PREPARATION AND CHARACTERIZATION OF NEW BIO-NANOCOMPOSITES.

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ABSTRACT

For the sake of sustainable development, new environmental regulations will request the use of biodegradable materials. Bacterial semi-crystalline polyhydroxyalkanoates (PHA) such as poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) and poly(3-hydroxybutyrate-co-4-hydroxybutyrate) (P(3HB-co-4HB)) have received considerable attention as potential alternative to fossil-based commodity polymers with applications for automotive and packaging products. At the end of their lifetime, such "ecomaterials“ could be composted. However, the development and the applications of such materials are limited because of their low mechanical properties, their low barrier properties to gas and high moisture absorption.
Nanocomposites are hybrid organic-inorganic materials including nanometer fillers. In the previous decade, they have attracted considerable attention as they hold the promise of enhancing polymer properties. As compared to pure polymers, organic-inorganic materials could improve mechanical, thermal and barrier properties

In the present work PHBV and P(3HB-co-4HB)) films containing organo-modified montmorillonite C30B nanoclays (2.5, 5, 7.5, 10 % wt/wt) were prepared by melt intercalation using an extruder. Size Exclusion Chromatography (SEC) measurements showed that only PHBV matrix was slightly degradated during the process. X-Ray Diffraction (XRD) measurements and transmission Electronic Microscopy (TEM) observations suggested that the nanoclays were intercalated in the polyester matrix. XRD patterns, Differential Scanning Calorimetry (DSC) measurements and optical microscopy observations (polarized light) showed that the nanoclays did not influence the crystalline structure of the matrix because they were mainly located in the amorphous phase[1].

The influence of the filler on the barrier properties of the film was evaluated by water diffusion, gas permeation (CO_2, N_2 O_2) and water sorption measurements. A decrease of the N_2 permeability was observed due to the tortuosity effect of the fillers and a decrease of the solubility within the matrix. The barrier effect was more marked for the PHBV/C30B nanocomposites because of their low nanoclay aggregate content. The best result was obtained for the PHBV nanocomposite containing 10%wt/wt C30B with a decrease of 60% for N_2 permeability coefficient (P = 0,014 barrer). The effect of the filler was less marked for P(3HB-co-4HB)/C30B due to an interface effect. On contrary, the CO_2 permeability increased for both nanocomposites whatever the filler content. This result was explained by a facilited transport mechanism due to the presence of ammonium groups on the C30B surface. Not any influence was observed with O_2.
A decrease of the water sorption was observed for P(3HB-co-4HB)/C30B also due to the tortuosity effect of the nanoclays. On the other hand, an increase of the water permeability of the PHBV/C30B films was observed and was explained by the affinity of nanoclays to water.

This work highlights the complexity of the mechanisms of the transport of small molecules inside nanocomposite materials, the dispersion state of the filler being one of the key factors.

References:

[1]Crétois, R.; Delbreilh, L.; Dargent, E.; Follain, N.; Lebrun, L.; Saiter, J.-M.; *Eur. Polym. J.* **2013**, *49*, 3434.