# PHOTO AND THERMAL DEGRADATION OF POLYLACTIDE / ZINC OXIDE NANOCOMPOSITES: EVOLUTION OF THERMAL AND MECHANICAL PROPERTIES

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To limit environmental impact of plastic waste and to ensure low cost of raw materials, development of biosourced biodegradable polymers such as polylactic acid (PLA) receives great interest. Recently, an awareness of general sanitation has led to the development of antimicrobial materials, e.g., using nanoparticles with photocatalytic properties such as zinc oxide (ZnO). For these reasons, PLA/ZnO nanocomposites are potential candidates for applications in packaging and in medical applications[1]. The impact of temperature and/or UV-light can provoke dramatic modifications of the chemical and physical structure of the polymer, with a degradation of the properties. The main objective of this work was to correlate the local modifications provoked by thermal/UV exposure of PLA and PLA/ZnO nanocomposites with the evolution of the mechanical and thermal properties, in the bulk and at the surface.

Changes in bulk mechanical and thermal properties were characterized by Differential Scanning Calorimetry (DSC), Dynamical Mechanical Thermal Analysis (DMTA) and MicroHardness tester. Surface evolution of films of PLA and PLA/ZnO nanocomposites was investigated using an Atomic Force Microscope (AFM) and techniques derived such as nano indentation and nano thermal analysis (Vita mode). Accelerated

artificial ageing of the samples was performed either by irradiation at λ>300 nm and 60°C in SEPAP 12-24 or in an oven at temperatures between 60°C and 100°C.

Photo- and thermal ageing provoke bulk crystallization, as observed by DSC and DMTA analysis, and chain-scissions that are evidenced by Size Exclusion Chromatography.

ZnO nanoparticles strongly absorb in the UV domain, which provokes heterogeneous degradation resulting from light absorption profile[2] within the PLA/ZnO nanocomposites films. At the surface of the samples, a progressive crystallization is evidenced by AFM images. As an example, after 300h of UV light-irradiation, glass transition temperature of PLA-3 % ZnO disappears, and the transition temperature detected at 103°C should be the melting temperature (Figure 1). By transition temperature analysis with the AFM Vita mode, we are able to discriminate crystallization and crosslinking reactions. Correlation between surface thermal transition temperature and nano hardness will be discussed.

1. Murariu M., Doumbia A., Bonnaud L., Dechief A.-L., Paint Y., Ferreira M., Campagne C., Devaux E., P. Dubois, Biomacromolecules, 12 (5) : 1762, 2011.
2. Larché J.F., Therias S., Bussière P.O., Gardette J.L., Murariu M., Dubois P., Biomacromolecules, submitted

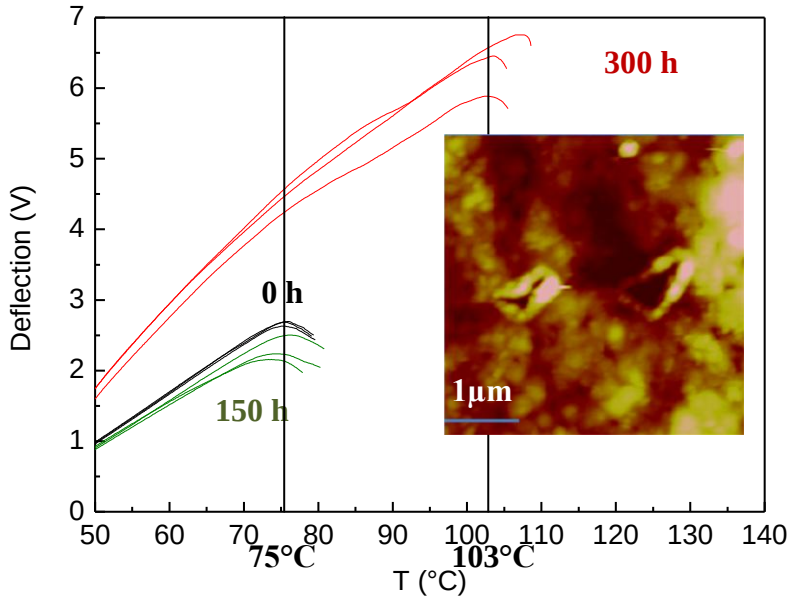


**Figure 1**: Evolution of the surface thermal transition temperature of PLA – 3% ZnO nanocomposite film during photo ageing in SEPAP 12-24 using an Atomic Force Microscope at various irradiation times (a) 0 h (b) 150 h (c) 300 h (inset) AFM image showing two holes obtained after surface thermal analysis of PLA – 3% ZnO photo irradiated 150 h.