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# Fabrication of patterned thermoplastic microphases between composite plies by inkjet printing

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## Abstract

We report on the pioneering application of inkjet printing in depositing patterned thermoplastic microphases between composite plies, and the beneficial effect of the printed thermoplastic on the interlaminar fracture toughness ~~and shear modulus~~ of carbon fibre reinforced polymer (CFRP) laminates. Double cantilever beam (DCB) test and short beam shear (SBS) test were employed to investigate the mechanical performances of the engineered composites. The results from this work revealed that by printing thermoplastic poly(ethylene glycol) (PEG) and poly(methyl methacrylate) (PMMA) between the CFRP plies, mode I interlaminar fracture toughness ( $G_{Ic}$ ) is noticeably enhanced. ~~Furthermore, the toughening process had a beneficial influence on the interlaminar shear modulus~~, whilst the shear strength has also been preserved. Scanning electron microscopy (SEM) was used to investigate the fracture surfaces generated during the DCB test. The microscopic addition of the thermoplastic polymers (approximately 0.015 wt.%) did not increase the weight of the composites significantly, which compares favourably to other conventional toughening methods.

## Keywords

Inkjet printing, composites, toughness, polymers, patterning

## Introduction

Composites have become increasingly important to mechanical, aeronautical, electrical and architectural engineering applications on account of their light weight, high specific stiffness and strength.<sup>1</sup> In advanced CFRP composites, carbon fibres are embedded in the composite to improve their mechanical properties such as strength and stiffness-to-weight ratio.<sup>2</sup> However, the less beneficial aspects involve their relatively poor performance under impact and fracture, especially in through-thickness and interlaminar directions.<sup>3-5</sup> Delamination is one of the critical damage propagation modes in advanced composite laminates, where the interlaminar fracture toughness plays a prominent role in controlling delamination growth.<sup>6,7</sup> Therefore, a significant increase in the interlaminar fracture toughness of advanced composite laminates can be a potential route towards

designing and manufacturing more durable composites with an extended lifetime.

Numerous types of interlaminar laminated CFRPs with different interlaminar toughening mechanisms have been reported to date. Arai et al.<sup>8</sup> used carbon nanofibre as an interlaminar toughener and successfully increased the  $G_{Ic}$  and mode II interlaminar fracture toughness ( $G_{IIc}$ ) by 50% and 300% respectively, compared to the base laminates. In terms of the method of their addition to the interlayer, Arai et al. manually applied the toughener onto CFRP prepregs using a metal roller. Similar work has been reported by White et al.<sup>6</sup> where a carbon nanotube/polyamide-12 epoxy thin film was used as a toughening layer. An increase in  $G_{IIc}$  values nearly 2.5 times higher compared to the virgin CFRP was reported. Hojo et al.<sup>9</sup> used the epoxy matrix as the interleaf material by sequentially laying up half-cured epoxy films and prepregs. It was reported that the  $G_{Ic}$  values of the laminates with the self-same epoxy interleaves were almost identical to those of the base laminates. However, the initial values and the propagation values of  $G_{IIc}$  in the laminates with interleaves were 1.6 times and 3.4 times higher than those of the base CFRPs respectively. Hamer et al.<sup>10</sup> demonstrated a three-fold improvement in  $G_{Ic}$  values compared to the base laminates using an electro-spun Nylon-6,6 nano-fibrous mat as the interlaminar toughener. Although these methods improved the interlaminar fracture toughness to a greater or lesser extent, the continuous film inserted between the plies interfered with the chemical adhesion within the interlaminar region that is critical to the mechanical properties and the design criteria in the composite components.<sup>6</sup>

Inkjet printing has been extensively explored as a manufacturing technique over the last two decades due to its ability to precisely print pico-litre droplets according to predefined patterns without masks. The direct write ability of inkjet printing makes it an attractive method for many areas such as printed electronics,<sup>11-14</sup> tissue engineered scaffolds,<sup>15,16</sup> cell seeding,<sup>17,18</sup> and protein printing.<sup>19,20</sup> As inkjet printing is a non-contact process, contamination is reduced; also inkjet's convenient fabrication procedures and minimum waste generation are advantages over conventional fabrication methods. The main consideration for using inkjet printing is in the physical and rheological properties of inks which are composed of either solutions or suspensions.<sup>20</sup> Viscosity and surface tension are the most important factors which determine the printability of inks,<sup>21,22</sup> since an ink cannot be printed if it is too viscous (typically, viscosity must be less than 20 mPa s).

This study reports on the use of inkjet printing to deposit thermoplastic microphases in pre-determined patterns between composite plies prior to the curing cycle with the aim of enhancing the structural performance of the composite without incurring any significant parasitic weight. A research grade inkjet printer was used to place discrete dots of polymer onto the surface of carbon fibre reinforced epoxy prepregs. The interface between the plies is likely to be the main source of micro-cracks<sup>23</sup> hence this strategic deposition imparts multifunctional properties whilst enhancing its structural integrity in service. The addition of the microphases contributed to improved  $G_{Ic}$  without sacrificing the interlaminar shear strength of composite laminates. By using inkjet printing, it is possible to vary the printed pattern easily. Moreover, the overall usage of the printed material is low, which not only reduces the cost but, more importantly, leads to a minimal weight increase of the final composite.

## Experimental

### *Ink preparation and properties*

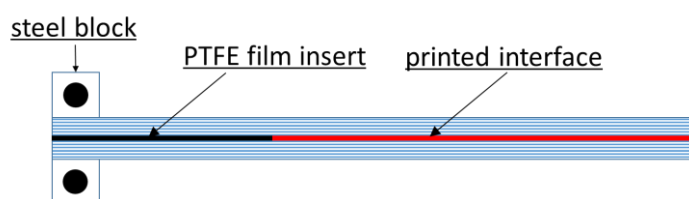
Two standard polymers were dissolved into appropriate solvents to make inks for printing. Poly(methyl methacrylate) (PMMA) was dissolved in N, N-dimethylformamide (DMF) at room temperature, whereas poly(ethylene glycol) (PEG) was dissolved in pure ethanol at 50°C. All chemicals were purchased from Sigma Aldrich (Sigma-Aldrich Co. Ltd., UK) and used as received. Viscosity and surface tension of PMMA ink were measured at room temperature using an A&D sine-wave vibro viscometer (European Instruments, UK) and a KRÜSS K11 tensiometer (KRÜSS GmbH, Germany). Since PEG ink is in a gelled solid state at room temperature, surface tension and viscosity data are not available. Table 1 shows some physical parameters of inks used in this work.

**Table 1.** A summary of the inks used in this study.

Ink name	Component solute/solvent	Mn/kDa	wt%	Surface tension /mN m <sup>-1</sup>	Viscosity /mPa.s
PMMA	PMMA/DMF	15	5	37	1.30
PEG	PEG/Ethanol	20	5	-	-

### *Mechanical tests*

Two [ISO standards](#)<sup>24,25</sup> were adopted to investigate the mechanical properties of composite laminates. Double cantilever beam test (DCB) and short beam shear test (SBS) were used to evaluate mode I interlaminar fracture toughness ( $G_{Ic}$ ) and apparent interlaminar shear strength respectively. [The speed of cross head of DCB and SBS tests were 5 mm/min and 1 mm/min respectively.](#) Figure 1 shows the sample configuration used for DCB Mode I test, where a polytetrafluoroethylene (PTFE) film was placed inside the laminate's mid-thickness during lay-up to simulate a crack. Table 2 shows the dimensions of both DCB and SBS test samples.



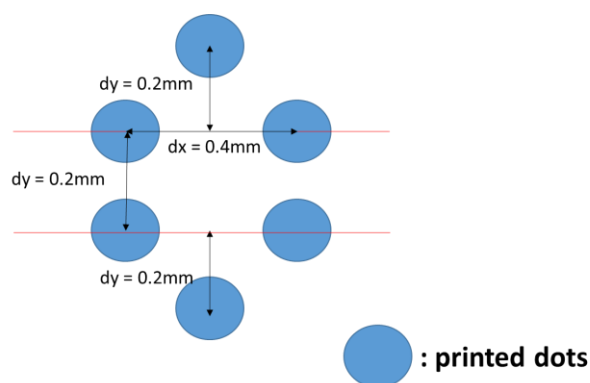
**Figure 1.** Schematic showing DCB test sample.

**Table 2.** Dimensions of DCB and SBS test samples.

Test	Length/mm	Width/mm	Thickness/mm
DCB	140±1	20±0.5	3±0.1
SBS	20±1	10±0.2	2±0.2

### *Printing and sample preparation*

PMMA ink was printed at room temperature using a drop-on-demand (DOD) JetLab 4xl printer equipped with a compatible MicroJet printhead, whereas the PEG ink was printed at 50°C using the same printing platform with a PolymerJet printhead. The diameter of printhead orifice used for all printing work was 60  $\mu\text{m}$ . All printing devices were purchased from MicroFab Inc. (Plano, TX, USA). The substrate used was CFRP pre-preg (Cycom 977-2, Cytac Industries Inc., USA). A hexagonal pattern which can cover an area with lowest material usage was chosen for printing as shown in Figure 2. Although the dot spacings,  $dx$  and  $dy$  can be changed to vary the density of pattern to be printed, those variations are not reported in this study; only the pattern shown in Figure 2 was printed for this work.



**Figure 2.** Hexagonal pattern of inkjet-printed dots.

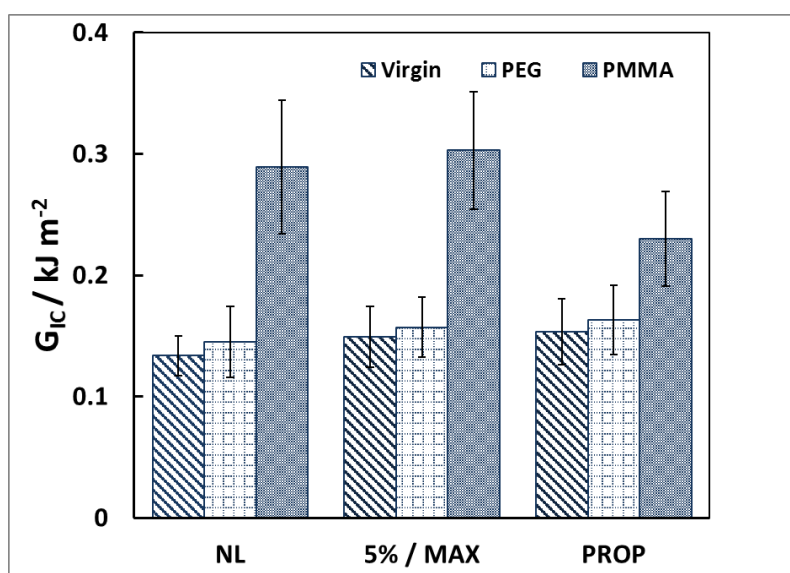
Prepregs were subsequently zero-degree unidirectionally laid-up after printing, then cured using an autoclave (Premier Autoclaves Ltd., UK). The curing cycles used refers to previous work.<sup>27</sup> Twelve and eight layers of prepregs were used for the DCB and SBS tests, respectively, in accordance with the requirement for sample thickness of the test standards. Test samples for both tests were cut from their original cured laminates. In order to investigate whether the inkjet-printed polymer has any effect on non-damaged and damaged samples before and after heat treatment, two groups of SBS samples [including non-damaged and damaged](#) were heated to 177°C for two hours as the harshest case scenario. Damaged samples were prepared by introducing barely visible impact damage (BVID) with a tensometer.

## **Results and Discussion**

### *Mechanical tests and fractographic analysis*

Figure 3 shows the  $G_{Ic}$  values of all three testing groups at their respective non-linear (NL) point and 5%/Maximum Load (Max) point, as well as the  $G_{Ic}$  values averaged on the corresponding propagation value (PROP) points. For an exact illustration of these three parameters in Figure 3 (NL, 5%/Max and PROP), please refer to the DCB test standard<sup>25</sup> adopted in this work. It can be seen that relative to the

original CFRP (Virgin) case, the inclusion of PMMA ink droplets remarkably enhanced the  $G_{IC}$  values on NL point, 5%/Max point and PROP points, whilst PEG ink droplets yielded a slightly higher  $G_{IC}$  than the Virgin sample. It is reasonable to conclude that the inkjet-printing of both PEG and PMMA inks has improved the mechanical performance of a composite laminate during the crack initiation and propagation.



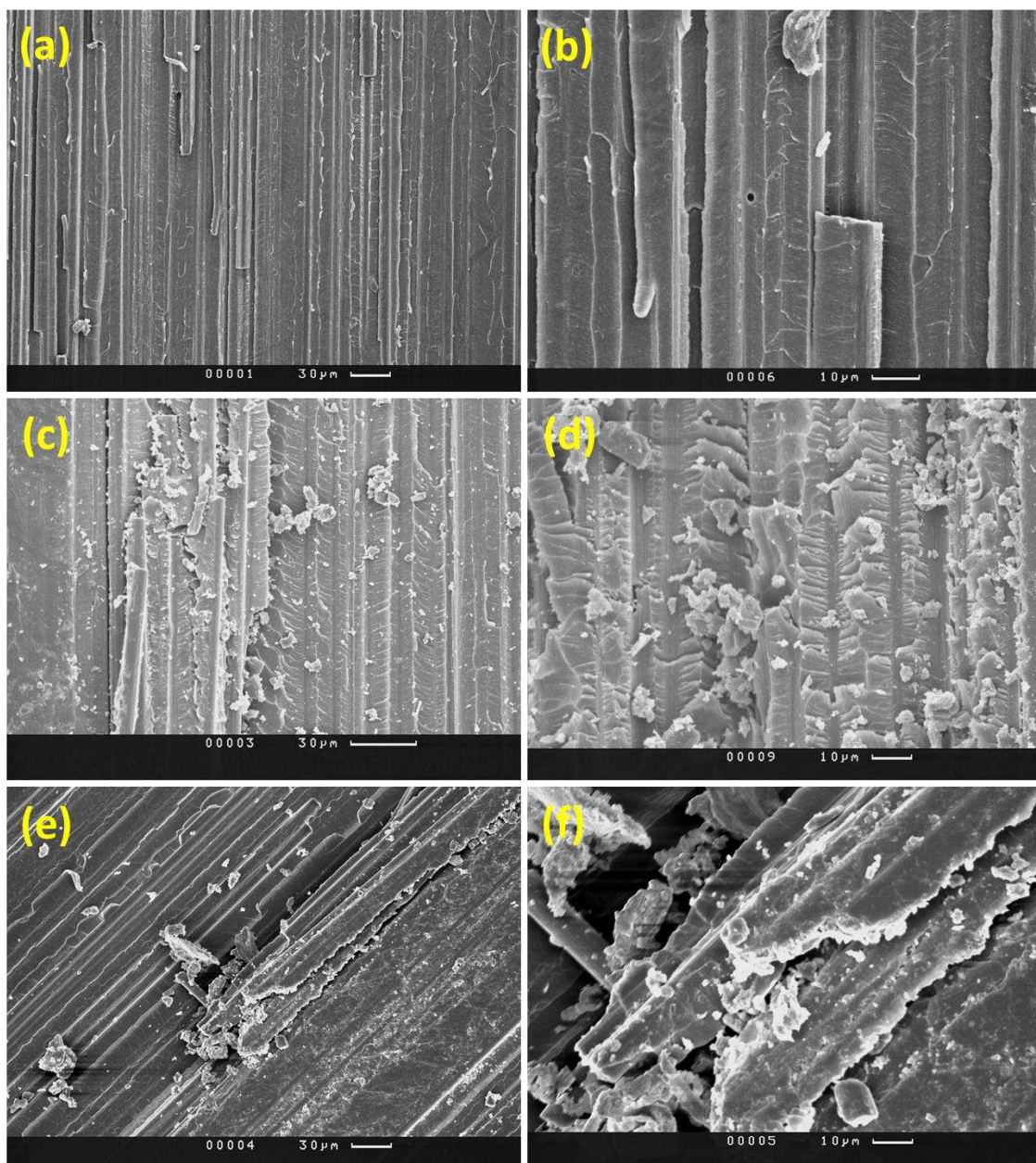
**Figure 3.**  $G_{IC}$  comparison between virgin and printed composite laminates.

The noticeable  $G_{IC}$  increase with the PMMA system may be partially obtained through the viscoelastic nature of the polymer. Herein, the microphases of inkjet-printed PMMA are well distributed throughout the printed region. Due to its viscoelasticity, PMMA provides an energy absorption path by deformation, which could decelerate crack growth, thus enhancing the interlaminar fracture toughness. Another possible contribution to the remarkable  $G_{IC}$  of our PMMA printed CFRP system, for the sake of argument, could be that due to the limited compatibility of PMMA with the epoxy resin, the interface between these two phases is relatively weak, thus deflecting the crack path. In the PEG system, the relatively small increase of  $G_{IC}$  could be attributed to the good miscibility of PEG with the epoxy. It has been demonstrated that PEG shows a compatibility with the epoxy resin<sup>26</sup>. Hereby, we postulate that during the curing process, PEG has shallowly penetrated into the epoxy resin phases of the adjacent two plies of composite laminates, between which the PEG dots were printed. As a result, the printed interface may not have such a distinct area with additional discrete plastic zones as with the PMMA system. However, the part of epoxy matrix where PEG penetrated into was toughened. Since the amount of PEG addition was quite small, this toughening effect can be limited, leading to a small amount of  $G_{IC}$  increase.

Considering that the other mechanical properties were either enhanced or preserved through this method, the likely cause behind  $G_{IC}$  increases, as further evidenced, would be through both preservation of the adhesion between PMMA and the epoxy, and the inclusion of distinct printed zones that deflected the crack propagation in the laminates.<sup>27</sup>

SEM was used to analyse the fracture surfaces of printed CFRPs after DCB tests. As seen in Figure

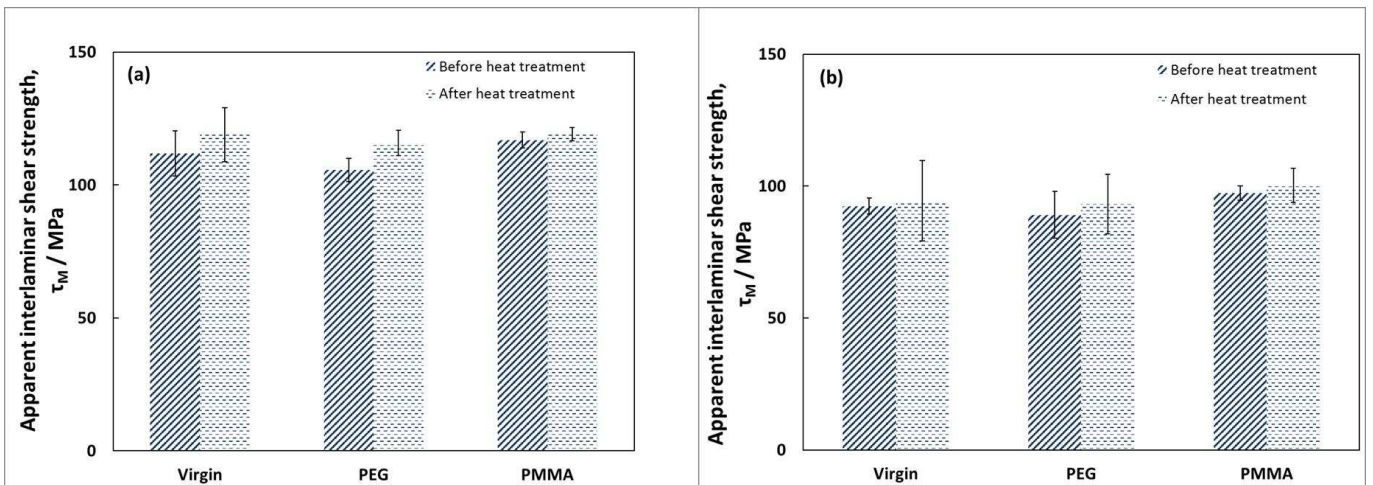
4(a) and 4(b), Virgin samples showed a relatively smooth and flat fracture surface. However, upon applying PEG as the ink, “hackles” appeared on the fractured surfaces (Figure 4(c) and 4(d)), which corresponds to the aforementioned explanation: toughened printed interfaces require more energy to delaminate, resulting in a more ductile failure. However, when PMMA droplets were printed between plies, crack path deflections and fibre debonding developed during DCB test (Figure 4(e) and 4(f)), implying that a considerable amount of energy has been absorbed during the crack development. Actually, the evidence of crack path deflection agrees well with our above postulation, that the inkjet-printed discrete dots of viscoelastic PMMA may guide crack growth, with the crack most likely taking place at the interface between PMMA and the epoxy/fibre.



**Figure 4.** SEM images of fracture surfaces in DCB samples. Fractographs in (a) and (b) show fracture surfaces from the virgin samples; (c) and (d) fracture surfaces from the samples with addition of PEG; and (e) and (f)

fracture surfaces from the samples with addition of PMMA.

Interlaminar shear strength (ILSS,  $\tau_M$ ) is another critical mechanical property of advanced composite laminates. ~~Short beam shear~~<sup>SBS</sup> tests were conducted to investigate structural integrity in the systems investigated in this study. Figure 5 shows that the printed thermoplastic microphases are of no detriment to this property of laminates both before and after heat treatment both in non-damaged and damaged groups, the two groups. Previous work<sup>27</sup> has even shown an increase in interfacial shear modulus by using discrete patterning of thermoplastic microphases by inkjet printing. The heat treatment was conducted to evaluate the self-repair or self-healing potential of these systems, due to the recovery of the reheated thermoplastic printed inclusions. However, more investigations need to be done in the future to confirm the mechanism.



**Figure 5.** The interlaminar shear strength comparison before and after heat treatment. (a) Samples without damage (to evaluate the ‘placebo’ effect due to postcured cross-linking) and (b) samples with damage initiated using the standard short beam shear test.

### Calculation of volume fraction and surface coverage

In the design of lightweight aircraft structures, component weight is a decisive parameter. More specifically, the overall weight of the final composite is of great importance. One advantage of using inkjet printing is its efficient material usage. Assuming the generated droplets are perfect spheres, and the diameter is the same as the printhead used to dispense the droplets, the volume of one single droplet is  $1.13 \times 10^{-13} \text{ m}^3$ . The volume fraction can be calculated using Equation (1):

$$\eta_V = \frac{V_{Printed}}{V_{Spec}} \times 100\% \quad (1)$$

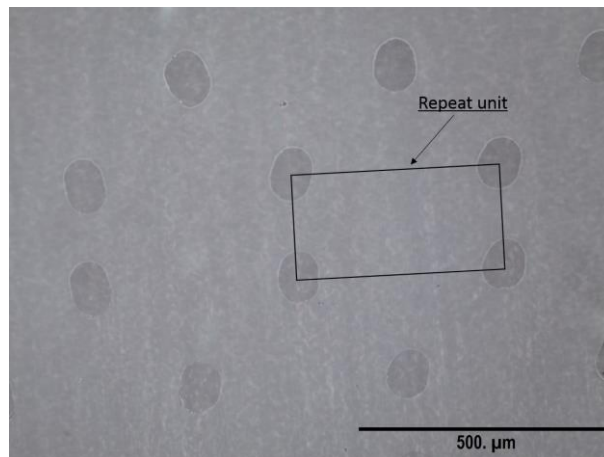
Where  $\eta_V$  is the volume fraction,  $V_{Printed}$  is the volume of printed material in one specimen, and  $V_{Spec}$  is the volume of one specimen. According to Equation (1) and considering the drop spacing of pattern that was used in this work ( $dx = 0.4 \text{ mm}$ ,  $dy = 0.2 \text{ mm}$ ), the volume fraction of additional material is calculated as approximately 0.025 vol.%. which This volume fraction of additional material is considerably lower than any of the aforementioned meanings of introducing additional toughening in composite laminates, which ranges from 1.2~6.1 vol.%, and which were discussed briefly in the

~~Introduction. conventional method currently used to toughen composite laminates.~~

In terms of surface coverage, Figure 6 is an image of printed PEG droplets on prepreg in a hexagonal pattern. The corners of the rectangle are made up of the sectors of each deposited droplet.

$$\eta_s = \frac{S_{\text{printed}}}{S_{\text{unit}}} \times 100\% \quad (2)$$

Where  $\eta_s$  is the surface coverage ratio,  $S_{\text{Printed}}$  is the printed area in one specimen and  $S_{\text{unit}}$  is the printed area of one repeat unit. With a deposit diameter of 98  $\mu\text{m}$ , Equation (2) yields a surface coverage of about 10%.



**Figure 6.** PEG ink was printed on 977-2 prepreg with a hexagonal pattern.

As mentioned earlier, the drop spacing  $dx$  and  $dy$  can be varied. Obviously,  $dx$  and  $dy$  affect the volume fraction and the surface coverage. Besides, droplets of inks with different wettability will spread onto the prepreg surface with different areas, which will affect the surface coverage. In this work, the deposit diameter of PMMA ink printed on prepreg is about 195  $\mu\text{m}$ , larger than that of PEG ink, thus the surface coverage is about 37%. Therefore, we printed an area with a minimum amount of material between composites plies to achieve efficient interlaminar fracture toughening, while preserving and even enhancing the structural properties.

## Conclusion

In summary, by employing the inkjet-printing technique to precisely deposit microscopically patterned droplets of thermoplastic PEG and PMMA onto CFRP prepreps, we have noticeably enhanced  $G_{Ic}$  while preserved the interlaminar shear strength of the resulting CFRP laminates. ~~Moreover, we found that our approach increased  $G_{Ic}$  values without detriment to, and in some cases noticeable benefit to, the interlaminar shear modulus.~~ As additional volume increase (or parasitic weight) is an important consideration in the lightweight aerospace structures, our method achieved a significant improvement in damage tolerance with minimum material addition of only 0.025 vol.%/0.015 wt.%, significantly lower than the allowable manufacturing variability margin of 0.4%. Hence, the new resulting system has shown a significant improvement in two important design parameters,  $G_{Ic}$  and the interlaminar shear modulus, without sacrificing any other aspect of the material's performance, including weight.

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