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Glass transition and segmental dynamics in poly(L-lactic acid)/graphene oxide nanocomposites

Panagiotis Klonos [a], Sotiria Kripotou [a], Apostolos Kyritsis [a], George Z. Papageorgiou [b], Dimitrios Bikiaris [c], Dimitrios Gournis [d], Polycarpos Pissis [a,*]

[a] Department of Physics, National Technical University of Athens, Zografou Campus 15780, Athens, Greece
[b] Chemistry Department, University of Ioannina, P.O. Box 1186, 45110 Ioannina, Greece
[c] Department of Chemistry, Laboratory of Polymer Chemistry and Technology, Aristotle University of Thessaloniki, GR-541 24 Thessaloniki, Greece
[d] Department of Materials Science and Engineering, University of Ioannina, GR-45110 Ioannina, Greece

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ABSTRACT

Effects of graphene oxide (GO) and GO modified with dodecylamine (org-GO) on glass transition and segmental dynamics of poly(L-lactic acid) (PLLA) were investigated by differential scanning calorimetry (DSC) and two dielectric techniques, broadband dielectric spectroscopy (BDS) and thermally stimulated depolarization currents (TSDC) techniques. Measurements were performed on initially amorphous and on crystallization annealed samples. Isothermal crystallization in the neat matrix and the nanocomposites was followed by DSC and BDS with the same thermal protocol. No change in the glass transition temperature is observed by DSC, whereas the heat capacity step decreases in the nanocomposites. The segmental α relaxation becomes faster and broader in the nanocomposites and its dielectric strength decreases. The results were rationalized in terms of a fraction of interfacial polymer becoming immobilized in the nanocomposites. Changes of this interfacial polymer fraction with composition and functionalization show similar trends in DSC and BDS, absolute values are, however, larger by BDS.

1. Introduction

It is commonly accepted nowadays in the scientific community that interfacial effects play a significant role for the improvement of various properties of polymer nanocomposites (PNCs) at much lower filler contents as compared to traditional polymer composites [1]. With interfacial effects we mean changes in structure and organization, thermal transitions, molecular dynamics and properties of the polymer at the interfaces with the filler extending up to a few nanometers into the polymer matrix [2–5]. Interfacial effects are significant also for thin films developed on solid substrates [6], as well as for many other soft matter devices and applications [7]. A better understanding of these effects is essential for the knowledge-based design of multicomponent materials and devices with predicted, tailor-made properties.

Over the last years we studied in detail interfacial effects in PNCs based on poly(dimethylsiloxane) (PDMS) and natural rubber (NR) as matrices and silica or titania as fillers, prepared by sol–gel techniques in the presence of the cross-linked polymer matrix [5,8–12]. This work has been recently extended to core–shell type PNCs, where PDMS has been physically adsorbed from a solution onto nano-oxides in powder form [13,14]. A methodology based on differential scanning calorimetry (DSC) to study glass transition and dielectric techniques to study segmental dynamics in PNCs with well characterized morphology has proved a powerful tool for such studies. DSC results have been analyzed and interpreted in terms of a fraction of polymer being immobilized in an interfacial layer around the nanoparticles (NPs). Dielectric techniques revealed the presence of a slower segmental relaxation in the interfacial layer next to the bulk segmental relaxation. Analysis of the results provided quantitative information on the interfacial polymer fraction (the fraction of polymer with modified behavior) and, in cases of well-defined morphology, the thickness of the interfacial layer [5,9–11,13].

The situation is more complex for PNCs based on thermoplastic matrices. DSC measurements, on the one hand, often show a reduction of the heat capacity step at the glass transition, ΔC_p, interpreted in terms of immobilization of polymer in the interfacial layer, similar to rubbers [15,16]. Dielectric measurements, on the other hand, typically reveal a behavior different than in rubbers and similar to that of DSC, namely only the bulk segmental relaxation with reduced, however, magnitude in the nanocomposites (NCs)

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[*] Corresponding author.
E-mail address: ppissis@central.ntua.gr (P. Pissis).

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[17,18]. Only in a few cases a separate, slower segmental relaxation, assigned to polymer in the interfacial layer, has been observed, in the raw data or after analysis [4,19]. So, for example, dielectric measurements in poly(2-vinylpyridine)/silica NCs have been analyzed in terms of a bulk and a slower interfacial segmental relaxation [19] against a single segmental relaxation with reduced magnitude in the NCs [18], resulting in significantly different numbers for the calculated interfacial polymer fraction and the thickness of the interfacial layer.

The present work deals with PNCs based on a thermoplastic matrix, poly(L-lactic acid) (PLLA), and graphene oxide (GO). Poly(lactic acid) (PLA) has attracted much interest in recent years because of the favorable combination of renewability, biodegradability, good mechanical properties and low cost. Properties may be further improved and tailor-modified to specific applications, mostly biomedical and packaging, by combining PLA with other polymers, typically in blends [20,21] and copolymers [22], or by reinforcing it with various fillers in the form of composites and NCs [23–26]. Regarding PLA NCs, the subject of interest here, we refer to two recent reviews [27,28], where further references can be found. The focus in most of the publications, including the two reviews mentioned above, is on the properties and routes for improving them in relation to applications [29–32]. Relatively less attention has been paid to effects of fillers on glass transition and molecular dynamics [23,33,34].

In a recent paper we presented results on the preparation and characterization of PLLA/GO NCs by a variety of experimental techniques [35]. Preliminary results there by DSC and dielectric techniques indicated significant effects of GO and GO modified with dodecylamine (org-GO) on glass transition and segmental dynamics of the PLLA matrix. Here we focus just on these effects. We employ DSC to study glass transition and crystallization/melting and two dielectric techniques, broadband dielectric spectroscopy (BDS) and thermally stimulated depolarization currents (TSDC) techniques, to study segmental dynamics of the polymer matrix for initially amorphous and for crystallization annealed samples. In a second part, following previous work on monitoring isothermal crystallization in neat PLLA by BDS [36–40], we monitor isothermal crystallization by DSC and by BDS with the same thermal protocol. By analyzing the data we calculate the interfacial polymer fraction by both DSC and BDS and compare results with each other.

2. Experimental

2.1. Materials

The preparation of GO and amino-functionalized GO (org-GO) has been described in [35]. According to measurements by atomic force microscopy (AFM), the layered GO consists of irregularly shaped sheets of ~5 nm in size and ~15.5 Å in average height. The mass density was estimated around 1.85 g/cm^3. According to wide angle X-ray diffraction (WAXD) the basal spacing between initial GO and org-GO sheets in bulk is 7.4 and 18.4 Å, respectively. Taking into consideration that the thickness of GO monolayer has been reported 6.1 Å (reference 33 in [35]), the intersheet separation for org-GO is equal to 12.3 Å (=18.4 – 6.1 Å), this being a result of successful insertion of the guest molecules in the interlayer space of GO.

Films of PLLA/GO and PLLA/org-GO NCs were prepared by solution casting, using N,N-dimethylformamide (DMF) as a solvent for the dispersion of GO and chloroform for PLLA, we refer to [35] for details. The filler amount was 0.5, 1.0 and 2.5 wt% (always referring to pure GO amount). GO and org-GO were found exfoliated in NCs of all compositions according to WAXD in combination with mechanical tensile measurements. Samples are designated by PLA/GO and PLA/org-GO for the NCs based on org-GO, followed by the filler weight fraction, e.g. PLA/GO 0.5 wt% or PLA/org-GO 2.5 wt%. Films of ~1 mm in thickness were produced by employing a thermal-press operating at 200 °C, for melting of the polymer and fixing the thickness of the sample. Finally, immediately after pressing, the samples were immersed into cold water, this procedure resulting in solid and fully amorphous samples. The latter was confirmed by both DSC and WAXD measurements [35].

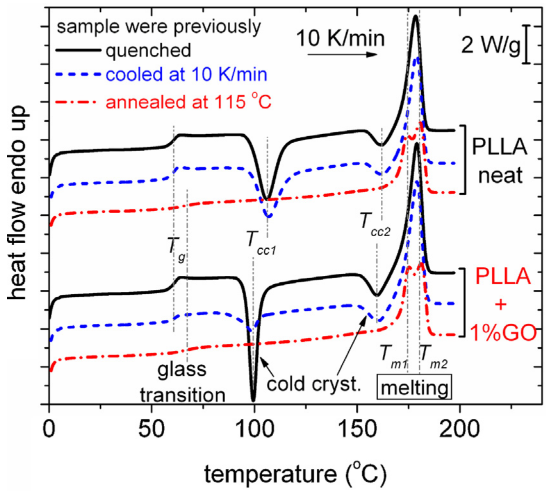

Fig. 1. DSC heating thermograms for the samples and the conditions of measurement indicated on the plot. Indicated on the plot are also the various events recorded, along with the characteristic temperatures; glass transition (T_g), cold crystallizations ($T_{cc1,2}$) and melting of crystals ($T_{m1,2}$). The curves are normalized to sample mass.

2.2. Differential scanning calorimetry (DSC)

Thermal transitions of the polymer matrix (glass transition and crystallization/melting) were investigated in nitrogen atmosphere in the temperature range from 0 to 200 °C using a TA Q200 series DSC instrument, calibrated with indium (for temperature and enthalpy) and sapphire (for heat capacity). Samples of ~8 mg in mass were closed in standard *T*-zero aluminum pans. Different thermal protocols were used, details being given later together with the results of measurements. Results are evaluated in terms of characteristic temperatures of the various thermal events, namely the characteristic temperature of glass transition, T_g, the temperature position of the two cold crystallization peaks, $T_{cc1,2}$, and the position of melting peaks (double melting peaks in some cases), $T_{m1,2}$ (examples are shown in Fig. 1). Finally, the various polymer fractions, namely crystalline (*CF*), mobile amorphous (*MAF*) and rigid amorphous (*RAF*), are evaluated by employing widely adopted models [16], which involve the melting and cold crystallization enthalpies (ΔH_m, $\Delta H_{cc1,2}$) and the change in specific heat capacity during glass transition ($\Delta C_{p,\mathrm{DSC}}$).

2.3. Dielectric techniques

For BDS measurements [41] the complex dielectric permittivity, $\varepsilon^* = \varepsilon' - i\varepsilon''$, was recorded isothermally as a function of frequency in the range from 10^{-1} to 10^6 Hz. Measurements were carried out on samples of ~1 mm in thickness and 20 mm in diameters, cut from the produced films, by means of a Novocontrol Alpha analyzer at selected temperatures, controlled to better than 0.5 K by a Novocontrol Quatro cryosystem. We refer to previous work for details of measurements and analysis of experimental data [9,13,17]. Several thermal protocols were employed, in correlation also to DSC measurements.