This study provides suitable selections for systems with both single and double PTC behaviour, which can be used to safely cure different CFRP composites OoO through self-regulating Joule heating.

ACKNOWLEDGEMENTS

The authors would like to acknowledge the financial support received from the Engineering and Physical Science Research Council (EPSRC) [ESTEEM project, EP/V037234/1].

REFERENCES

[1] “Carbon fiber market by raw material (PAN, Pitch), fiber type (Virgin, Recycled), product type, modulus, application (Composite, non-composite), end-use industry (A&D, Automotive, wind energy) and region – Global Forecast to 2031”. *Markets and Markets*, July 2021.

[2] J. Zhang, V. Chevalier, H. Wang and C.-H. Wang “Current status of carbon fibre and carbon fibre composites recycling”. *Composites Part B*, 193, pp 108053, 2020.

[3] Y. Liu, T. Vietnamese, Y. Tao, JJC Busfield, T. Peijs, E. Bilotti, H. Zhang “Sustainable and self-regulating out-of-oven manufacturing of FRPs with integrated multifunctional capabilities”. *Composite Science and Technology*, 190, pp 108032, 2020.

[4] Y. Liu, E. Asare, H. Porwal, E. Barbieri, S. Goutianos, J. Evans, M. Newton, JJC Busfield, T. Peijs, H. Zhang, E. Bilotti “The effect of conductive network on positive temperature coefficient behaviour in conductive polymer composites”. *Composites Part A*, 139, pp 106074, 2020.

[5] Y. Liu, H. Zhang, H. Porwal, W. Tu, K. Wan, J. Evans, M. Newton, JJC Busfield, T. Peijs, E. Bilotti “Tailored pyroresistive performance and flexibility by introducing a secondary thermoplastic elastomeric phase into graphene nanoplatelet (GNP) filled polymer composites for self-regulating heating devices”. *Journal of Materials Chemistry C*, 6, pp 2760, 2018.

[6] Y. Liu, H. Zhang, H. Porwal, W. Tu, K. Wan, J. Evans, M. Newton, JJC Busfield, T. Peijs, E. Bilott “Universal Control on Pyroresistive Behavior of Flexible Self-Regulating Heating Devices”. *Advanced Functional Materials*, 27, pp 1702253, 2017.

[7] X. Yao, SC Hawkins, BG Falzon “An advanced anti-icing/de-icing system utilizing highly aligned carbon nanotube webs”. *Carbon*, 136, pp 130, 2018.