THERMALLY TREATED POLY(HYDROXYBUTYRATE-*CO*-HYDROXYVALERATE): MOLECULAR MOBILITY VS. MICROSTRUCTURE

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ABSTRACT

Polyhydroxyalkanoates (PHAs) are bio-sourced linear polyesters spontaneously produced by some bacteria via the fermentation of sugars or lipids to store energy in conditions of physiological stress[1]. The most common bacterial PHA is poly(hydroxybutyrate) (PHB), but hydroxybutyrate (HB) repeating units can also be associated to either hydroxyvalerate (HV) or hydroxyhexanoate (HHx) repeating units to obtain PHBV or PHBHHx copolymers with different morphologies. It is possible to control PHA morphology by adding specific nucleating agents such as boron nitride[2,3]. Whatever the nucleating agent, PHAs are prone to develop high crystallinity degrees; in any case, the microstructure strictly depends on the thermal treatment applied to the polymer. The literature provides several examples of works focusing on the study of the crystalline phase developed as a consequence of a given thermal treatment[4-6]. However, there are no works exploring the molecular mobility of the amorphous phase at its glass transition as a consequence of the microstructure developed after a given thermal treatment. A comparison of PHAs with poly (ethylene terephthalate) (PET) and poly (lactic acid) (PLA) is interesting as these polyesters showed a clear dependence of the coupling between amorphous and crystalline phase (and therefore of the molecular mobility in the amorphous phase) as a function of the thermal treatment to which they were subjected[7,8].

In this work, the molecular mobility of a PHBV copolymer with 3% HV repeating units was investigated as a function of the semicrystalline morphology developed by different thermal treatments (quenching from the melt, crystallization from the melt and cold crystallization in the rubbery state from the glassy state). The size of the Cooperative Rearranging Regions (CRR) was calculated by performing Temperature Modulated Differential Scanning Calorimetry (TM-DSC) measurements and using Donth's approach. CRR data were then interpreted by considering the microstructure or the sample as revealed by the thermal analysis as well as Wide Angle X-ray Diffraction (WAXD), Small Angle X-ray Scattering (SAXS) and Positron Lifetime Annihilation Spectroscopy (PALS).

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