https://doi.org/10.2352/ISSN.2169-4451.2017.32.482

Multi-functional Carbon Fibre Reinforced Composites Obtained using Inkjet Printed Polymers

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Abstract

Tougher and stronger carbon fibre reinforced composites have been prepared using inkjet printing to deposit discrete polymer droplets onto the composite precursor. The polymer system that has been inkjet printed is a dual material system, in which half of the deposited droplets contain PMMA and the other half contain PEG.

The resultant uni-directional carbon fibre reinforced composite exhibits improved mechanical properties with a barely noticeable increase in weight. For the dual material PMMA & PEG system, mode I interlaminar fracture toughness is increased by 40%, with evidence that higher values are possible. Additionally, initial experiments indicate that a significant increase (~5%) in apparent interlaminar shear strength is also observed.

Introduction

Carbon fibre composites

Carbon fibre composite materials are increasingly employed in aerospace applications (e.g. Boeing's 787 Dreamliner) on account of their high specific stiffness and strength, as well as their low weight. It has been calculated that for every kilogram reduction in weight in an aircraft there is a corresponding reduction of 200 litres in annual fuel consumption [1].

Although there are clear financial and environmental benefits to using lightweight composites, some of their inherent properties such as low fracture toughness and brittleness compared to metallic alloys can lead to time consuming maintenance protocols.

The most common mode of failure in carbon fibre composites is by delamination, whereby cracks grow along the interface region between adjacent plies [2][3]. The brittle nature of epoxy means that it is prone to develop microcracks when subjected to stress. These microcracks tend to develop between laminate plies due to the laminated materials lacking reinforcement in the through thickness direction [4]. This phenomenon, of the cracks propagating between the plies, eventually leads to delamination, which is a typical failure mode commonly seen in laminated carbon fibre composites.

A variety of methods have been investigated to inhibit and prevent delamination occurring in carbon fibre composites with interleaving being shown to be effective [5]. Interleaving involves placing thin sheets of high toughness material between laminate plies [6]. However, a major trade off exists in employing the interleaving toughening method as the overall weight of the composites system increases, which compromises the high stiffness-weight and strength-weight ratios of carbon fibre composites. Furthermore, there is a reduction in the interlaminar shear properties and fibre volume fraction [6]. It is, therefore, of interests to the composites community to investigate alternative means to improving the toughness of carbon fibre composites without significantly increasing the overall weight of the system.

Inkjet printing

Drop-on-demand inkjet printing is an attractive technique which can generate uniform droplets in the picolitre volume range and precisely dispense those droplets directly into pre-designed patterns without masks [7][8]. Two of the major advantages of using inkjet printing are the ease of pattern change-over since patterns are digitally stored and an efficient material usage as droplets are printed only at places where needed. Inkjet printing has been used in a variety of applications such as fabricating scaffolds for tissue engineering [9], printing electronics [10] and delivery of biological factors [11][12].

Inkjet printing and carbon fibre reinforced composites

Recently, it has been reported that inkjet printing has been used to toughen carbon fibre composites [13][14], and to introduce an organic system which possesses self-healing capability into carbon fibre composite [15]. As regards the toughening approach, a solution of poly(methyl methacrylate) (PMMA) was inkjet printed onto the carbon fibre precursor, known as pre-preg. The PMMA droplets were patterned in a hexagonal pattern, as shown in Fig. 1. After printing was complete, the sheets of pre-preg were laid up and thermally processed under pressure to form the final carbon fibre composite material.

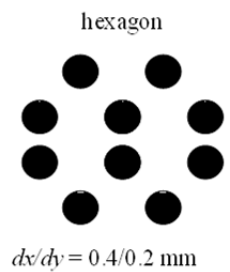

Figure 1. *The standard printing pattern that has been employed in producing toughened carbon fibre composites by inkjet printing. Each dot corresponds to a printed droplet of PMMA, where the dot-spacing in X (dx) was 0.4 mm and dot-spacing in Y (dy) was 0.2 mm.*

The resultant uni-directional carbon fibre reinforced composites that have been prepared employing an inkjet printing step exhibit improved mechanical properties with a barely noticeable increase in weight (e.g. if using 10 wt% PMMA solution and a hexagonal discrete dot pattern, dx = 0.4 mm, dy = 0.2 mm, for printing, approximately 0.036 wt% increase in the final composites). As can be seen in Fig. 2, for a single material PMMA system, mode I interlaminar fracture toughness (G_{Ic}) increased by 40%; compare the non-printed (NP) control to the printed 'Hexagon' sample [16]. Higher values are possible, as can be seen in the printed 'Film' sample in Fig. 2 [16].

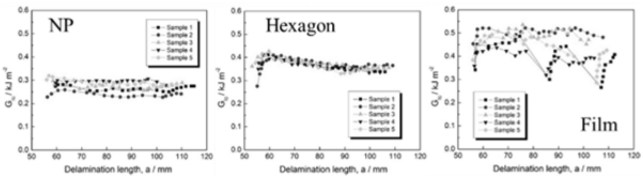

Figure 2. A comparison of mode I interlaminar fracture toughness measurements, G_{Ic} for a non-printed control (NP) and two experiments containing inkjet printed PMMA. One of the experiments contained a printed hexagonal pattern of PMMA dots whilst the other contained a continuous film of PMMA. The HEXAGON sample exhibits higher G_{Ic} when compared to the control, NP and greater reproducibility when compared to the FILM sample [17].

The left hand side of Fig. 3 shows the crack initiation and propagation for the three sample types. It can be seen that the both printed systems exhibit improved toughness, with film showing higher values but the printed hexagon displaying higher repeatability. The right hand side of Fig. 3 illustrates the apparent interlaminar shear strength (aILSS) of the three samples. It can be seen that whilst the printed hexagon sample is comparable to the control the printed film sample is lower on average and exhibits a wide variability.

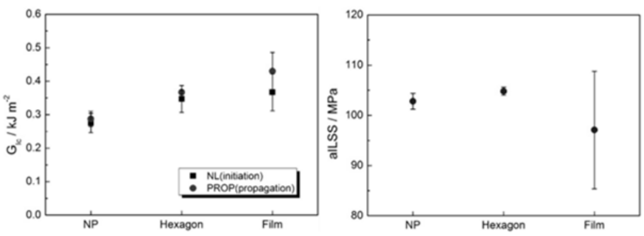

Figure 3. Crack initiation and propagation in the left hand figure and the apparent Interlaminar Shear Strength (aILSS) on the right for the control (NP), the printed hexagon and printed film samples. In all cases n = 5. [17]

In the work discussed in this paper, the effect of printing a polyethylene glycol (PEG) solution and a dual material system in which half of the dots are PMMA and the other half are PEG is discussed.

Results and Discussion

Variation of PEG concentration and solvent

PEG can be dissolved in both organic and inorganic solvents and although the solvent should not affect the mechanical properties of the composites since it should fully evaporate before lay-up, it is worth investigating to ensure this is the case. In order to minimise the potential effect of solvent evaporation rate on the possible amount of residue trapped in PEG deposits, solvents with similar boiling point (Deionised water, Dw, 100°C; 1-Propanol, Pp, 97°C) were used.

As expected, changing the solvent used for the PEG contained solutions does not have much influence on aILSS of the printed samples compared to non-printed group (NP) as shown in Fig. 4, which indicates that the solvent evaporates from the substrate before layup, presumably because the volume of an inkjet printed droplet is sufficient small.

It is also can be seen from Fig. 4 that varying the concentration of PEG in the solutions has little difference on the aILSS of the printed samples, when compared to the control (NP). However, it is also worth noting that the aILSS of PEG printed CFRP laminates was retained compared to the control.

A comparison between 5 wt% solutions of PMMA and PEG and their effect on mode I interlaminar fracture toughness, G_{Ic}, is shown in Fig. 5. It can be seen that the PMMA addition has a marked effect, whereas the PEG addition has less of an effect, with much of its improvement being within the scatter of the non-printed control. As PMMA showed a better toughening efficiency, the majority of subsequent work focussed on the PMMA system, which has been reported elsewhere [13][14][17]. It is pertinent to report the data here as it helps inform the discussion with the dual material system.

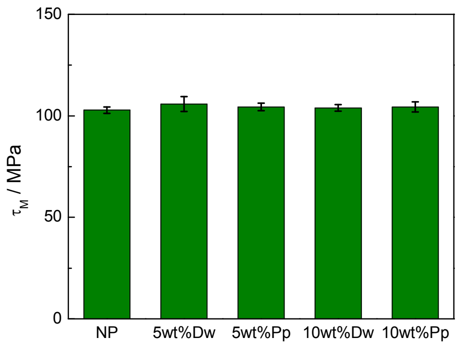

Figure 4. aILSS comparisons of samples printed using different PEG concentrations and solvents, where Dw stands for deionised water and Pp is 1-Propanol. The pattern employed was the hexagon shown in Fig. 1. n = 5 for all cases.

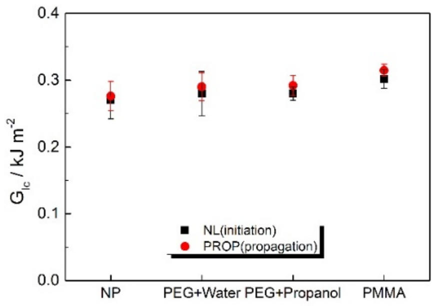

Figure 5. G_{Ic} comparisons (initiation and propagation) for 5 wt% solutions of PEG in water, PEG in 1-propanol and PMMA in DMF compared to a non-printed control (NP) (n = 5).

Dual material (PMMA & PEG) system

The motivation for the dual material experiment was to explore one of the advantages of inkjet printing, namely the ability to deposit more than one material [18]. In this particular case, 10 wt% PMMA and 10 wt% PEG solutions was used to alternatively print deposits patterned in a hexagon pattern as shown in Fig. 6. The resultant composite samples were tested for both mode I interlaminar fracture toughness, G_{Ic} and apparent interlaminar shear strength, aILSS, with the measurements shown in Fig. 7.

It can be seen from Fig. 7 that the dual material system delivers an improvement in G_{Ic} that is similar to that for the 10 wt% PMMA. This is a remarkable result since previous experiments have shown that increasing the dot spacing of the PMMA system or reducing the concentration of PMMA reduces the improvement in G_{Ic}. Similarly, earlier research had shown that PEG had little effect on G_{Ic} (Fig. 5).

When the values for aILSS are observed, the right-hand side of Fig 7, it can be seen that the dual material system exhibits a significant increase (in this case significant implies that the result is outside the variation of the control) compared to the PMMA system and the control. Although this work is still at an early stage, it seems that the combination of PMMA and PEG has a beneficial effect on the mechanical performance of carbon fibre reinforced composites, both in terms of mode I interlaminar fracture toughness and apparent interlaminar shear strength but the exact reasons for why this is have yet to be determined. At this stage, it is, however, reasonable to suggest that inkjet printing's ability to print more than one material in a single pass confers an advantage of carbon fibre reinforced composites. Moreover, it is fascinating to observe that usually one would expect a decrease in aILSS for a toughened system (Fig. 3, right-hand side) but it seems that the discrete dots produced by inkjet printing prevent this drawback.

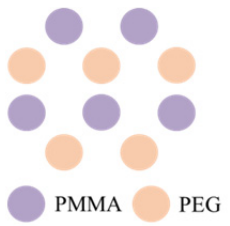

***Figure 6**. Alternatively printed hexagon pattern (dx/dy = 0.4/0.2 mm) using PMMA and PEG solutions.*

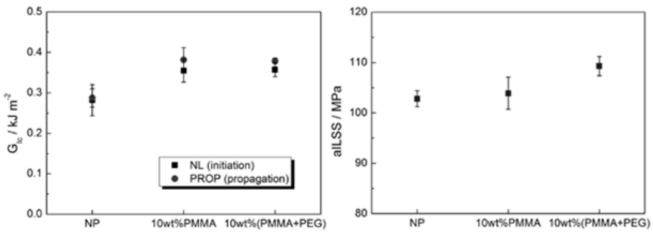

***Figure 7.** The values of G_{Ic} and aILSS measured for three sample sets. One of the sample sets was the non-printed (NP) control, the second was the optimised PMMA single material system, and the third was a dual material PMMA/PEG system. [17]*

Conclusions

Inkjet printing has been used to deposit droplets of solution that either contain PEG (polyethylene glycol) or PMMA (poly(methyl methacrylate)) onto a carbon fibre composite precursor, pre-preg. After the final composite has been obtained the resultant uni-directional carbon fibre reinforced composite exhibits improved mechanical properties with a barely noticeable increase in weight. For the dual material PMMA & PEG system, mode I interlaminar fracture toughness is increased by 40%, which is similar to that obtained for the PMMA single material system, and a noticeable increase in apparent interlaminar shear strength is also observed.

Materials and Methods

Solution preparation and inkjet printing

PMMA (Mw ~ 15 kDa) and PEG (Mn ~ 20 kDa) were dissolved in N, N-dimethylformamide (DMF) and deionised water and 1-Propanol with different weight percentage respectively to form the solutions for printing. All chemicals were purchased from Sigma Aldrich (Sigma-Aldrich Co. Ltd., UK) and used as received. Ultrasonic agitation was used to aid the dissolution of PMMA in DMF. A drop-on-demand (DOD) JetLab 4xl printer equipped with a compatible MicroJet printhead was employed as the deposition tool (MicroFab Inc. Plano, USA).

Test procedures

A tensometer (TA500 Texture Analyser, Lloyd Instruments, UK) equipped with a 500N load cell was used to conduct the DCB (double cantilever beam) test in tension mode. The speed of crosshead was 5 mm/min. The test samples were first pre-cracked using a mode I opening load to avoid any resin rich pockets and generate a sharp crack tip for subsequent test. A high definition camcorder was used to record the DCB test for determining the delamination length for data reduction.

The short beam shear (SBS) test was carried out using a benchtop tester (H25KS, Tinius Olsen Ltd., UK) equipped with a 25KN load cell in three-point compression mode. The speed of crosshead was 1 mm/min. The span/thickness ratio was 5 which is recommended by the test standard.

Sample fabrication

Unidirectional CFRP prepreg tape (CYCOM®977-2, Cytec Industries Inc., USA) was used to fabricate the carbon fibre laminates. Twelve (DCB) and eight (SBS) printed plies of prepreg were laid-up unidirectionally for subsequent curing into laminates respectively. A non-stick polytetrafluoroethylene (PTFE) film was inserted at the mid-thickness ply of DCB panel to simulate a crack to allow the crack propagation at the interested interface. A customised autoclave (Premier Autoclaves Ltd., UK) was used to consolidate the laid-up panels. For the detailed curing cycles please refer to previous work [14]. DCB and SBS samples were cut into 140 ± 1 mm × 20 ± 0.5 mm × 3 ± 0.1 mm and 20 ± 1 mm × 10 ± 0.2 mm × 2 ± 0.2 mm in accordance with the test standards [19][20]. Two 11.9 mm x 11.9 mm centre-drilled metal blocks were bonded to each PTFE inserted DCB samples ends for fitting into the test machine. For improving the visibility of the crack propagation, the edges of DCB test samples were paint with a white correction fluid.

Acknowledgements

The research reported in this paper was sponsored initially by the Air Force Office of Scientific Research, Air Force Material Command, USAF, under grant numbers FA8655-11-1-3072 and FA8655-13-1-3090 then by the US Army under grant number W911NF-14-1-0581. The authors wish to acknowledge colleagues from the European Office of Aerospace Research and Development (a detachment of the Air Force Office of Scientific Research) for their guidance and support. In particular, we wish to thank Dr Lee Byung (Les), Dr Randall Pollak (Ty), Mr John Preston and Dr Matthew Snyder for their strong support of our research. The authors also wish to thank the Department of Mechanical Engineering, University of Sheffield for their financial support connected to the lab class inkjet printer, and the US Army for continuing to finance and to patent our ongoing research.

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