TOUGHENING COMPOSITES WITH SELF-AMELIORATING CAPABILITY USING INKJET PRINTING TECHNIQUE

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Abstract

Poly(methyl methacrylate) (PMMA) ink was accurately deposited in a pre-defined microscopic hexagonal pattern onto carbon fibre prepreg substrate using an inkjet printing method before curing cycle, leading to a significant increase in mode I interlaminar fracture toughness (G_{Ic}) of the final aerospace grade advanced carbon fibre reinforced polymer (CFRP) composite system. This improvement was further optimised by increasing the concentration of PMMA in the ink and the density of printed pattern on the substrate, resulting in a proportional increase in toughening mechanism and the mechanical properties of the system.

1. Introduction

Carbon fibre reinforced polymer (CFRP) offers distinct advantages such as high specific stiffness and strength while maintaining lower weight for manufacturing. However, this superior material has some vital limitations in service. The main limitation in using laminated composite materials is the poor damage resistance on through-thickness and interlaminar directions [1]. Delamination is one of the most common damage modes in CFRP laminated composites, it develops from micro-cracks which can be generated from a localised impact loading such as impacting by a dropped tool and debris [2, 3]; these micro-cracks are difficult to detect before they develop into cracks potentially leading to catastrophic failure [4]. Thus, enhancing the interlaminar fracture toughness, as one of the key parameters for evaluating structural integrity of laminated composites, extends the lifetime of this material.

Inkjet printing is a material-efficient deposition technique that uses liquid phase materials as printing inks. Its ability to precisely place pico-litre droplets according to predefined patterns directly upon substrates makes this technique attractive to areas such as printing scaffolds for tissue engineering and integrated printing electronics [5-9]. Various materials have been used in inkjet printing such as polymers, ceramics, nanoparticles and bioactive substances [10-12].

As inkjet printing deposits droplets at predetermined locations material usage and waste are minimised. This advantage is important to composites toughening as introduced weight to final engineered composites needs to be balanced with the increase in mechanical properties. Physical and rheological properties of liquid inks are important to enable successful printing. Amongst them, viscosity and surface tension are the most important factors that determine the printability of inks [13-15].

This inkjet printing technique can be used to selectively toughen composite areas where higher damage resistance is required, such as holes, joints and high-load areas, on account of inkjet's ability to deposit a vast range of patterns that can be designed ahead of time. In the work reported here, thermoplastic micro-droplets were printed onto prepreg before curing, and remained arrested between composite plies without direct contact with the neighbouring micro-droplets after curing, which preserved the structural integrity of the novel composite system. As the thickness of deposits on substrate by inkjet printing is sub-micron, the introduced thickness to the composite is negligible, which is an advantage over conventional interleave toughening methods. Since the interface between the plies is likely to be the main source of micro-cracks [16, 17], discrete thermoplastic microdroplet deposition imparts multifunctional properties whilst enhancing its structural integrity in service.

2. Experimental

2.1 Materials

An aerospace grade unidirectional carbon fibre prepreg (Cycom 977-2, Cytec Industries Inc., USA) was chosen as substrate in this work. Poly(methyl methacrylate) (PMMA) (Mn = 15 kDa) was dissolved in N, N-dimethylformamide (DMF) with different concentrations. All chemicals were purchased from Sigma Aldrich (Sigma-Aldrich Co. Ltd., UK) and used as received. As aforementioned, the viscosity of ink is an important parameter for inkjet printing, hence viscosities of all inks used in this work were measured at room temperature using an A&D sine-wave vibro viscometer (European Instruments, UK) as shown in Table 1.

Table 1. Viscosities the PMMA inks used in this study.

Ink No.	wt.%	Viscosity / mPa.s
1	5	1.30
2	10	2.05
3	20	6.32

2.2 Fabrication of specimens

A drop-on-demand (DOD) JetLab 4xl printer equipped with a compatible MicroJet printhead was used to print the prepregs before the curing cycle. The diameter of printhead orifice was 60 μm, all printing devices were purchased from MicroFab Inc. (Plano, USA). Prepreg sheets were cut into 150×140 mm and 100×100 mm for DCB test and impact test respectively. For DCB test, only the mid-thickness ply was printed with PMMA solution. For impact test, PMMA ink was deposited between all the plies. A hexagon pattern was chosen for printing as shown in Figure 1. Parameters *dx* and *dy* can be verified to change shape and density of patterns. After printing, the plies were laid-up unidirectionally in accordance with the test standard BS ISO 15024:2001 [18]. A non-adhesive polytetrafluoroethylene (PTFE) film was inserted at the mid-thickness of the panel during lay-up to simulate a sharp starter crack. Autoclave (Premier Autoclaves Ltd., UK) was used to cure panels. For the detailed curing cycles please refer to our previous work [19]. DCB test specimens were cut from cured laminates with the required dimensions as described in the standard.

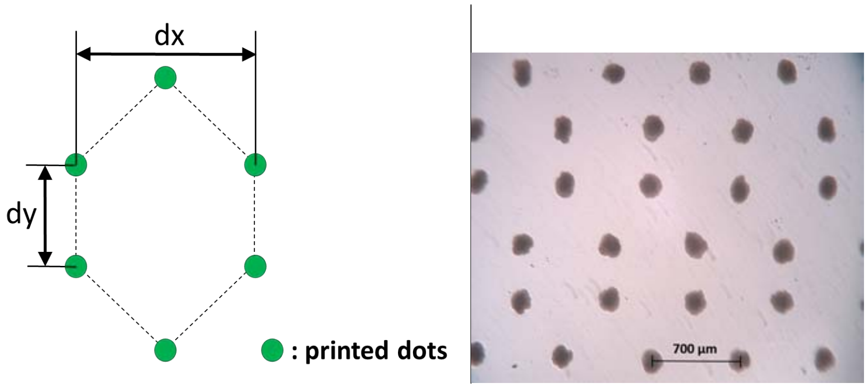

Figure 1. Hexagonal pattern and PMMA droplets deposited on glass slide with the hexagonal pattern.

2.3 Experimental procedure

DCB test was adopted to measure the Mode I interlaminar fracture toughness (G_{Ic}). Figure 2 schematically shows the DCB test specimen with printed PMMA. The DCB test was carried out using a tensometer equipped with a 500 N load cell (TA500 Texture Analyser, Lloyd Instruments, UK) with a crosshead speed of 5 mm/min. A mode I pre-loading was carried out to avoid resin rich regions and to generate a real crack for the subsequent DCB test.

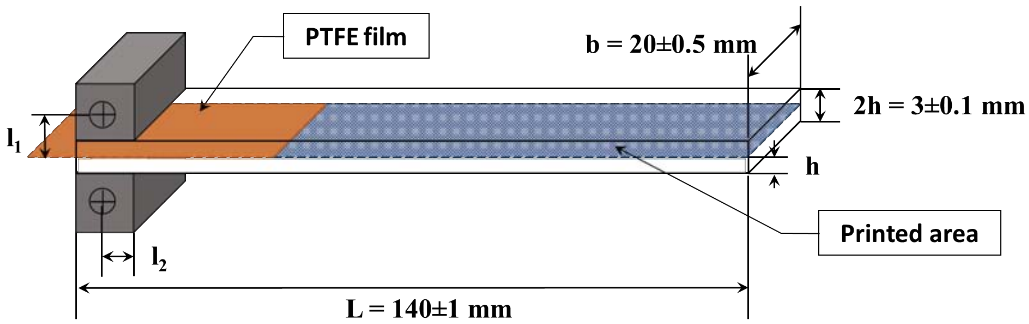

Figure 2. Schematic view of DCB test specimen.

The critical energy release rate (G_{Ic}) is calculated by:

$$G_{Ic} = \frac{3P\delta}{2b\,(a+\Delta)} \times \frac{F}{N} \tag{1}$$

Where *P* is the load, *δ* is the load curve displacement, *b* is the specimen width, *a* is the total delamination length, *Δ* is a function of total delamination length *a* (for more details please refer to reference [18]), *F* is the large-displacement correction which is calculated by equation (2) and *N* is the load block correction which is calculated by equation (3):

$$F = 1 - \frac{3}{10}\left(\frac{\delta}{a}\right)^2 - \frac{2}{3}\left(\frac{\delta l_1}{a^2}\right) \tag{2}$$

$$N = 1 - \left(\frac{l_2}{a}\right)^3 \frac{9}{8}\left[1 - \left(\frac{l_2}{a}\right)^2\right]\frac{\delta l_1}{a^2} - \frac{9}{35}\left(\frac{\delta}{a}\right)^2 \tag{3}$$

Where l_1 is the distance from the centre of the loading pin to the mid-plane of the specimen beam and l_2 is the distance from the loading-pin centre to its edge (see Figure 2).

Impact test was conducted to investigate the damage tolerance of composite laminates with inkjet printed PMMA deposits. Two 100×100×2 mm cured composite plates (non-printed and PMMA printed) were impacted by a drop weight impact tower using 1 J as impact energy. For each plate, five different places were impacted followed by x-ray tomography to scan the impacted areas.

2.4 X-ray tomography inspection

Custom design Nikon/Metris dual source high-energy micro-focus walk-in room system at The University of Southampton was used to conduct non-destructive x-ray tomography analysis of the microcracks in non-printed and PMMA printed CFRPs. The scan used the 225kV source with and 1621 PerkinElmer cesium-iodide detector. The current was set at 157uA (8.6W) and 100×10×2 mm composite panel brought forward so that the source-imaging distance was ~700mm. At this power, the focal spot is spread slightly to prevent melting of the target. 3142 projections were taken over the 360 degree rotation, with 4 frames per projection being averaged in order to improve signal to noise. Exposure time of each projection was 354 ms and the gain set to 30 dB. To reduce the effect of ring artefacts, shuttling was used with a maximum displacement of 5 pixels.

3. Results and discussion

3.1 DCB test

In our previous work, it was demonstrated that specimens with inkjet-printed PMMA micro-patterns showed increased G_{Ic} values [19]. This observation has been ascribed to the establishment of discrete plastic zones, which arrested damage development and deflected crack paths by absorbing energy [3, 19, 20]. The normalised values of initial or non-linear (NL) and propagation (PROP) values from the fracture toughness Mode I test on the printed CFRP systems before and after the secondary heat treatment (used as self-ameliorating process) are shown in Table 2.

Table 2. Non-linear and propagation values of G_{IC} in printed CFRP systems before and after heat treatment, normalised by the non-printed CFRP values.

G_{IC} normalised by Virgin CFRP values (before/after HT)				
System	NL before HT	NL after HT	PROP before HT	PROP after HT
Virgin CFRP	1	0.5/1	1	0.49/1
5%PEG	1.09	0.72/1.44	1.06	0.56/1.16
5%PMMA	2.16	1.21/2.43	1.5	0.91/1.87

The increase in both initial and propagation values of G_{IC} were noticeable in PMMA printed system, leading to the maximum increases in fracture toughness by over 100% of the initial value before the secondary heat treatment, and by 87% of the propagation value after the heat treatment, compared to the virgin CFRP values. The results are normalised by the virgin CFRP system properties before and after the secondary heat treatment, to provide the information on the relative improvement and the overall achieved increase in properties respectively. These results were accompanied by 35% increase in the interlaminar shear modulus in the undamaged PMMA printed samples [19], compared to the virgin CFRP system, and 8% increase in the same property after the damage (introduced as the onset of delamination during the first test) and secondary heat treatment. The interlaminar shear strength was also fully preserved, both before and after the secondary heat treatment.

This significant improvement is further optimised by increasing polymer concentration in the ink, yielding a proportional increase in G_{Ic} of final PMMA printed composites. Figure 3 shows the G_{Ic} comparison of specimens with different concentrations of PMMA addition using the same printing pattern and pattern density. It can be clearly seen that specimens with printed PMMA possessed higher G_{Ic} at their respective non-linear (NL) point, 5%/MAX point and the propagation G_{Ic} on the corresponding propagation (PROP) points, especially, specimens with 10 wt.% PMMA showed the highest improvement compared to the other systems. For an exact illustration of NL, 5%/MAX and PROP points in Figure 3, please refer to the DCB test standard adopted in this work.

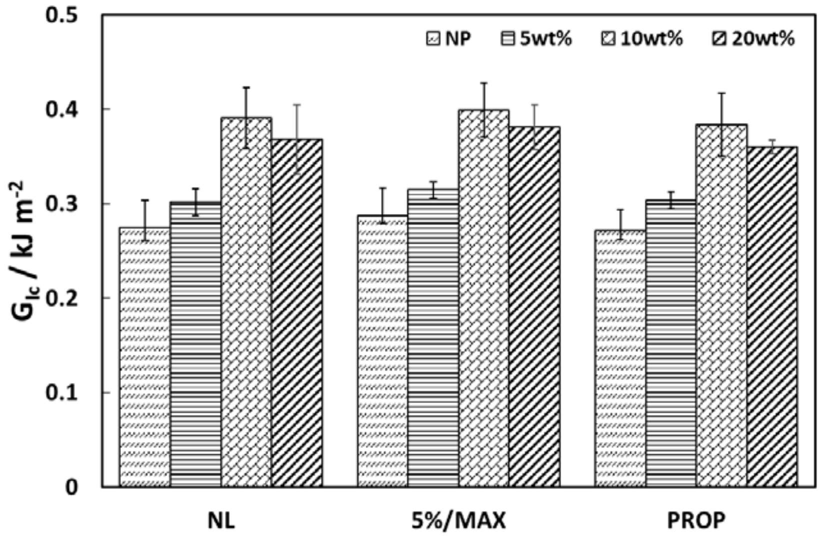

Figure 3. G_{Ic} comparison of different PMMA concentrations in printing inks, deposited between CFRP unidirectional plies.

As shown in Figure 1, dx and dy can be varied to determine the pattern density deposited on a substrate. Figure 4 shows the effect of printing pattern densities on G_{Ic} in printed laminated composites. The specimens with dx/dy = 0.4/0.2 mm as the printing pattern density exhibited higher G_{Ic} than that of dx/dy = 0.7/0.35 mm specimens as expected. Higher pattern density means more PMMA was deposited onto that specific region where the cracks are expected to propagate, requiring more energy to fracture numerous discrete PMMA zones.

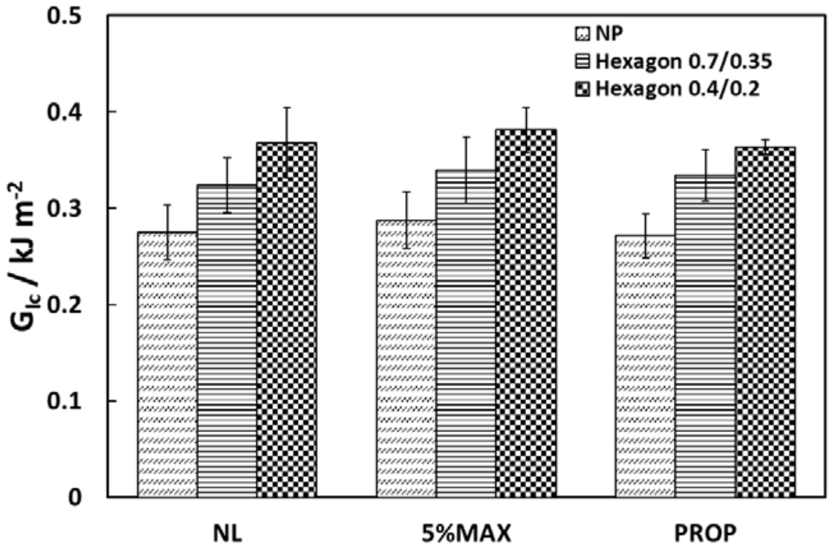

Figure 4. G_{Ic} comparison of different printed pattern densities (hexagon dx/dy).

Since applying an interleave to enhance the interlaminar fracture toughness has proved a successful method to toughen composite laminates, and has been adopted in industry, it is worthwhile to investigate the difference between the systems with discretely deposited microscopic patterns, and that with the fully printed surface. Hereby printing 10 wt.% and 20 wt.% of PMMA inks as a thin film between the plies was carried out to investigate the effect of PMMA surface deposition. As shown in Figure 5, when a continuous thin film instead of a discrete dot-pattern was printed between plies, the increased PMMA concentration led to the increase in G_{Ic}. Comparing the two systems by the volume fraction of the deposited PMMA, 10 wt.% film deposition should be equivalent to 20 wt.% discrete pattern deposition; however, the ratio is closer to 1.8 due to overlapping during film printing using inkjet technique. The results showed that 20 wt.% PMMA concentration in printed patterns provided better resistance to crack propagation than its 10 wt.% film counterpart, and improved the predictability of the results in these typically rigid systems. The results provided the evidence to support discrete dots printing pattern to improve the mechanical properties of CFRP laminates.

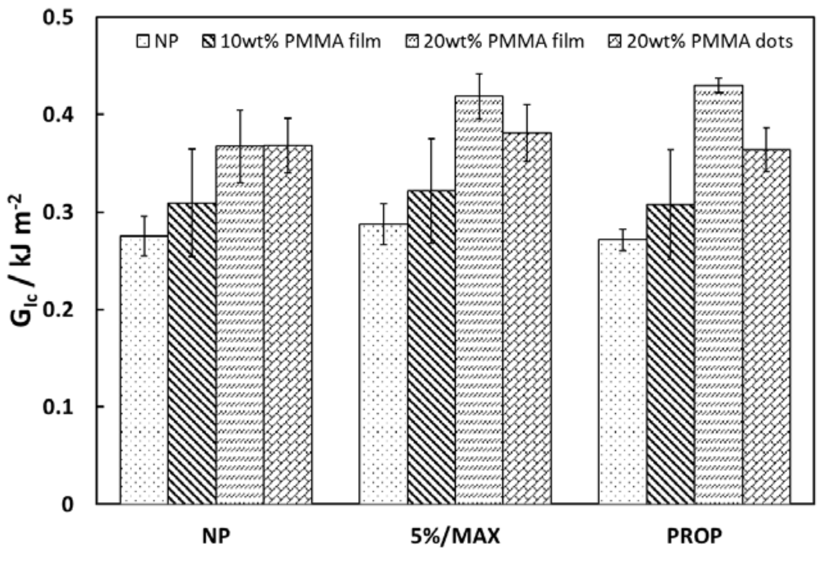

Figure 5. G_{Ic} comparison of specimens with printed thin film and discrete dots pattern.

3.2 X-ray tomography

Since DCB Mode I results showed that PMMA imparted a good toughening efficiency in CFRP laminates, it was deemed important to investigate whether this thermoplastic material offered other benefits to composite structures. X-ray tomography was used to investigate the damage tolerance of inkjet-printed laminates after impact test. Figure 6 shows the non-printed laminates having visible micro-cracks after impact with only 1 J impact energy, however, laminates with 20 wt.% PMMA addition did not show any micro-cracks after the same impact test. This promising result indicated that inkjet printing of PMMA into CFRP laminates is a suitable method to generate a more durable material in service, especially in load bearing structures where high damage tolerance capability is needed such as holes, joints and impact-prone regions.

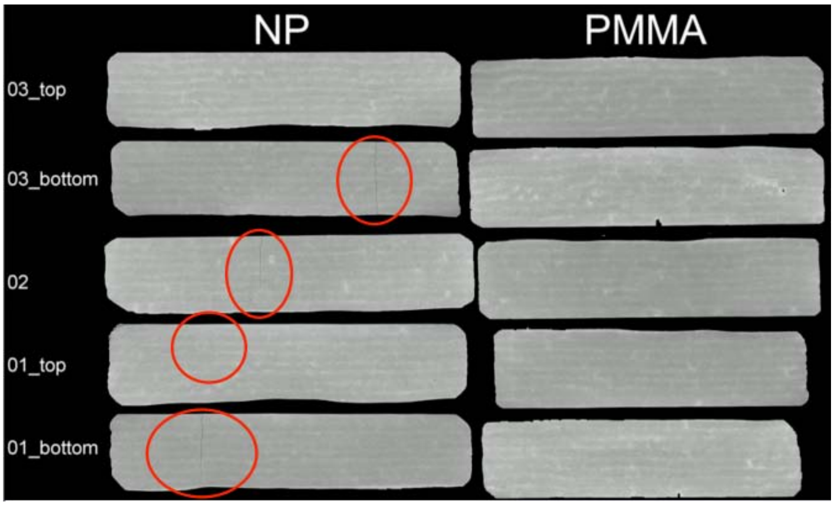

Figure 6. X-ray tomography of impacted laminates showing hairline cracks occurring after only 1J impact force in aerospace grade composites (non-printed), whereas discretely printed composite (on the right) retained the structural integrity, without added weight. Each section is approximately 10 mm wide.

4. Conclusions

Based on our previous demonstration of the unique advantages of applying inkjet printing to improve interlaminar fracture toughness of CFRP laminates, we have elaborated the influence of ink concentration and printing density on G_{Ic} of the corresponding laminates. It was reported that PMMA concentration 10-20 wt.% provided the optimal effect in CFRP, by imparting the highest G_{Ic} values. Also, with a hexagonal printing pattern, a higher printing density generally resulted in a proportionally increased G_{Ic}. Moreover, further x-ray tomographical study revealed a better impact resistance due to PMMA dot deposits between the CFRP plies. This study presented the experimental evidence to support the use of discrete inkjet printing in toughening of CFRP laminates. Most importantly, the improvements to the aerospace accredited CFRP systems were achieved without imparting any parasitic weight. Future work will focus on investigation of an accurate crack arrest mechanism leading to improved engineering prediction in these systems.

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