

Effect of Different POSS Structures on Thermal and Morphological Properties of a Biodegradable Polyester [†]

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The quest for materials with properties similar to those of engineering plastics but derived from renewable resources remains a continuous need of our time. Poly(lactic acid) (PLA) is a linear aliphatic thermoplastic polyester, intensively studied and currently used for various applications because of its biodegradability and availability on the market at a price close to polypropylene [1]. However, its slow crystallization rate, low thermal stability, and excessive brittleness are disadvantages that limit the wider applicability of PLA [2]. Extensive research has showed that an effective way to improve PLA properties is the addition of nanofillers. Because of their nanoscale dimensions, biocompatibility, recyclability, nonflammability, nonabrasive, and nonmigrating features, polyhedral oligomeric silsesquioxanes (POSS) could be an interesting choice as fillers for PLA [3]. The aim of this study was to evaluate the POSS influence on the thermal, morphological, and mechanical behavior of a poly(l-lactic acid) matrix (PLLA). POSS fillers (trisilanol-isooctyl polyhedral oligomeric silsesquioxanes—TSio-POSS, allyl-heptaisobutyl—ALib-POSS, and aminopropyl-heptaisobutyl polyhedral oligomeric silsesquioxane—APib-POSS) (Sigma-Aldrich) were incorporated into a PLLA matrix (4043D, NatureWorks Ingeo) by a melt compounding method. The morphological, thermal, mechanical, and surface properties of PLLA/POSS nanocomposites were evaluated by atomic force microscopy (AFM), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), and water contact angle measurements (CA). AFM analysis showed a more organized structure for the TSio-POSS nanocomposite, whereas some aggregates were detected mainly on the surface of the PLLA/ALib-POSS film. CA results indicated that POSS improved the hydrophobicity of the PLLA matrix, with the exception of the nanocomposite containing APib-POSS—probably due to the better incorporation of APib-POSS in the PLLA matrix, as also shown by AFM. The addition of POSS improved the thermal stability of the PLLA matrix, as demonstrated from the characteristic temperatures of the TG/DTG curves. A slight shift of T_m nanocomposites towards lower values was observed as a result of the plasticizing effect of POSS and good miscibility between PLLA and POSS. The downward shift of T_c indicated that ALib and APib-POSS nanoparticles enhanced the nucleating activity and the rate of crystallization of the PLLA, which was also confirmed by the higher degree of crystallinity values. Incorporation of POSS led to a decrease of the storage modulus and increased PLLA flexibility, which was noticed in the glassy state, below T_g ; beyond the T_g region, all the PLLA/POSS nanocomposites displayed higher storage modulus values as compared with neat PLLA. The loss modulus curves

indicated that POSS addition decreases the melt viscosity of the corresponding PLLA nanocomposites. The self-assembled POSS molecules were well dispersed in the PLLA matrix, as shown by AFM images. Furthermore, an increase in thermal stability was noticed, and both T_{on} and $T_{5\%}$ were modified, depending on the POSS type. Except for TSio-POSS, the fillers acted as plasticizers, lowering the E' of the PLLA matrix in the glassy region and increasing the E'' above the glass transition temperature (T_g).

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