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The role of the constrained amorphous interphase on physical and mechanical properties of bio-based polymeric materials

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The micro- and nanophase structure of semi-crystalline polymers is determined by competition between crystallization and vitrification, which leads to the development of different amorphous regions, which, due to different distance from the crystalline domains, can exhibit different molecular dynamics. A detailed description of the micro- and nanophase structure of semi-crystalline polymers is decisive for a full understanding of the physical properties of these materials. It has been recently proved that many macroscopic properties of semi-crystalline polymers, as for example mechanical and barrier properties, are defined not only by the degree of crystallinity, but also by the percentage of constrained amorphous nanophase present at the amorphous/crystal interface. The quantification of this nanophase is therefore a crucial step in the characterization of a polymeric material, since different processing conditions affect in different ways the evolution of the crystalline and amorphous fractions.

Due to the coupling between the crystalline and amorphous phases, the amorphous phase of semi-crystalline polymers is constituted by regions with different mobility: a mobile amorphous fraction (MAF), which vitrifies and devitrifies at the bulk glass transition temperature (T_g), and a constrained amorphous interphase, or rigid amorphous fraction (RAF), located at the amorphous/crystal interface, which vitrifies and devitrifies at temperatures higher than the bulk T_g. Many macroscopic properties of semi-crystalline materials (e.g., thermal, mechanical, and gas permeability properties) can be accurately explained by considering not only the relative percentage of the crystalline and amorphous phases, but also the amount of RAF interphase. Thus, the quantification of this interphase is a crucial step in the characterization of a polymeric material, because different processing conditions affect the evolution of crystalline and amorphous fractions in different ways.

The subject of the presentation will be the evolution, during solidification, of the constrained amorphous interphase in some bio-based polymers, as poly(L-lactic acid) (PLLA), poly(3-hydroxybutyrate) (PHB), poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBV) and poly(butylene succinate) (PBS), which, owing to their biodegradability, can be utilized for a variety of applications.

The contribution of the constrained amorphous nanophase to physical ageing of PLLA, as well as to the mechanical properties of PLLA, PHB and PHBV will be presented and discussed. In

particular, a quantitative estimation of the elastic modulus of the constrained amorphous nanophase in PLLA and some PHBV copolymers will be described. The calculated elastic modulus turned out to be in agreement with theoretical expectations.

Biography

Maria Cristina Righetti is Senior Researcher at National Research Council of Italy. She has 25 years of experience on materials characterization for the study of correlations between molecular structure and physical properties (morphology, thermal, volumetric, mechanical, rheological and viscoelastic properties) of polymers and bio-polymers, copolymers, polymeric mixtures, composites and nanocomposites. Her latest interest is the study of the nanometric interphases in polymeric and bio-polymeric systems, with the aim to obtain more detailed and accurate interpretation and prediction of the macroscopic properties of these materials. She is author and co-author of more than 100 publications in international journals indexed by Web of Science and Scopus (50% as corresponding author), 10 book chapters, 80 contributions to national and international conferences and a patent.