Biocompatible reinforcement of poly(lactic acid) with graphene nanoplatelets

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Improved mechanical properties of composites produced by melt blending is achieved at low filler loadings.

Graphene—a single layer of carbon atoms arranged in a honeycomb structure—possesses extraordinary mechanical strength and an extremely high surface area. In particular, commercially available graphene nanoplatelets (GNPs) have lower costs than single-layer graphene. These GNPs consist of a few stacked graphene layers that have oxygen-containing functional groups at their edges. In addition, GNPs provide a high aspect ratio and can thus form a percolated network in composites. In these networks there is a large interfacial interaction between the platelets and the polymer matrix (mainly at the edges), which results in effective load transfer and increased strength. Despite the benefits of using GNPs as fillers within polymer composites, however, previous methods that have been used to incorporate the GNPs are associated with problems of toxicity.

In previous work, for instance, we have demonstrated the potential of GNPs as polymer fillers, i.e., we achieved improvements to the mechanical properties of poly(lactic acid)—PLA—thin films for filler loadings below 1 wt%. Moreover, we showed that the GNPs were non-toxic when they were incorporated into the PLA at these low proportions. In this earlier work, we used solvent mixing for the GNP incorporation, but the use of solvents should generally be avoided because of the toxicity of the residues that remain in the materials (presenting a problem for industrial workers). In another approach—used to improve the mechanical properties of ultra-high-molecular-weight polyethylene—the composites were produced by electrostatic deposition of GNPs (at the 1 wt% level). The resultant composites in this study, however, were toxic to osteoblasts (bone-forming cells) because filler leaching had occurred.

In this work, we have thus investigated the use of melt blending—as a ‘green’ method—to ensure complete embedding of GNPs in a polymer matrix for the production of PLA/GNP composites. For this study,
we purchased the PLA (2003D) from NatureWorks and the GNPs from XG Sciences. The GNP grade we obtained (C-750) is a recently available form (which we refer to as GNP-C) and (to our knowledge) our work is the first time it has been studied as a reinforcement filler for PLA. With these materials, we prepared the PLA/GNP-C composites by melt blending, under different conditions, in a Thermo Scientific Haake PolyLab. We then molded the composites into thin sheets (with dimensions of 60 × 15mm and a thickness of 300–500μm) in a hot press (at 190°C for 2 minutes). We also measured the tensile properties of our resultant composites (at room temperature) with the use of a Mecmesin MultiTest-Id motorized test frame. To evaluate the biocompatibility of our materials, we used HFF-1 cells (human fibroblasts) cultured at the surface of the films (with diameter of about 5.5mm). In the last parts of our procedure, the cells were seeded, a resazurin solution (a fluorescent dye) was added, and the mixture was incubated for three hours. We subsequently measured the fluorescence of the mixture (at an excitation wavelength to emission wavelength ratio of 530/590nm) and evaluated the metabolic activity.

Initially, we prepared the PLA/GNP-C blends by mixing at 180°C for 20 minutes and at 50 revolutions per minute (rpm). For these composites (see Figure 1), we obtained maximum Young’s modulus and tensile strength values at a loading of 0.25wt%. We also observed a 20% increase in tensile strength, a 12% increase in Young’s modulus, and a 16% increase in toughness for the composite with a 0.25wt% filler content compared with the neat PLA. In addition, we found that a decrease in the mechanical performance of the composites occurs when the loading is increased to 0.5wt%. We attribute this change to an increased level of platelet agglomeration, which introduces defects into the polymer matrix. We have also investigated the variation in the mechanical

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**Figure 2.** The effect of mixing time and rotation speed on the mechanical properties of PLA/GNP-C composites (with filler content of 0.25wt%) processed at 180°C. Error bars represent the SD of the measurement (for n of 10).

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**Figure 3.** (a) Cumulative number of GNP agglomerates per unit area, as a function of agglomerate length, for PLA/GNP-C composites (produced at 180°C and 50rpm for 20 minutes) with different loadings. (b) Scanning electron microscope images (5000× magnification) of fracture surfaces within the three different composites.
properties of our composites as a function of mixing time and rotation speed (see Figure 2). These results show that we obtained a brittle material at 75rpm, which was probably caused by PLA degradation under high shear. Furthermore, we find that the best processing conditions were mixing for 20 minutes at 50rpm. We believe that shorter mixing times or slower rotation speeds probably provide worse GNP dispersion and thus the poor mechanical properties. We also tested a higher mixing temperature (200°C), but this yielded very brittle materials (probably because of thermo-oxidative degradation of the PLA).

From our scanning electron microscope images (see Figure 3) we measured the density of platelet agglomerates in the composites. We display the cumulative number of agglomerates per unit area, as a function of agglomerate length, for different GNP-C loadings in Figure 3(a). These results show that the composites with loadings of 0.1 and 0.25wt% have similar agglomerate densities, but the composite with a loading of 0.5wt% has a substantially higher concentration of agglomerates (of all sizes).

In the last part of our study, we examined the metabolic activity of our composites. The results shown in Figure 4 indicate that the metabolic activity of the HFF-1 cells on the PLA/GNP-C composite with a 0.25wt% loading never decreased below 97% (expressed as a percentage of the metabolic activity of cells cultured on a PLA surface). Furthermore, we obtained immunocytochemistry images (see Figure 4) that show no morphological differences between the PLA and the PLA/GNP-C composite with 0.25wt% loading.

In summary, we have studied a non-toxic and green melt blending approach to achieve the incorporation of graphene nanoplatelets within PLA/GNP composites. We examined the mechanical properties of our composites (with different loading levels) and found an optimum loading of 0.25wt%. At higher loading levels, defects in the matrix (caused by filler agglomerations) caused a decrease in mechanical performance. In addition, we have found that the metabolic activity and morphology of human skin cells (cultured on the surface of the materials) were unaffected by the incorporation of 0.25wt% GNP-C into the PLA. The improved mechanical performance of our composites, at low filler loadings, and their associated biocompatibility means that our approach may have interesting future uses in biomaterial applications. In the next step of our work we will conduct an in vivo evaluation of the biocomposites’ biocompatibility.

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References