Biodegradation influence on PLA/graphene-nanoplatelets composite biomaterials mechanical properties and biocompatibility

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Abstract

Two types of graphene-nanoplatelets (GNPs) were incorporated in PLA (poly(lactic acid)) by melt blending. Materials were biodegraded during 6 months and characterized by XRD, tensile tests, DMA and biocompatibility assays. For both fillers, low loadings (0.25 wt.%) improved mechanical properties and decreased decay until 6 months biodegradation. PLA degradation decreased its toughness (AUC) by 10 fold, while for PLA/GNP-M and C, toughness was only reduced by 3.3 and 1.7 fold, respectively. Comparing with PLA, PLA/GNP-M and C composites presented similar (HFF-1) fibroblasts adhesion and proliferation at the surface and did not released toxic products (6 months).

Introduction

A commercial available product, with reduced cost comparing with single layer graphene, GNPs, are constituted by few stacked graphene layers. These materials present high aspect ratio and possess oxygen-containing functional groups in the platelet edges, which may facilitate extensive interfacial interaction with polymer matrices. [1] Some typical composite production techniques like solvent mixing and electrostatic deposition lead to obtainment of toxic materials. [1,2] Thus, melt blending, which assures complete embedding of GNPs in polymer matrix preventing filler leaching, is studied in this work as a green method for production of PLA/GNPs composites.

Materials and Methods

PLA 2003D (Natureworks), GNPs (XG Sciences). Composites were prepared by melt blending and moulded in a hot press into thin sheets (0.3-0.5 mm). Samples were immersed in PBS and incubated for 6 months (37 °C, 100 rpm). Tensile properties were measured (Mecmesin Multitest-1d, Mecmesin BF 1000N) using a strain rate of 10 mm min^{-1}. Creep/recovery assays were performed using a DMA 242 E Artemis (Netzsch). Biocompatibility of materials was evaluated using HFF-1 cells cultured at the surface of composite films and in direct contact with materials extracts obtained after 6 months degradation. Metabolic activity was determined using resazurin assay.

Results and discussion

XRD

GNP-M and C powders present similar XRD spectra, typical of carbon materials. PLA, before (0M) and after 6 months (6M) biodegradation, presents similar spectra, also typical for this polymer. In composites PLA and GNPs peaks were observed. Degradation did not affected spectra.

Tensile tests

Incorporation of GNP-C and M in PLA increased its Young´s modulus by 14 %. Also, tensile strength is increased by 20% for GNP-C and by 6% for GNP-M. After 6 months biodegradation, decreases in tensile strength, elongation at break, and toughness are respectively, for PLA of 2.6, 2.5, and 10 fold, for PLA/GNP-M of 1.6, 1.8 and 3.3 fold, and for GNP-C of 1.4, 1.4 and 1.7 fold.

Creep/recovery

Figure 1 shows that for undegraded PLA, dL_f (final, at 6N) after 10 creep/recovery cycles was of 14.2 µm, being of 13.7 and 13.2 µm for PLA/GNP-M and C 0.25 wt.%, respectively. After 6 months degradation, PLA sample ruptured after 4 cycles (1.A) reaching a dL_f of 56.3 µm. PLA/GNP-M and C 0.25 wt.% did not rupture (1.B,C) and presented only a slight increase in dL_f, of 16.8 and 16.7 µm, respectively. Materials degradation was confirmed in terms of molecular weight decrease and changes in surface morphology (results not shown).

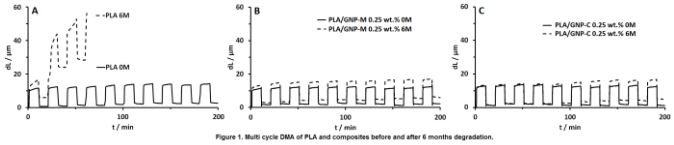

Figure 1. Multi cycle DMA of PLA and composites before and after 6 months degradation.

Biocompatibility evaluation

PLA/GNP-M and C 0.25 wt.%, metabolic activity never decreased below 90%, for both composites in comparison with PLA. Composites degradation products are not toxic (24, 48, 72h), comparing with PLA 6M. Also, cell morphology is normal and similar for all conditions tested (images not shown).

Conclusions

GNP-M and GNP-C incorporation in PLA (0.25 wt.%) improved mechanical properties and decreased their decay after 6 months biodegradation. GNPs can be used to tune PLA mechanical performance during biodegradation in biomedical applications, since they did not decrease cell proliferation or cause toxicity.

References

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