PLA-clay nanocomposites for food packaging: Water absorption and its effects in the structure.

F.R. Beltrán, E. Ortega, H. Bernabéu, S. Lorenzo, J. Moreno, A. Arenas, E. Guijarro, M. Martín, V. Lorenzo, M.U. de la Orden, J. Martínez-Urreaga.

Universidad Politécnica de Madrid, ETSI Industriales, Dpto. Ingeniería Química Industrial y Medio Ambiente, Grupo "Polímeros, Caracterización y Aplicaciones", 28006 Madrid, Spain. <u>freddysbeltran@gmail.com</u>

Abstract

The massive use of petroleum-based plastics in the manufacture of food packaging has brought concern about the environmental impact of these materials, which has driven the development of biodegradable materials as an environmental friendly alternative. Among these materials stands out the poly(lactic acid) (PLA), an aliphatic polyester produced from the fermentation of sugars, starch and other renewable resources [1]. The PLA has seen its popularity increased due to its good optical properties, easy processability with currently available technologies and lower cost of production in comparison with other biopolymers. However, among their main drawbacks for its application in food packaging are its fragility and moderate gas barrier properties compared to those of the conventional polymers. Different alternatives have been investigated over the past years to overcome these drawbacks, being one of the more attractive the use of nanoclays as reinforcement particles, thus improving the performance of the PLA [2].

Another drawback of PLA becomes from its easy hydrolytic degradation, which leads to a significant decrease in the performance of the material, so it is important to know the behavior of the PLA when is exposed to water [3]. The objective of this work is to study the water absorption of PLA nanocomposites at different temperatures, and the effect of this absorption on the polymer structure.

In this study, a commercial PLA (Ingeo 2003D, NatureWorksTM) was used. This grade is designed for packaging applications. A commercial organically modified montmorillonite (Cloisite 30BTM) was used as reinforcement of the polymer matrix. Nanocomposites with 2% wt. clay were manufactured by melt compounding. The prepared nanocomposites were then compression molded into films, which were immersed in a phosphate buffer (pH 7.4) at 37 ° C and 58 ° C. After definite periods of time, samples were withdrawn from the buffer solution and analysed. The water absorption was monitored measuring the weight increase after different test durations. The changes in the structure of the samples were studied by ATR-FTIR.

Fig. 1 shows that the water absorption curve of the nanocomposite at 37 °C is not simple. At high immersion times the water absorption becomes faster due to the hydrolytic degradation of PLA, which generates hydrophylic terminal groups. However, absorption of water at low immersion times can be accurately described using a Fickian diffusion model. The absorption curve at 58 °C is similar but the nanocomposite absorbs more water due to the proximity of this temperature to the glass transition temperature of PLA (55-60 °C), which causes increased mobility of the molecular segments and a growth in the free volume, thus facilitating the absorption of higher amounts of water. However, the apparent diffusion coefficient at 58 °C is lower than at 37 °C. This result has been explained by considering the crystallization of PLA at 58 °C, which was observed in the analysis of the infrared spectra of the materials.

Fig. 2 shows the FTIR spectra recorded at different immersion times. Changes can be seen in different regions of the spectrum. The absorption band appearing at 3400 cm⁻¹ is mainly due to water absorption of the material. Changes seen in the bands located at 1747, 1266, 1207, 956 and 920 cm⁻¹ are due to the increase in the crystallinity of PLA during water absorption, due to the hydrolytic degradation of the polymer [4, 5]. Finally, the appearance of the band located at 1600 cm⁻¹ could be explained by the formation of carboxylate ions during the degradation process [6].

The results obtained in this work reveal the effect of the nanoclay on the water absorption. When compared to the neat polymer, the nanocomposite shows increased water absorption at long times, due to the hydrophylic nature of the clay. However, the nanoclay reduces the diffusion coefficient of the polymer, probably due to the barrier effect of the layered silicate.

References

[1] M. P. Arrieta, J. López, A. Hernández and E. Rayón, "Ternary PLA–PHB–Limonene blends intended for biodegradable food packaging applications," *European Polymer Journal*, vol. 50, pp. 255-270, 1, 2014.

[2] S. Molinaro, M. Cruz Romero, M. Boaro, A. Sensidoni, C. Lagazio, M. Morris and J. Kerry, "Effect of nanoclay-type and PLA optical purity on the characteristics of PLA-based nanocomposite films," *J. Food Eng.*, vol. 117, pp. 113-123, 7, 2013.

[3] P. K. Roy, M. Hakkarainen and A. Albertsson, "Nanoclay effects on the degradation process and product patterns of polylactide," *Polym. Degrad. Stab.*, vol. 97, pp. 1254-1260, 8, 2012.

[4] E. Meaurio, N. López-Rodríguez and J. R. Sarasua, "Infrared Spectrum of Poly(I-lactide): Application to Crystallinity Studies," *Macromolecules*, vol. 39, pp. 9291-9301, 12/01, 2006.

[5] J. D. Badia, L. Santonja-Blasco, A. Martínez-Felipe and A. Ribes-Greus, "Hygrothermal ageing of reprocessed polylactide," *Polym. Degrad. Stab.*, vol. 97, pp. 1881-1890, 10, 2012.

[6] X. Shi, J. Jiang, L. Sun and Z. Gan, "Hydrolysis and biomineralization of porous PLA microspheres and their influence on cell growth," *Colloids and Surfaces B: Biointerfaces,* vol. 85, pp. 73-80, 6/15, 2011.

Figures



Fig. 1. Water absorption data for the PLA nanocomposite at 37 °C.



Fig. 2. FTIR Spectra of the PLA nanocomposite without inmersion (blue), after 14 days (red) and after 44 days of inmersion (green).