Study of properties of Poly(L-lactic acid)/Graphene Oxide nanocomposites

George Z. Papageorgiou¹, Panagiotis Klonos², Elias Giannoulidis², Zoe Terzopoulou¹, Dimitrios Gournis³, Dimitrios N. Bikiaris¹, Polycarpos Pissis²

¹Laboratory of Organic Chemical Technology, Department of Chemistry, Aristotle University of Thessaloniki, GR-541 24, Thessaloniki, Greece ²Physics Department, National Technical University of Athens, Heroon Polytechneiou 9, Zografou Campous, 15780, Athens, Greece ³Ceramics and Composites Laboratory, Department of Materials Science and Engineering, GR-45110 Joannina, Greece

Introduction

Poly(L-lactic acid) (PLLA) is one of the most important biodegradable polymers with numerous applications. It is used for the development of green materials including nanocomposites, always keeping its biodegradation characteristics.



Graphene and Graphene Oxide (GO) are novel materials, with impressive properties such high specific surface, electrical and mechanical properties and low weight. Combining Graphene Oxide with polymers can lead to nanocomposite materials with improved properties. Graphi



In this work PLLA/GO nanocomposites were preparared and their thermal and dielectric properties were studied.

Experimental

GO was produced through a modified Staudenmaier's method. The nanocomposites, were prepared by solvent casting using N,Ndimethylformamide and chloroform as solvents. Two series of nanocomposites were prepared, one using GO and one using modified GO. GO content in the nanocomposites was 0.5, 1 or 2.5wt%. The materials were studied by means of Differential Scanning Calorimetry (DSC), Thermally Stimulated Depolarization Currents (TSDC) and Dielectric Relaxation Spectroscopy (DRS) and Xray Diffreactometry (WAXD). Tensile properties and FTIR spectra were also investigated.

Results and Discussion

DSC study of crystallization from the melt or from the glass showed enhancement of crystallization rates with increasing GO content in both series of nanocomposites and increase of crystallinity (Figure 1). WAXD patterns did not show any significant change in crystal reflections. Tensile properties increased slightly. For 2.5wt% GO or modified GO a 10% increase in Young's modulus was observed.

In Figure 2a comparative TSDC thermograms for PLA and PLA/GO nanocomposites are presented. The α_s relaxation, related to the segmental mobility of polymer chains (glass transition) of PLA, is at around 50 °C.



Figure 1. DSC heating scans for quenched PLLA and PLLA/2.5wt% org GO nanocomposite.

In Figure 2a comparative TSDC thermograms for PLA and PLA/GO nanocomposites are presented. The α_s relaxation, related to the segmental mobility of polymer chains (glass transition) of PLA, is at around 50 °C. At higher temperatures the $\alpha_{_N}$ (normal mode) relaxation is observed, originating from the motions of dipoles on the backbone of the polymer chains. No systematic changes in the temperature position and the magnitude of the relaxations were observed with filler loading.



temperature (°C) $T-T_{max}$ (°C) **Figure 2.** Comparative TSDC thermograms for PLA and PLA/GO nanocomposites a) in the range from -150 to 100 °C (inset shows glass transition region) and b) in the temperature range of segmental dynamics. (Results after normalizing the 'shape' of α_N relaxation).

Figure 3a shows the comparative isothermal DRS plot of the real part of dielectric permittivity, ε' , versus frequency at -150 °C. Reduction of ε' values with the addition of GO at low temperature is observed. The values of PLA are reduced with GO. Expect for the sample with 2.5 wt% unmodified GO, the changes are stronger for the organomodified filler, as compared to unmodified. The changes cannot be described by additivity. So, polymerfiller interactions should contribute on these changes, directly by reducing the molecular mobility which contributes to ε' , and/or indirectly by affecting the volume of polymer crystals in the systems. It is possible also that the modifier contributes to these changes by its own dielectric response. Further work is needed to follow these points. Figure 3b the variations of the secondary β relaxation of PLA with different filler loadings. This relaxation is probably related to local movements of PLA. As expected, θ relaxation is not affected by the presence of GO. On the other hand, α_s relaxation becomes faster after the addition of GO, recorded at higher frequencies compared to unfilled PLA at 70 °C. The dielectric relaxation strength, $\Delta \varepsilon$, of β relaxation does not change with increasing of temperature. The dielectric strength of α_s relaxation was slightly suppressed for the low GO filled samples. These changes maybe related with crystallinity.







