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Reviewed Paper

Additive Manufacturing of Carbon Fiber and Graphene – Polymer Composites using the technique of Fused Deposition Modelling.

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Abstract

Adding micro or nano-carbon reinforcements to polymers enhances their mechanical and electrical properties. In this paper, the effects of the addition of short carbon fibres (SCF) and graphene into acrylonitrile butadiene styrene (ABS) and polylactic acid (PLA) polymer to create composite filaments for fused deposition modelling (FDM) are investigated. After creating carbon polymer composite filaments, using a commercial 3D printer, samples were printed and tested for mechanical and electrical properties. The measured values for these composites were compared to those obtained for pure ABS and pure PLA. It was found that by using only 2% SCF it was possible to achieve a 22% increase in tensile strength with no significant impact on printability. With addition of graphene, PLA was made to be conductive. These results show the feasibility of developing new materials for 3D printing that will create structurally sound and conductive designs.

Introduction

Additive manufacturing processes have the potential to alter the engineering landscape. The untapped resource of carbon polymer composite printing has the ability to create lightweight components of high strength, taking advantage of the repeatability and intricacy of additive manufacturing. It is also possible to use these materials to create electrical components due to the electrical properties of some carbon polymer composites.

The carbon structures used throughout this investigation were graphene and short carbon fibres. Graphene is an incredibly strong material with a tensile strength of 130000 MPa (Potts et al. 2011) over 70 times greater than that of steel. It is composed of a single layer of carbon atoms formed inside a honeycomb lattice (Akhaven. 2009). Graphene also provides a high conductivity, measured up to 3500S/m in stacked graphene oxide (Potts et al. 2011). Carbon fibre is currently used widely in applications demanding high strength and low weight, such as aerospace, high performance marine, automotive and sporting equipment (Fu et al. 2000). Composed of interlocking sheets of graphite (MIT, 2015), it has a tensile strength greater than 3GPa (Chen et al. 2004), and low electrical resistivity of 10^{-2}-10^{-3} Ωcm (Chen et al. 2004).

It is well known that the addition of a small amount of carbon nanostructures within a polymer matrix can lead to enhanced material properties. Kuilla et al. (2010) find that by adding 0.1% by weight of graphene to an epoxy matrix improved flexural strength by 87%. Similarly, addition of 0.1% by volume of graphene sheets to a polystyrene matrix increased electrical conductivity by a factor of 4 x 10^{14}. Cong et al. (2015) found a 21% increase in ultimate tensile stress with the addition of 7.5% short carbon fibers in an ABS polymer matrix. In this work these carbon polymer composites with enhanced material properties were combined with the 3D printing process. This was done to examine the extent to which these material properties were conserved through the 3D printing process and the viability of this production technique.

Experimental Techniques

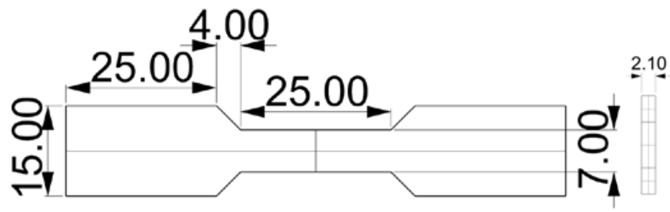

Figure 1- Schematic of specimens (dimensions in mm)

The investigation involved analysis of structural and electrical properties of 3D printed carbon polymer composite components. To achieve this, short carbon fibres of 212µm were mixed with commercially available ABS pellets in a single screw Filabot filament extruder in specified ratios. These filaments were then extruded at approximately 178^{o}C and printed into tensile test coupons. The 3D printer used was a commercially available Leapfrog 3D Creatr. The printing parameters used were a print temperature of 230^{o}C with a bed temperature of 80 ^{o}C. Test coupons were then analysed for conductivity using a high accuracy ohm meter and in tension until failure using a MTS Criterion loading frame. Pure ABS, 1wt% SCF/ABS, 2wt% SCF/ABS, PLA and PLA/Graphene coupons were subject to this test regime. The PLA/Graphene filament was sourced from Black Magic 3D (2015).

Results

The tests show that it is possible to use the enhanced properties of carbon polymer composites in the 3D printing process. Figure 2 shows the stress strain curve of ABS printed samples against the curves of 1wt% and 2wt% SCF composite printed samples. Table 1 compiles these results showing that a strength increase of 22% was observed with only 2wt% addition of SCF to the polymer matrix. Whilst this increase in tensile strength is significant, Figure 2 also shows that whilst ABS exhibits plastic yielding, the SCF composite specimens do not behave in the same manner and their ductility is reduced.

Figure 3 shows the stress strain interaction of the PLA samples against those containing PLA/Graphene. It can be seen that despite the superior properties of graphene, the printed samples do not display the enhanced material properties, with these samples having a 54% lower tensile strength. Similar to the SCF composite samples, the specimens exhibit brittle failure characteristics.

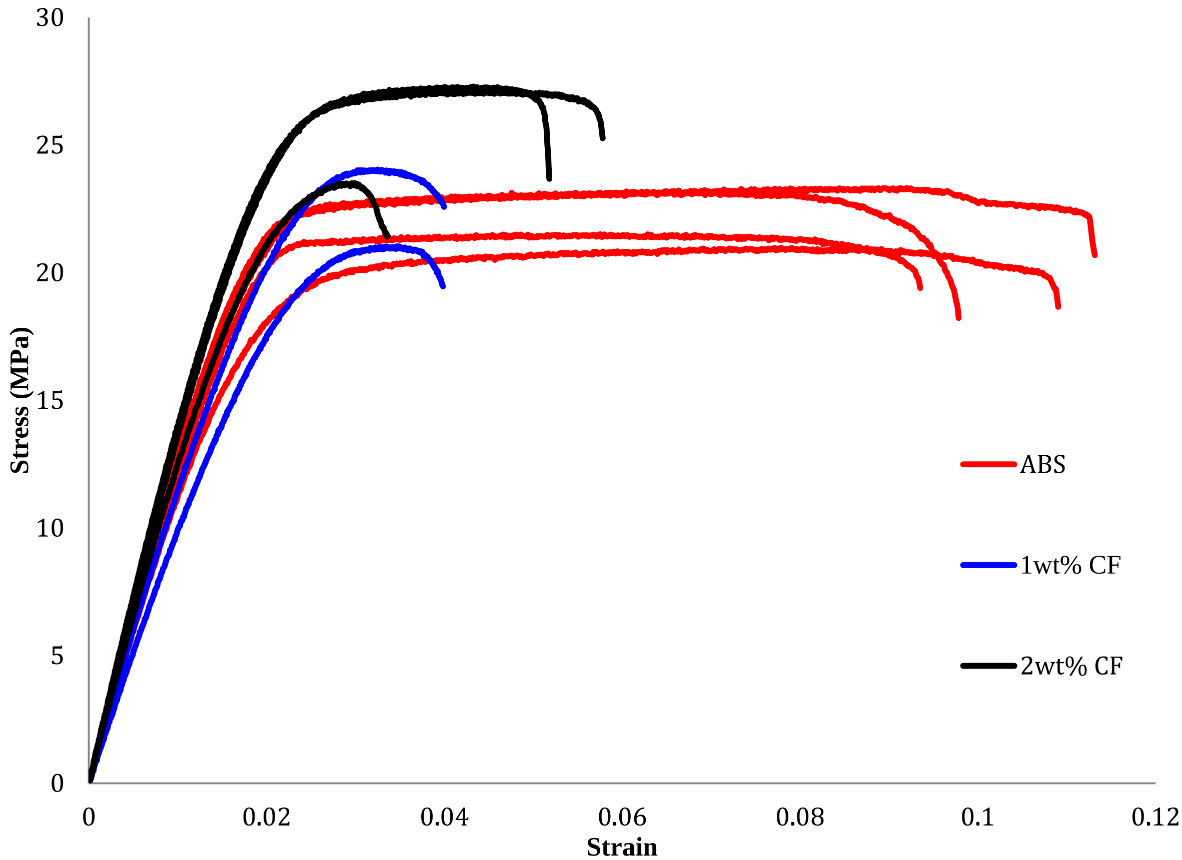

Figure 2 – Stress strain response of ABS and ABS/SCF composite specimens

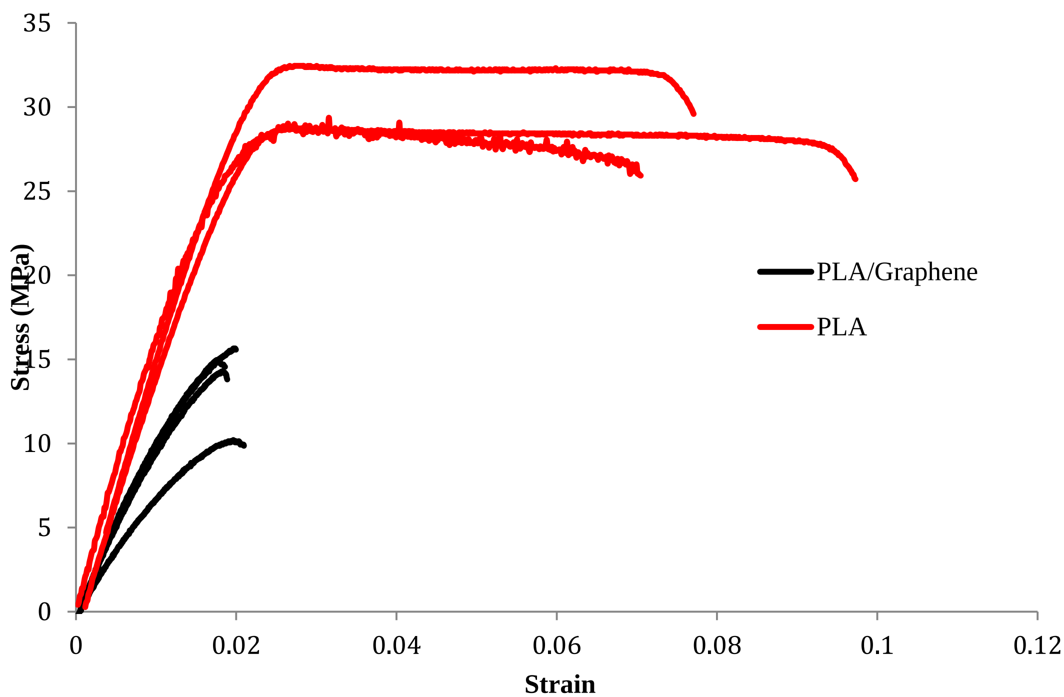

Figure 3– Stress strain response of PLA and PLA/Graphene composite specimens

Table 1 – Comparison of average maximum tensile stresses

Sample	Average Tensile Strength (MPa)	Theoretical tensile strength at 100% infill (MPa)	% Increase compared with Pure Material
PLA	30.2	43.77	N/A
PLA-Graphene	13.78	19.97	-54%
ABS	22.24	32.23	N/A
ABS-1wt% SCF	22.54	32.67	1%
ABS-2wt% SCF	27.23	39.46	22%

As each specimen was printed at only a 20% infill, it was necessary to scale results in order to obtain material properties. Using density analysis, it was found that a 20% infill lead to the printed cross section being 69% of the total area. Using this analysis, the material properties were calculated and are listed in Table 1. As shown by Table 1, even with theoretical scaling, the PLA coupons do not achieve the usual tensile strength of 56.6MPa (Tymerak et al. 2014) whilst the ABS coupons also do not reach the usual value of 42.5MPa (Teststandards. 2015). This may be due to a lack of bonding of layers within the 3D printing process, and delamination occurring between the layers of printed material.

The addition of carbon structures to a polymer matrix did affect the conductivity of the materials. As seen in Table 2, addition of SCF did not change the conductivity of the ABS drastically, whilst the graphene samples provided conductivities five orders of magnitude higher than the SCF specimens. A reading could not be obtained for the PLA samples due to the apparent insulating property of the material. However through the 3D printing process, the conductivity of the sample was reduced as shown through the pure filament having a conductivity over three times higher than that of the printed PLA/Graphene specimen.

Table 2 – Conductivity of Tested samples

Specimen	Conductivity (S/m)
Pure PLA Coupon	N/A
PLA-graphene Coupon	11.24416
PLA – graphene Filament	38.75969
Pure ABS Coupon	3.39E-05
1wt% SCF-ABS Coupon	3.80E-05
2wt%SCF-ABS Coupon	3.82E-05

One of the largest factors that influences the results obtained is the printability of filaments. Using the Leapfrog Creatr 3D in this investigation, the print head diameter was 0.5mm. Throughout the printing process, the clogging of this nozzle was the most significant hindrance of results, causing many prints to be incomplete. Whilst higher compositions of carbon structures were intended to be explored, the 2wt% SCF formed the highest printable filament and hence shows a limitation of this investigation.

Discussion

It is not surprising that an introduction of SCF into an ABS matrix increases tensile stresses, confirming previous results from Cong. Et al (2015). However this investigation shows that a significant increase in tensile strength of 22% is achievable with a low percentage of SCF and no impact on printability. Whilst Cong. et al (2015) were able to achieve a 21% increase in their printed samples with 7.5% SCF introduction, this investigation shows that it is possible to achieve a greater increase of 22% with only a 2wt% addition. This may be attributed to the fact that Cong et al (2015) used 150μm long SCF whilst this investigation used 212 long μm fibres. Cong et al. (2015) also find that increasing the fibre length from 100 to 150μm increases tensile strength by close to 10%, which is consistent with our result.

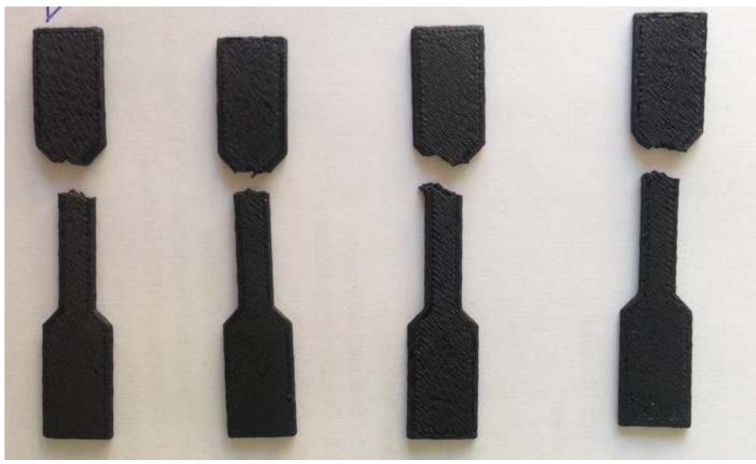

Figure 4 – Image of failed Graphene – PLA specimens

The introduction of the carbon structures into the polymer matrix also altered the failure mode. The ABS samples failed after a large amount of plastic deformation was seen by the material, whilst the SCF and graphene composite samples exhibited brittle characteristics as shown in Figure 3. Figure 4 shows that the failure did not exhibit signs of yielding, suggesting a brittle failure mode. Similarly It was observed on most samples that the failure occurred along a 45 degree axis. This is largely due to the structure of the 3D printed sample, determined by the pattern of infill set up in the gcode of the 3D printer process. Determined by the gcode, for all infill, material was laid down by the printer head at an angle of 45 degrees to the coupon's longitudinal axis. This explains the 45 degree failure observed in most sample's infill, as the strands of material did not have to break, but rather, the bond between each strand of printed material failed first. This shows that it is not entirely the material failing, but rather a structural flaw in the design of the coupon leading to premature failure.

However, it may not have been the carbon structures themselves that lead to brittle failure, as the tensile strength for SCF and graphene are 2950 MPa (Fu et al. 2000) and 130000MPa (Potts et al. 2011) respectively, and it is unlikely that these values were reached during the testing process. Instead however it is more likely that the bonds between the polymer and the carbon structures within the matrix fail with brittle characteristics. This effect may be reduced with an increase in length of the carbon structures. Potts et al. (2011) sight this effect, stating that as a result of scanning electron microscopy study, two dimensional stiffness of graphene is unable to be utilised by three dimensional polymer sample. To reduce the influence of this effect, Mark Forged (2015) increased length of printed sampled by developing a process to lay continuous strands of carbon fibres within a polymer matrix. The company claims strength increase up to 27 times compared with a pure ABS print. However, this process requires specialised equipment and does not follow the standard FDM printing process.

Both SCF and graphene are highly conductive. However this conductivity is not reflected in the printed composite materials. Whilst carbon fibres have a low electrical resistivity of 100-1000 S/m (Chen et al. 2004) and graphene has a high conductivity of up to 3500S/m (Potts et al. 2011), as shown by Table 2, the conductivities of the SCF composite samples were near zero rendering them poor conductors, and the conductivity of the graphene filament was roughly 10 times lower than the value measured by Potts et al. (2011). A low concentration of the carbon structures within the sample provides one possible explanation for the lack of conductivity observed in the samples. The printing process also significantly altered the conductivity of samples. As shown in Table 2, the PLA/graphene filament provided conductivity over three times greater than the printed sample. Inherent in the FDM printing process is a deposition of very fine material that is often laid in an orientation not following the path of current flow. Similarly, between layers there may not be a path for electrons to flow due to small air voids or a lack of contact of conductive carbon structures within the sample. These variables significantly alter the conductivity of samples through the printing process when compared to the corresponding filament.

Conclusion

It can be seen from the investigation that it is possible to enhance the mechanical and conductive properties of 3D printed structures with the addition of carbon structures within the polymer matrix. The conductivity of a pure PLA sample was increased with the introduction of graphene into the polymer. Hence the 3D printing process involving the addition of graphene to polymer filaments was effective in increasing the conductivity of printed structures. This could lead to potential application of this process for 3D printed electrically conductive components such as circuit boards. The 3D printed coupons comprised of PLA-graphene composite materials exhibited reduced tensile strength and stiffness characteristics. These structures also exhibited brittle failure and no yielding compared with the ductile PLA coupons. Hence the 3D printing process involving graphene additives was ineffective in enhancing the material properties of polymer structures. The investigation showed that it was possible to enhance the tensile strength of ABS 3D printed structures with the addition of SCF. 2wt% SCF-ABS 3D printed structures exhibited higher tensile strengths, however showed less ductility than pure polymer structures. These enhanced properties show potential application of this process in creating stronger 3D printed components for high accuracy applications such as aerospace and industry. The conductivity of ABS filament was not increased to highly conductive levels by the introduction of SCF filaments. The addition of the SCF at the 2wt% level was unable to create viable conductivity within the sample for applications requiring electrical conductivity.

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