Article:

Zhang, Y., Stringer, J., Grainger, R. et al. (2 more authors) (2015) Fabrication of patterned thermoplastic microphases between composite plies by inkjet printing. Journal of Composite Materials, 49 (15). pp. 1907-1913. ISSN 0021-9983

https://doi.org/10.1177/0021998314533715

Fabrication of patterned thermoplastic microphases between composite plies by inkjet printing

Yi Zhang[1], Jonathan Stringer[1], Richard Grainger[2], Patrick J Smith[1] and Alma Hodzic[1]

[1] Composite Systems Innovation Centre, Department of Mechanical Engineering, The University of Sheffield, UK

[2]Advanced Manufacturing Research Centre with Boeing, The University of Sheffield, UK

Corresponding author: Patrick J Smith
Composite Systems Innovation Centre, Department of Mechanical Engineering, The University of Sheffield, Sheffield S1 3JD, UK.
Email: patrick.smith@sheffield.ac.uk

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.[1] In advanced CFRP composites, carbon fibres are embedded in the composite to improve their mechanical properties such as strength and stiffness-to-weight ratio.[2] However, the less beneficial aspects involve their relatively poor performance under impact and fracture, especially in through-thickness and interlaminar directions.[3-5] 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.[6,7] 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.[8] 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.[6] 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.[9] 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.[10] 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.[6]

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,[11-14] tissue engineered scaffolds,[15,16] cell seeding,[17,18] and protein printing.[19,20] 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.[20] Viscosity and surface tension are the most important factors which determine the printability of inks,[21,22] 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[23] 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^{-1}	Viscosity /mPa.s
PMMA	PMMA/DMF	15	5	37	1.30
PEG	PEG/Ethanol	20	5	-	-

Mechanical tests

Two ISO standards[24,25] 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.

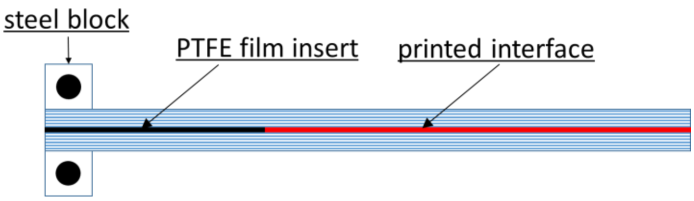

Figure 1. Schematic showing DCB test sample.

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 µm. All printing devices were purchased from MicroFab Inc. (Plano, TX, USA). The substrate used was CFRP pre-preg (Cycom 977-2, Cytec 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.

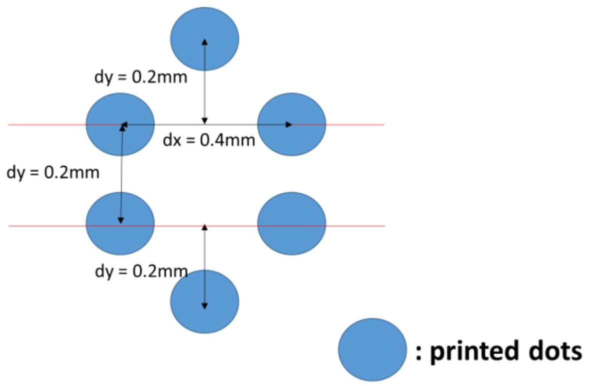

Figure 2. Hexagonal pattern of inkjet-printed dots.

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.[27] 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[25] 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.

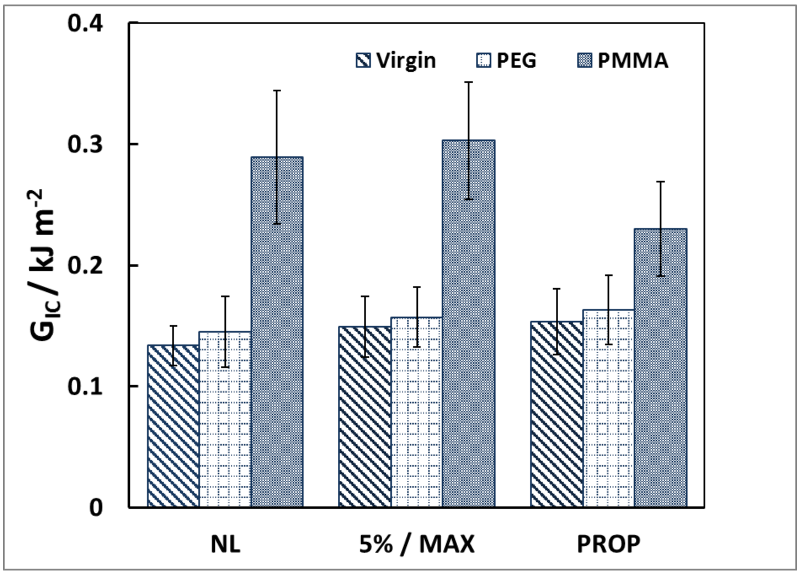

Figure 3. G_{Ic} comparison between virgin and printed composite laminates.

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[26]. 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.[27]

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.

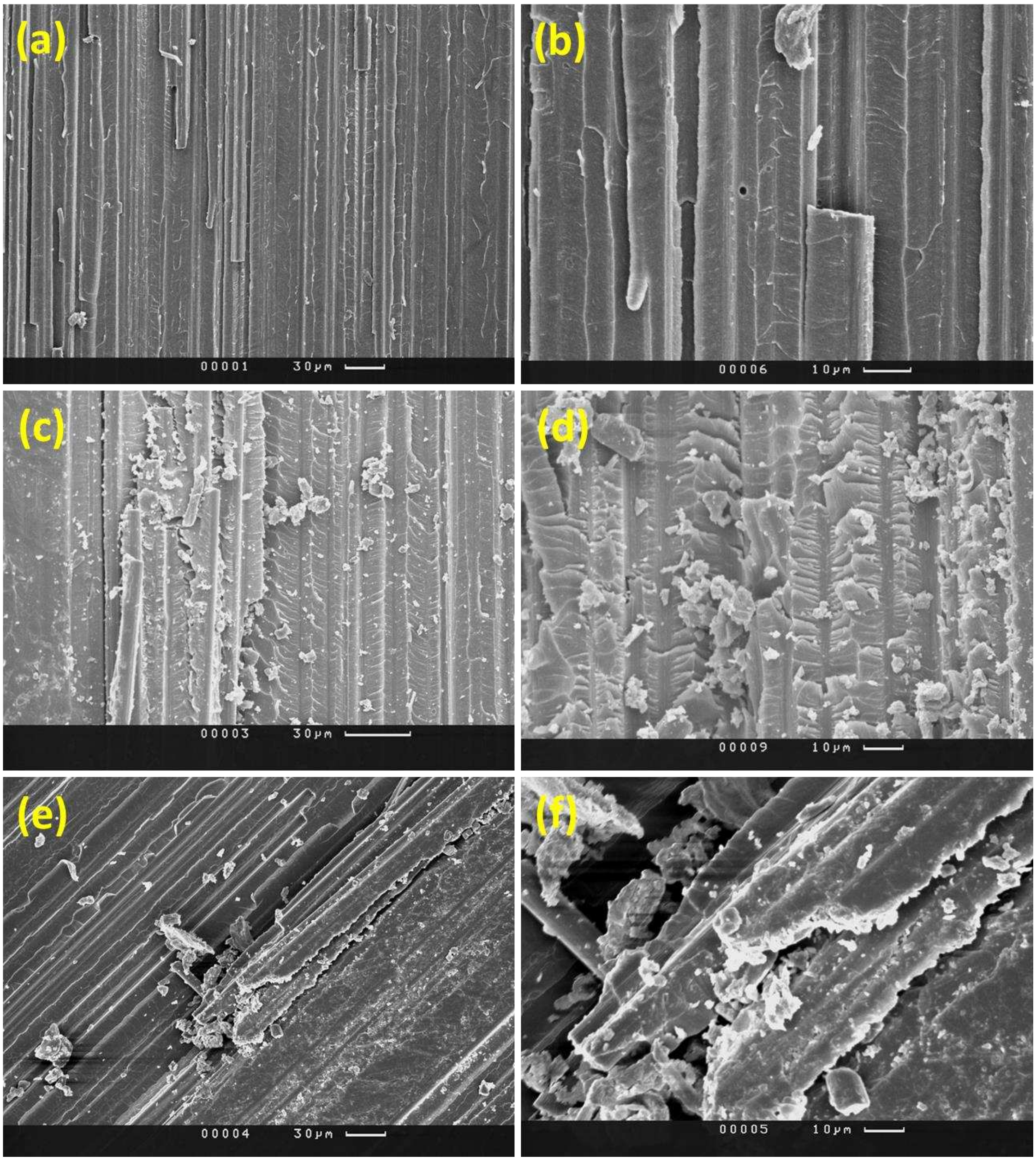

Figure 4. SEM images of fracture surfaces in DCB samples. Fractographs in (a) and (b) show fracture surfaces from the virgin samples; (c) and (d) fracture surfaces from the samples with addition of PEG; and (e) and (f)

fracture surfaces from the samples with addition of PMMA.

Interlaminar shear strength (ILSS, τ_M) is another critical mechanical property of advanced composite laminates. ~~Short beam shear~~SBS 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[27] 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.

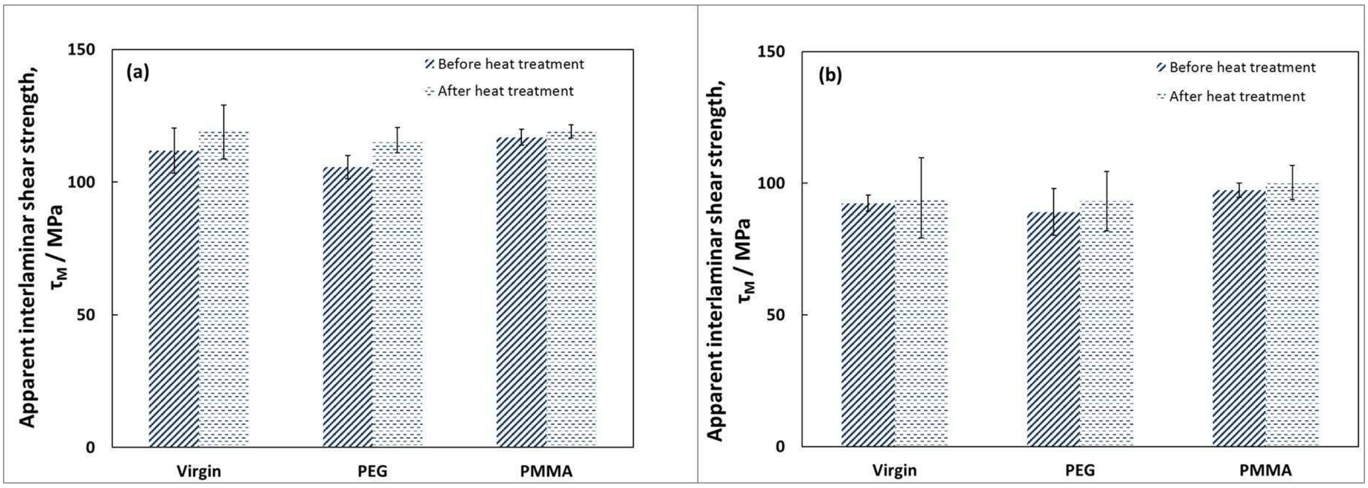

Figure 5. The interlaminar shear strength comparison before and after heat treatment. (a) Samples without damage (to evaluate the 'placebo' effect due to postcured cross-linking) and (b) samples with damage initiated using the standard short beam shear test.

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 1.13×10^{-13}m^3. The volume fraction can be calculated using Equation (1):

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

Where η_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 mm, dy = 0.2 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 mean~~ing~~s of introducing additional toughening in composite laminates, which range~~s~~ 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.

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

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

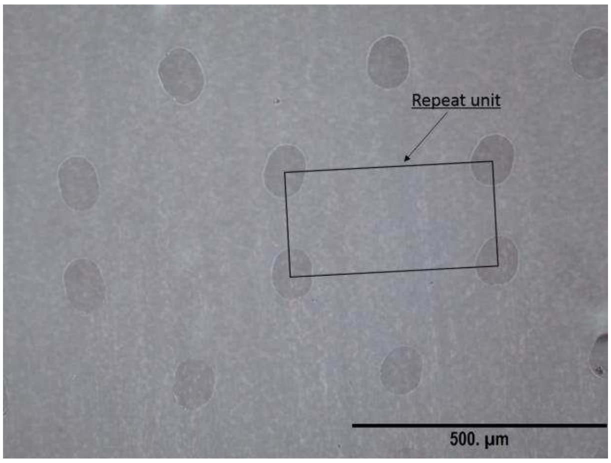

Figure 6. PEG ink was printed on 977-2 prepreg with a hexagonal pattern.

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 μm, 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 prepregs, 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.

Acknowledgements
The research reported in this manuscript was sponsored by the Air Force Office of Scientific Research, Air Force Material Command, USAF, under grant number FA8655-11-1-3072. The U.S. Government is authorised to reproduce and distribute reprints for Governmental purpose notwithstanding any copyright notation thereon. 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. The authors also wish to thank the Department of Mechanical Engineering, University of Sheffield for financial support connected to the inkjet printer.

References
1. Wang WX, Nakata M, Takao Y, et al. Experimental investigation on test methods for mode II interlaminar fracture testing of carbon fiber reinforced composites. *Compos Part A-Appl S* 2009; 40(9): 1447-55.
2. Morton J and Godwin EW. Impact response of tough carbon fibre composites. *Compos Struct* 1989; 13(1): 1-19.
3. Lee SH, Kim H, Hang S, et al. Interlaminar fracture toughness of composite laminates with CNT-enhanced nonwoven carbon tissue interleave. *Compos Sci Technol* 2012; 73(0): 1-8.
4. Sebaey TA, Blanco N, Costa J, et al. Characterization of crack propagation in mode I delamination of multidirectional CFRP laminates. *Compos Sci Technol* 2012; 72(11): 1251-6.
5. Cantwell WJ and Morton J. Detection of impact damage in CFRP laminates. *Compos Struct* 1985; 3(3–4): 241-57.
6. White KL and Sue HJ. Delamination toughness of fiber-reinforced composites containing a carbon nanotube/polyamide-12 epoxy thin film interlayer. *Polymer* 2012; 53(1): 37-42.
7. Masaki H, Shojiro O, Gustafson C-G, et al. Effect of matrix resin on delamination fatigue crack growth in CFRP laminates. *Eng Fract Mech* 1994; 49(1): 35-47.
8. Arai M, Noro Y, Sugimoto KI, et al. Mode I and mode II interlaminar fracture toughness of CFRP laminates toughened by carbon nanofiber interlayer. *Compos Sci Technol* 2008; 68(2): 516-25.
9. Hojo M, Ando T, Tanaka M, Adachi T, et al. Modes I and II interlaminar fracture toughness and fatigue delamination of CF/epoxy laminates with self-same epoxy interleaf. *Int J Fatigue* 2006; 28(10): 1154-65.
10. Hamer S, Leibovich H, Green A, et al. Mode I interlaminar fracture toughness of Nylon 66 nanofibrilmat interleaved carbon/epoxy laminates. *Polym Composite* 2011; 32(11): 1781-9.
11. Tekin E, Smith PJ, Hoeppener S, et al. Inkjet printing of luminescent CdTe nanocrystal-polymer composites. *Adv Funct Mater* 2007; 17(1): 23-8.
12. Sirringhaus H, Kawase T, Friend RH, et al. High-resolution inkjet printing of all-polymer transistor circuits. *Science* 2000; 290(5499): 2123-6.
13. Liu Y, Cui T and Varahramyan K. All-polymer capacitor fabricated with inkjet printing technique. *Solid State Electron* 2003; 47(9): 1543-8.
14. Perelaer J, Smith PJ, Mager D, et al. Printed electronics: the challenges involved in printing devices, interconnects, and contacts based on inorganic materials. *J Mater Chem* 2010; 20(39): 8446-53.
15. Mondrinos MJ, Dembzynski R, Lu L, et al. Porogen-based solid freeform fabrication of

polycaprolactone–calcium phosphate scaffolds for tissue engineering. *Biomaterials* 2006; 27(25): 4399-408.
16. Zhang Y, Tse C, Rouholamin D, et al. Scaffolds for tissue engineering produced by inkjet printing. *Cent Eur J Eng* 2012; 2(3): 325-35.
17. Saunders RE, Gough JE and Derby B. Delivery of human fibroblast cells by piezoelectric drop-on-demand inkjet printing. *Biomaterials* 2008; 29(2): 193-203.
18. Di Biase M, Saunders RE, Tirelli N, et al. Inkjet printing and cell seeding thermoreversible photocurable gel structures. *Soft Matter* 2011; 7(6): 2639-46.
19. Delaney JT, Smith PJ and Schubert US. Inkjet printing of proteins. *Soft Matter* 2009; 5(24): 4866-77.
20. Derby B. Bioprinting: Inkjet printing proteins and hybrid cell-containing materials and structures. *J Mater Chem* 2008; 18(47): 5717-21.
21. Dearden AL, Smith PJ, Shin DY, et al. A low curing temperature silver ink for use in ink-jet printing and subsequent production of conductive tracks. *Macromol Rapid Comm* 2005; 26(4): 315-8.
22. Van Den Berg AMJ, Smith PJ, Perelaer J, et al. Inkjet printing of polyurethane colloidal suspensions. *Soft Matter* 2007; 3(2): 238-43.
23. Carlsson LA. Fracture of laminated composites with interleaves. *Key Eng Mat* 1996; 120: 489-520.
24. ISO 14130:1998. Fibre-reinforced plastic composites-Determination of apparent interlaminar shear strength by short-beam method.
25. ISO 27799:2001. Fibre-reinforced plastic composites-Determination of mode I interlaminar fracture toughness.
26. Huang YP and Woo EM. Effects of entrapment on spherulite morphology and growth kinetics in poly(ethylene oxide)/epoxy networks. *Polymer* 2001; 42(15): 6493-502.
27. Zhang Y, Stringer J, Grainger R, et al. Improvements in carbon fibre reinforced composites by inkjet printing of thermoplastic polymer patterns *Phys Status Solidi-R* 2014; 8(1): 56–60.