EFFECT OF COMPOSITION ON THE MECHANICAL PROPERTIES OF 3D PRINTED POLYMER NANOCOMPOSITES

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Introduction

Fused filament fabrication (FFF) is one of the most widely employed techniques of additive manufacturing, which produces three dimensional (3D) printed objects by the layering of melt-extruded thermoplastic filaments. Despite its ease of use and environmentally friendly nature, FFF has demonstrated a narrow range of applications due to the limited number of materials compatible with this technique. Furthermore, 3D printed[1] parts exhibit inferior mechanical properties compared to that of their conventionally-manufactured counterparts.

An approach for tailoring the properties of printing materials and extending the applicability of FFF is the addition of nanoparticles (e.g. organomodified nanoclays) to the feedstock polymer, in order to produce polymer/nanoclay composite filaments. Up to date, there has been only limited research in the incorporation of nanocomposites in FFF that has shown improved properties[2,3]. In the current work, polylactide (PLA)/nanoclay composite filaments were prepared and 3D printed by FFF. The properties of the acquired samples were evaluated with regards to the clay type and content.

Experimental details

Materials

The polymer utilised was PLA (grade: Ingeo™ Biopolymer 2003D, NatureWorks), while the clays employed were the organomodified nanoclays under the trade name CLOISITE®5 (Clo5) and CLOISITE®20 (Clo20), produced by BYK-Chemie. Both clays are bis(hydrogenated tallow alkyl) dimethyl, salts with bentonite. The pristine materials were processed by BYK-Chemie into filaments with an average diameter of 1.75mm and clay content of 1 wt% and 5 wt% of each clay type in PLA.

Sample preparation

Specimens for tensile & flexural tests were designed following the ASTM D638-10 Type IV and ISO 178:2003 standards respectively. An open-source RepRapPro Huxley 3D printer (0.5mm nozzle diameter) was employed in this work. All specimens were printed with their smallest dimension (thickness) perpendicular to the printing platform, as well as with identical printing parameters: 200°C nozzle temperature, 60 mm/s printing speed, 1 perimeter, rectilinear cross-hatched infill orientation (0°/90°), 0.3mm layer thickness and 100% infill density.

Mechanical testing

Tensile and flexural tests of 3D printed samples were performed on a Tinius Olsen H25KS universal testing machine. Tensile tests were performed at a crosshead speed of 5mm/min. Flexural three-point bending tests were carried out with a crosshead speed of 2mm/min. The flexural stress and strain were calculated using the following equations (ISO 178:2003):

$$\sigma_f = \frac{3FL}{2bh^2} \qquad \varepsilon_f = \frac{6sh}{L^2}$$

where σ_f is the flexural stress, F is the applied load [N], L is the span [mm], b is the width of the specimen [mm], h is the thickness of the specimen [mm], ε_f is the flexural strain and s is the deflection [mm].

Results and discussion

Tensile properties

The mean values of the measured tensile properties of the 3D printed PLA/clay samples are presented in Fig.1 and Fig.2, along with their standard deviations. Fig.1 shows that the modulus of elasticity increases for both clay types (e.g. 8% and 12% increase in modulus observed for the samples with 1 wt% and 5 wt% Clo5 clay in PLA respectively). For 1 wt% clay content in PLA, Clo5 clay appears to exhibit better enhancement than Clo20 clay.

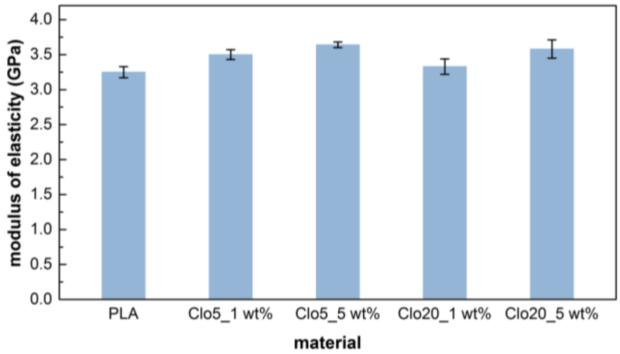

Fig.1: Modulus of elasticity of PLA and PLA/clay 3D printed specimens.

Fig.2 shows the effect of clays on the tensile strength and the ductility of the 3D printed specimens.

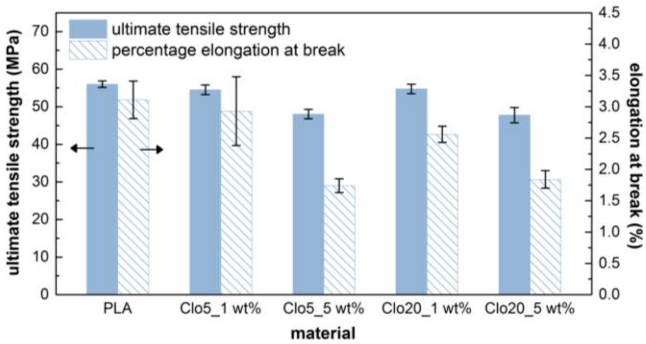

Fig.2: Ultimate tensile strength and percentage elongation at break of PLA and PLA/clay 3D printed specimens.

Compared to pure PLA, a 15% reduction in the tensile strength is observed for the samples of 5 wt% clay content, for both clay types. However, no decrease in tensile strength is observed for the samples with 1 wt% clay content. The addition of clays in PLA also resulted in a significant decrease in the ductility of the 3D printed samples with 5 wt% clay content (e.g. 44% decrease for the 5 wt% Clo5 clay and 41% decrease for the 5 wt% Clo20 clay.)

Flexural properties

Fig.3 and Fig.4 show the measured flexural properties of the 3D printed PLA/clay specimens. The results follow a similar trend to that obtained from the tensile tests. Flexural modulus (Fig.3) increased by 14% with the addition of 5 wt% Clo5 clay and by 15% with the addition of 5 wt% Clo20 clay in PLA.

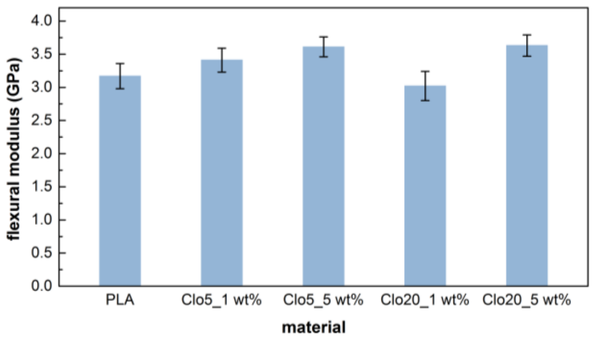

Fig.3: Flexural modulus of PLA and PLA/clay 3D printed specimens.

Compared with the pure PLA sample, there is a 24% reduction in the flexural strength of the 5 wt% Clo5 clay sample (Fig.4) and an 18% reduction for the 5 wt% Clo20 clay sample, while the 1 wt% Clo5 clay sample (Fig.4) exhibits similar flexural strain at break to the pure PLA sample, but a 27% reduction is observed for the 5 wt% Clo5 clay. As for the Clo20 clay samples, the flexural strain at break decreased by 13%, but it appears that this reduction is not affected by the clay content.

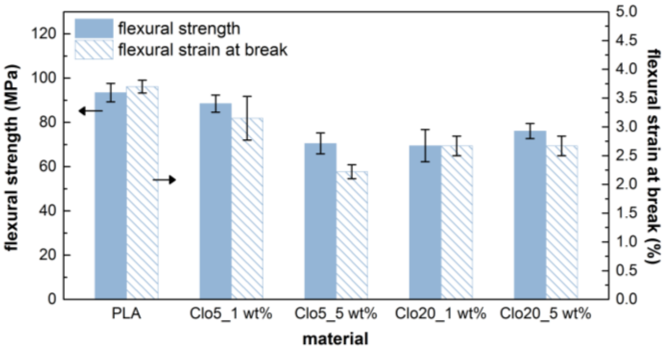

Fig.4: Flexural strength and flexural strain at break of PLA and PLA/clay 3D printed specimens.

Failure mechanism

The presence of hard phases (e.g. clays) in the polymer matrix usually results in higher stiffness and more brittle nature. Similar behaviour has been reported by Zaidi et al.[4] for moulded samples of similar PLA/clay system. Their work shows that the degree of intercalation/exfoliation of the clays in the PLA matrix (which in turn affects the PLA/clay interfacial area) affected the mechanical behaviour of the PLA/clay nanocomposites.

The observed mechanical performance of the 3D printed composite samples is related to the mesostructure formed during the 3D printing process. It was observed that the individual PLA/clay beads that build up the printed specimens exhibited smaller diameter than that of their PLA counterparts, printed under the same conditions. Such behaviour could be attributed to the reduced melt flow rate of the composites, due to the presence of solid nanophases that interact with the PLA matrix. The intercalation/exfoliation of nanoclays in PLA could generally account for the higher melt viscosity. The latter affects the rheological behavior of the composite filaments during the 3D printing process and finally the structure of the printed samples.

Furthermore, air bubbles were observed within the PLA/5 wt% Clo20 clay filament, which remained in the printed specimens (Fig.5), thus decreasing the load-bearing area and significantly lowering the strength of the corresponding samples (Fig.2 and Fig.4). These bubbles were not observed in the pure PLA filaments/specimens. The formation of the air bubbles in the filament could be related to the dispersion of the clays in the PLA matrix. Fig.5 (left) shows that the PLA/clay filaments also exhibited irregularities in their diameter. These irregularities could be related to an inconsistent melt flow during the extrusion process, which in turn might be attributed to a non-uniform dispersion of the clays in the PLA matrix. Further work is ongoing in order to address the issues mentioned above.

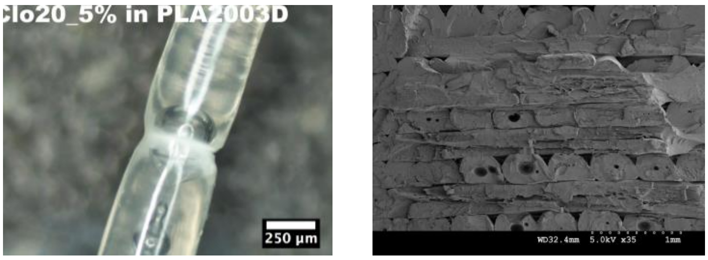

Fig.5: Optical micrograph of extruded material through the nozzle of the 3D printer of 5 wt% Clo20 clay in PLA (left), and field-emission scanning electron microscopy micrograph of the fracture surface of tensile specimen of 5 wt% Clo20 clay in PLA (right).

Conclusions

- Pure PLA and PLA/clay composites were successfully printed by an open-source 3D printer.
- The tensile and flexural moduli of the printed composites were increased by 12% and 15% respectively at the 5 wt% clay level.
- The tensile strength and ductility were found to be dependent on the clay content. Samples with 1 wt% clay content exhibited similar behaviour to pure PLA, while those with 5 wt% clay content showed a significant reduction in strength and ductility.
- The rheological behaviour of the composites strongly affected the development of properties of the printed composites.

References

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