

11th International Conference on Advanced Materials

Rio de Janeiro Brazil September 20 - 25

Addition of Starch Nanocrystals as Filler to PHB Biodegradable Films

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Abstract – In this work, waxymaize starch nanocrystals (SNC) was investigated as a potential filler for poly-3hydroxybutyrate (PHB) films. Cast films of PHB and SNC were characterized by X-ray diffraction, differential scanning calorimetry and scanning electron microscopy. SNC agglomerates were visualized in films even with low filler content. It was found that the degree of crystallinity of PHB matrix decreased with addition of nanocrystals. The addition of nanocrystals content higher than 2wt% led to the increase of unit cell parameters, which may indicated that SNC would be located within PHB molecules. SNC with amount of 2wt% probably acted as nucleating agent.

In the recent years, the ecological awareness impelled the development for new biodegradable materials, especially for single-use plastic items. Poly-3-hydroxybutyrate (PHB) is a biodegradable, microbial polyester. Although it possesses some mechanical properties like Young's modulus and tensile strength close to those of isotactic polypropylene, a more intensive commercial application of PHB is imparted mainly by its high cost, high crystallinity and narrow thermal processing window. In the context of both biomass valorization and nanocomposite materials development, in this work, starch nanocrystals (SNC) was investigated as a potential filler for PHB films as an alternative to overcome these drawbacks. Starch is an inexpensive, totally biodegradable polysaccharide, which is produced in abundance beyond available market. SNC were obtained from acid hydrolysis of waxymaize starch granules [2] followed by lyophilization. PHB/SNC films with lyophilized nanocrystals content varied from 0 to 20wt% were prepared by solvent evaporation technique. The samples was characterized by scanning electron microscopy (SEM), differential scanning calorimetry (DSC) and X-ray diffraction. SNC presented platelet-like morphology with 8 nm in height and 100 nm in lateral size, approximately. SNC have a strong tendency to agglomerate, as can be visualized in Fig. 1. Cross-section images of PHB/SNC films suggested the formation of SNC agglomerates, even with low content of filler (Fig. 2). X-ray diffractograms of PHB/SNC films suggested that no new structure was formed due to the addition of SNC. It was observed a progressive decrease in crystallinity degree of PHB/SNC films as compared to pure PHB films. The a, b and c parameters of the PHB rhombic unit cell were calculated from the (110), (020) and (021) crystalline planes, respectively [3]. Except for films with 2wt% SNC, there was a slight increase of unit cell parameters of PHB/SNC films compared to pure PHB, which could be an indicative that SNC would be located within PHB molecules, impairing crystallites formation and thus decreasing crystallinity degree of these films. Different from other PHB/SNC and PHB pure film, DSC thermograms of PHB/SNC films with 2wt% SNC in second heating scan did not show cold crystallization peak, suggesting that 2wt% SNC induced all PHB crystallization at first cooling scan. It can be supposed that, in these cases, nanocrystals may act as nucleating agent. With higher filler amounts, PHB chain movements would be progressively hindered by SNC presented within PHB molecules inhibiting the crystallization.



Figure 1: SEM images of starch nanocrystals agglomerates.



Figure 2: SEM image of the fractured surface of (a) pure PHB film and (b) PHB/SNC film with 2wt% SNC.

Acknowledgements - CNPq and CAPES for financial support and PHB Industrial and Corn Products do Brasil for raw material supply.

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