The influence of process conditions on the structure and properties of melt processed poly (lactic acid) nanohydroxyapatite composites

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Introduction

Poly (lactic acid) (PLA) is a biodegradable and bioresorbable thermoplastic polymer with good optical clarity, radio-translucency and biocompatibility. These properties make it a desirable material for medical implant application. At present, the use of PLA implants has been restricted to non-structural functions such as mandibular fracture plates due to its limited mechanical performance [1]. An area where PLA implants have been successfully employed is in bioresorbable interference screws. PLA screws for the fixation of bone-tendon and soft tissue grafts during ACL and PCL reconstruction procedures are proving favourable [2]. The work presented here is part of an effort to incorporate novel nano-sized hydroxyapatite particles (nHA) into bioresorbable PLA for healthcare applications via melt-processing, in order to broaden the application range of such bioresorbable materials. In this study the focus is on the effects of atmospheric process conditions on the post-processed molecular weight and mechanical properties of these novel nanocomposites.

Experimental

The medical grade PLA employed in this study was RESOMER® LR706S (Evonik Industries) 70:30 poly (L-lactide-co-D,L-lactide) (PLDLLA). The nHA is produced through a novel continuous flow reactor, and can be synthesised to produce large batches of specific morphologies, with the potential to modify the surfaces of the HA with many different surfactants [3]. Composites have been compounded using a Haake MiniLab recirculating extruder at 210 °C for 15 minutes in different atmospheres.

Extrudates were compression moulded at 170 °C for 15 minutes to produce specimens for mechanical testing. Mechanical tests were carried out using an in-house custom miniature 3-point bending rig with specimen sizes of 7 x 2 x 0.5 mm. The molecular weights of the compression-moulded virgin polymer and extrudates were analysed using size-exclusion chromatography (SEC) in THF, calibrated with polystyrene standards.

Results and discussion

It is well known that melt processing of PLA is very sensitive to the presence of water. Fig. 1b reports measurements of the peak molar mass M_p as a function of process conditions. Relative to the pre-processed conditions, compounding under a blanket of bottled nitrogen gas causes a significant decline in the molar mass. A drop in mechanical properties is also observed as a result of compounding, as shown in Fig 1a for flexural strength. The introduction of just 2.5wt% nHA platelets provided a small improvement in the flexural strength. The addition of nHA platelets results in both an improvement in the flexural strength and to the post-processed molar mass, possibly due to the nHA's interaction with the residual water.

In an attempt to reduce the water content, bottled nitrogen was passed through a cold trap to remove residual moisture. This mostly led to an improved flexural strength and molar mass after processing. With the nHA particles, the flexural strength of the unprocessed polymer was recovered, but the compounding still caused a significant reduction in molar mass.

The most significant improvement in post-processed molar mass was observed when the nHA was separately dried at a high temperature. This is believed to remove any remaining water from the PLA during processing, significantly reducing the effect of the depolymerisation ordinarily taking place at the compounding temperatures. Although the mechanical properties of the nanocomposites are not significantly affected by the moisture content, the reduced drop in molar mass is likely to play a significant role once these materials experience hydrolytic degradation in service.

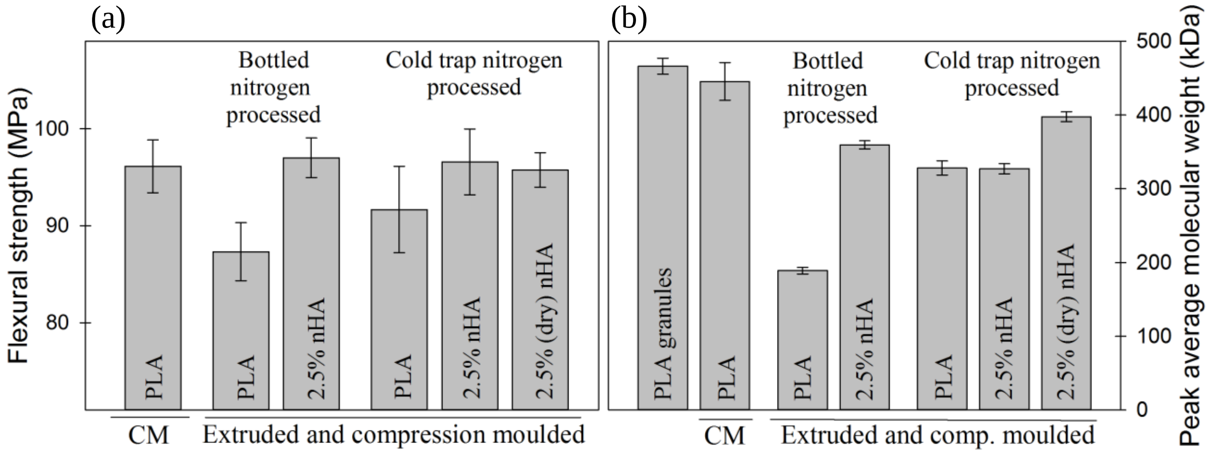

Fig. 1 *Properties of PLA and 2.5% nHA-PLA composites after melt processing in different conditions. (a) Flexural strength (b) Peak average molecular weight*

Conclusions

This work has investigated the effect of processing conditions on the molar mass and flexural strength of PLA and PLA nHA nanocomposites. Although compounding causes a drop in molar mass and flexural strength, much of this drop can be offset by compounding under dry nitrogen and by pre-drying the nanoparticles.

References

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