CRYSTALLIZATION AND MOLECULAR DYNAMICS IN POLY(L-LACTIC ACID) FILLED WITH GRAPHENE OXIDE NANOSHEETS AND SILICA NANOPARTICLES

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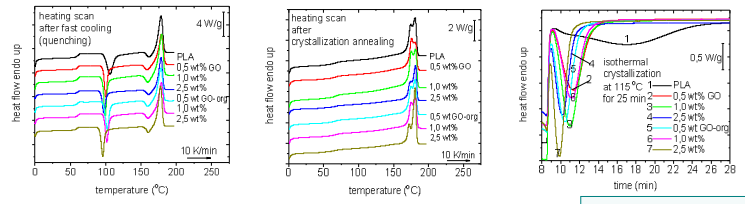
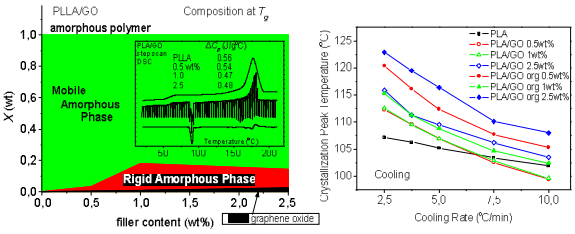
In the present work we studied the thermal transitions and molecular dynamics of Poly(L-Lactic acid) (**PLLA**) (*MW*~100 kDa) in two series of nanocomposites. PLLA was filled with (i) **Graphene Oxide** (GO) nanosheets (unmodified and modified with 1-dodecylamine) and (ii) **silica nanoparticles** (Aerosil, specific surface area S_{bet}~200 m^2/g, ~12 nm in diameter). The preparation involved solution mixing, stirring, sonication and, finally, evaporation of the solvent at elevated temperatures. Differential Scanning Calorimetry (**DSC**), Polarized Light Microscopy (**PLM**), Wide Angle X-Ray Diffractometry (**WAXD**) and Dielectric Relaxation Spectroscopy (**DRS, TSDC**) techniques were employed for the characterization of these systems. The nanocomposites suffered various thermal-crystallization treatments, aiming on the specific study of crystallization mechanism on the macromolecular dynamics.

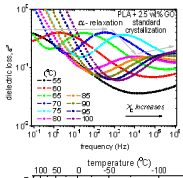
PLLA – graphene oxide

DSC

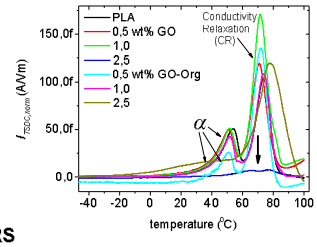




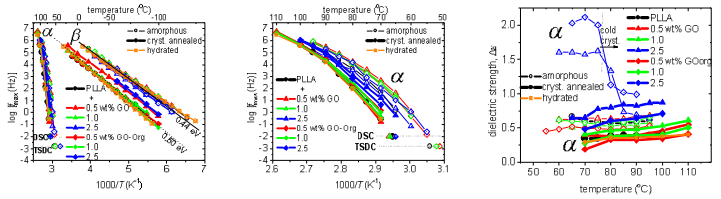
α relaxation mechanism is related to glass transition (segmental dynamics) and **β relaxation** represents local (-COOH) molecular mobility of the polymer.



TSDC

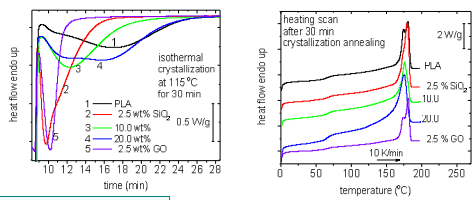


DRS

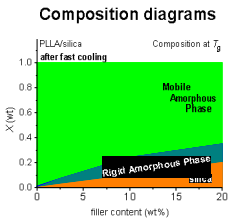


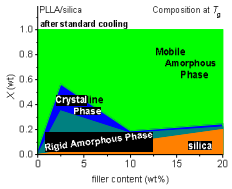
PLLA – silica

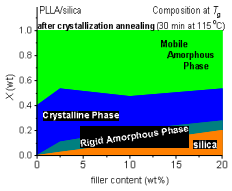
DSC

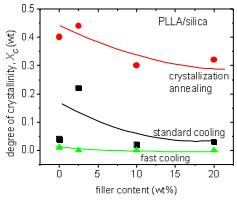


Composition diagrams



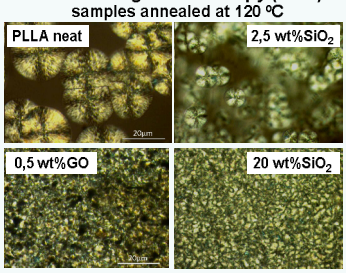




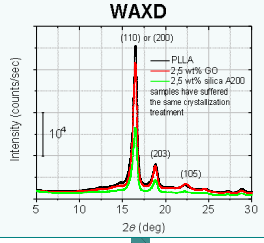


Polarized Light Microscopy (PLM)

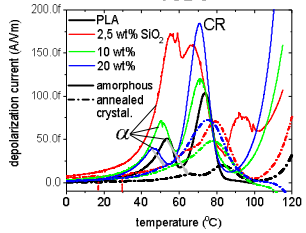
samples annealed at 120 °C



WAXD

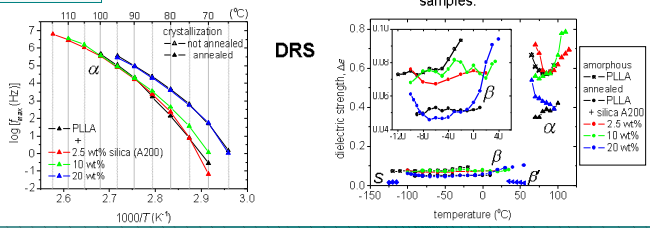


TSDC



α relaxation becomes faster (immigrates towards lower temperatures / higher frequencies) **with filler addition**, in either amorphous or highly crystallized samples.

DRS



DSC was used to study the crystallization of the nanocomposites under isothermal and nonisothermal conditions, from the melt to subglassy phase. In general, the dispersed nanofillers increase the degree of PLLA crystallinity, *Xc*, and the crystallization rates. The organomodified-GO showed more significant nucleation activity, as evidenced also by PLM. WAXD did not reveal additional type of polymer crystallite. Dielectric techniques showed effects of nanofillrers on the local (*β* relaxation) and segmental mobility (*α* relaxation) of PLLA. The presence of nanofillers affects polymer dynamics indirectly, through the increasing of *Xc*. *α* relaxation, related to glass transition, becomes faster for lower GO loadings and slower for the higher contents. In general, the presence of silica leads to faster *α* relaxation (agreement between DSC-dielectric techniques) For the higher loadings of silica (i.e. 10 and 20 wt%) extra secondary relaxations were revealed (*β´* and *S*). The overall dielectric permittivity of the samples is suppressed with the addition of filler, suggesting strong polymer-filler interactions.

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