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Degradable Polymer Nanocomposites for Fused Filament Fabrication Applications

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Introduction

The use of plastics in everyday life has increased dramatically during the course of the 20th and 21st century which is primarily due to the characteristics plastics offer in the development of new products to meet the challenges of modern society. It has been reported that in 2015 approximately 300 million tons of plastic material was produced around the world, most of which was derived from the ever depleting petroleum feedstocks [1]. This has resulted in polymers attracting increased interest owing to the growing concern with regards to both the environment and decrease in fossil resources and as a direct result has led to a substantial interest in switching to suitable eco-friendly alternatives of already existing polymers which afford similar properties to their depleting counterparts. Over the last number of decades, the study of both resorbable and degradable polymers has been investigated to a great extent [2] including their use as implants, stents, drug delivery devices and in the area of personalized medicine, with the vast majority, e.g. poly(ε-caprolactone), polyvinyl alcohol and polylactide acid, being produced from renewable sources. Although non-degradable polymers may be utilized in such applications it can become problematic if an implant or small device has to be retrieved *via* surgical intervention illustrating why degradable polymers may be advantageous in such applications. Furthermore, emerging technologies have also become intertwined with such applications and Fused Filament Fabrication (FFF), a form of 3-Dimensional (3D) printing, has demonstrated the possibilities of using degradable polymers in the production of solid dosage forms [3].

Aims

The main objective was to investigate the possibility of developing a degradable nanocomposite, incorporating the polymers poly(ethylene oxide) (PEO) and poly(ε-caprolactone) (PCL) and the nanoclay halloysite nanotubes (HNTs) by utilization of hot melt extrusion (HME). Furthermore, the research study aims to develop a suitable polymeric filament that would be suitable to be utilized as a feedstock in Fused Filament Fabrication.

Methods

Poly(ε-caprolactone) and poly(ethylene oxide) of varying ratios were prepared by HME with the extruded blends characterised using common polymer testing techniques, melt flow indexing, mechanical testing, differential scanning calorimetry and scanning electron microscopy. From the characterisation the most favourable blend was selected and HNTs of 2 and 6 weight percent were added with the same testing techniques employed to evaluate their influence on the material.



The resultant extruded filament was utilized as the feedstock in a MakerBot Replicator 2X 3D printer in order to print a stent demonstrating the possibilities it offers for personalized medical uses.

Results

It was found that the addition of PCL to the PEO matrix provided a plasticizing effect which was apparent with the melt flow index and melting point of the blends reducing with an increase in PCL content (data not shown).

From the inclusion of the nanoclay filler, HNTs, it can be observed **Figure 1.** and **Figure 2.**, that their addition, at low loadings, had a negligible effect on both the melting behaviour and melt viscosity of the Blend 4 matrix with no discernable pattern emerging.

Furthermore, upon reinforcing the matrix with HNTs, there was a significant improvement in the mechanical properties. The addition of the HNTs significantly increased the Young's modulus 11 % and 25 % when the loading was 2 wt.% and 6 wt.% respectively **Figure 3.**

The scanning electron microscopy images, **Figure 4.**, show no obvious HNT aggregation at the surface of the sample and that most of the HNTs have been incorporated into the bulk of the Blend 4 matrix which suggests that HME imparted high mixing efficiency. A small almond shaped accumulation of HNTs was observed on the surface of Blend 4A as shown with this accumulation was identified as HNTs using energy-dispersive x-ray spectroscopy.

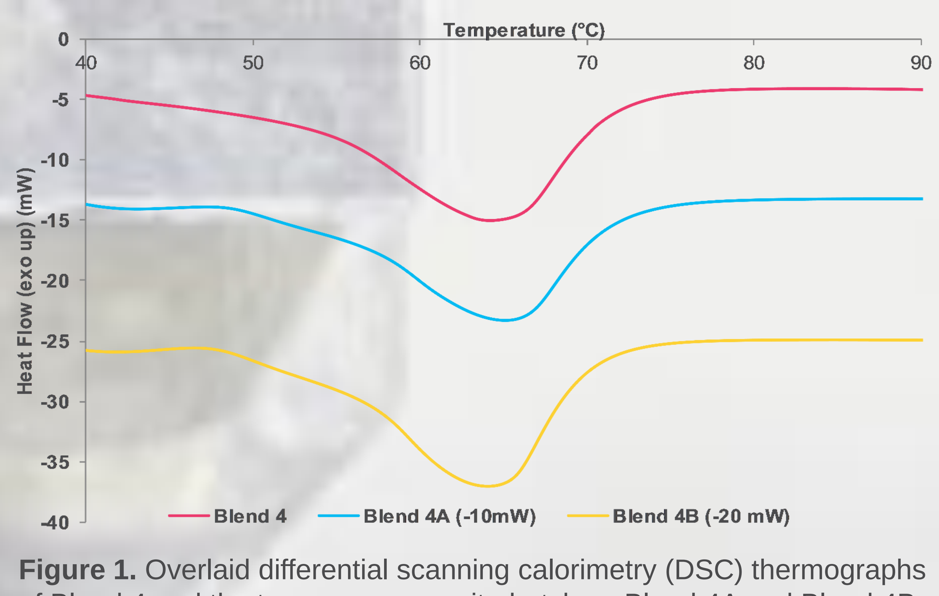

Figure 1. Overlaid differential scanning calorimetry (DSC) thermographs of Blend 4 and the two nanocomposite batches, Blend 4A and Blend 4B.

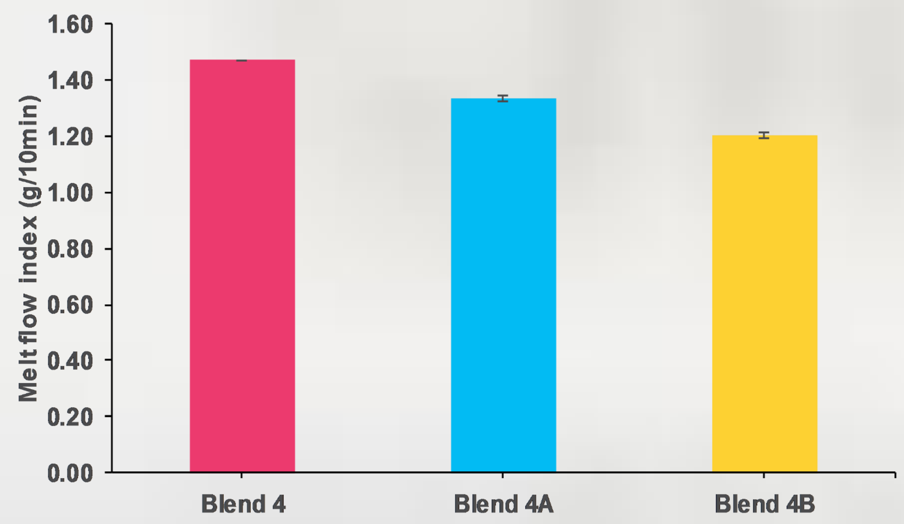

Figure 2. Melt flow index results of Blend 4 and the two nanocomposite batches, Blend 4A and Blend 4B (n=3).

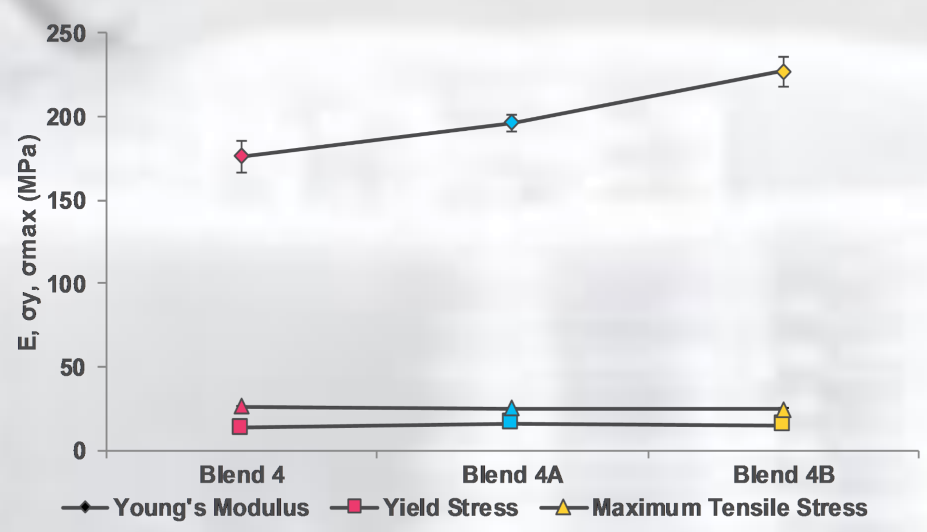

Figure 3. Selected mechanical data for the batches under investigation where, E represents the Young's modulus, σ_y is the yield stress and σ_{max} is the maximum tensile stress (n=5).

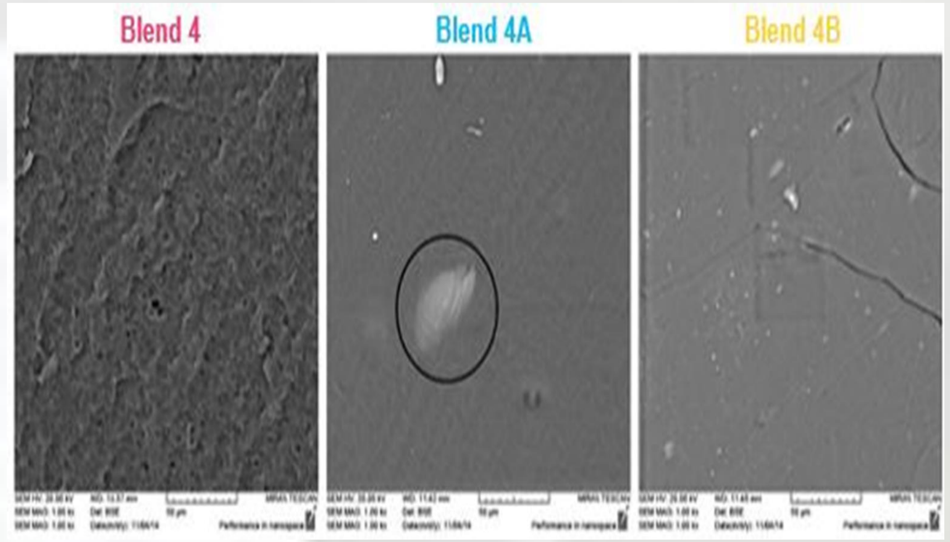

Figure 4. Scanning electron microscopy (SEM) images of Blend 4 and the two nanocomposite batches, Blend 4A and Blend 4B.

Conclusion

The work described the successful development of a filament feedstock from known degradable materials for use in Fused Filament Fabrication with the produced filament utilized in the fabrication of a stent. The use of this technology is promising as it may allow for the fabrication of stents tailored to a patient's specific needs.

Furthermore, there is also the potential application for loading drug molecules in the large lumen space of the HNTs which could slowly release as the device slowly degrades within the body.

References

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