

IMPROVED MECHANICAL AND BARRIER PROPERTIES OF AMORPHOUS POLYAMIDE FILMS BY THE ADDITION OF A HIGHLY EXFOLIATED NANOCCLAY

Pablo Santamaría and Jose Ignacio Eguiazábal

Department of Polymer Science and Technology and POLYMAT
Faculty of Chemistry UPV/EHU
P^o Manuel de Lardizabal 3, 20018 San Sebastián (SPAIN)
pablo.santamaria@ehu.es

Abstract

It is known that many of the most relevant polymers have been successfully used to produce nanoclay-based polymer nanocomposites (NCs) with improved properties by melt blending. Among them, NCs based on polyamides (PAs) have received the greatest industrial and scientific attention, as they have shown the highest levels of exfoliation of the nanoclay.[1] Among the application fields of PAs, packaging is probably one of the most important, as it comprises an important part of the total PA production. In this field, the incorporation of highly exfoliated nanoclays is very attractive, as the nanoclay could offer an improved performance (mainly mechanical and barrier) to the base film. This has triggered the development of PA based NC films, and the aim of the present work has been to examine the structure, and the mechanical and barrier properties of uniaxially drawn films of amorphous PA (aPA) based NCs with Nanomer I30 nanoclay, which is modified with a one-tailed surfactant and is one of the most performing commercially available nanoclays.

The NC films were obtained by melt extrusion-kneading followed by flat film extrusion. The draw ratio (DR), which varied from a minimum of 5 to the maximum allowed for the polymer, and the nanoclay content, which ranged from 0 to 6 wt.%, were the studied variables. The effects of both variables on the nanostructure (X-ray diffraction (XRD) and transmission electron microscopy (TEM)) as well as on the mechanical properties (measured both in the machine (MD) and the transverse (TD) directions) and the barrier behaviour (water sorption, acetone vapor transmission rate and permeability to O₂ and CO₂) were determined.

In Figure 1, a micrograph of the 4% NC film obtained at the lowest DR is shown. The presence of uniformly dispersed individual nanoclay platelets indicates a high degree of exfoliation of the nanoclay. As also seen in Figure 1, the nanoclay platelets appear preferentially oriented along the drawing direction due to the fact that the molten and oriented polymeric chains orientate the nanoclay sheets in their own direction. Regarding the mechanical properties, Figure 2 shows the tensile modulus of the films both in the MD (a) and the TD (b) directions as a function of the DR and the nanoclay content. As can be seen, the important increases in the MD resulting from the presence of nanoclay are additional to those produced by drawing. This means that the two independent increases contribute to a combined modulus increase, which goes from 2700 MPa in the aPA to 4450 in the drawn 6% NC films (65%). Along the TD the moduli appear always lower than those in the MD, and they decrease with DR, as a consequence of the orientation in the draw (MD) direction. However, the nanoclay presence leads to an important modulus increase also in the TD. These unusual increases in the two directions of the film, which are not common in films filled with fibrillar reinforcements, are attributed to the planar geometry of the nanoclay which, upon drawing, is oriented on the plane of the film and reinforces the film in both directions. With respect to the transport properties, representative water sorption plots of aPA and the 6% NC films are collected in Figure 3. The diffusion coefficients (D) can be calculated from the plots, and the obtained values indicate that the presence of nanoclay leads to a reduction of the D of aPA which is attributed to the fact that it creates obstacles in the solvent pathway, and hinders the transport through the polymer.[2] As also seen in Figure 3, the height of the plateau, i.e., the maximum water uptake (solubility) decreases in the presence of nanoclay. Both observations indicate a clear reduction in the water uptake of the aPA. As one of the most characteristic properties of aPA is its very low O₂ permeability, it was also studied as a function of the nanoclay content and the DR. As expected, O₂ permeability of the pure aPA decreases gradually upon the addition of nanoclay from 0.024 barrers in the aPA to 0.013 barrers in the 6%NC. This is almost a 50% improvement in the barrier capacity of aPA that i) is attributed to the tortuous path created by the nanoclay,[2] ii) is of particular interest taking into account the initial very low permeability of the aPA, and iii) shows the adequacy of this laminar nanoclay for improving transport properties. The nanoclay addition also produces a decrease in the CO₂ permeability and in the acetone vapor transmission rate of aPA films.

As a conclusion, the results show that the nanoclay, which is highly exfoliated and oriented along the drawing direction, produces an important tensile modulus increase both in MD and TD, and also leads to reduced water transport, permeability to O₂ and CO₂ as well as to lower acetone vapor transmission rate. Both properties improvements are attributed to the planar geometry of the oriented and exfoliated nanoclay.

Acknowledgements: The financial support of the Spanish “Ministerio de Economía y Competitividad” (Project MAT2010-16171), the Basque Government (IT-234-07) and the University of the Basque Country (UFI 11/56) is gratefully acknowledged. P. Santamaría also acknowledges the grant awarded by the Basque Government.

References

- [1] F. Chavarria, D.R. Paul, *Polymer*, **45** (2004) 8501-8515.
 [2] G. Choudalakis, A.D. Gotsis, *European Polymer Journal*, **45** (2009) 967-984

Figures

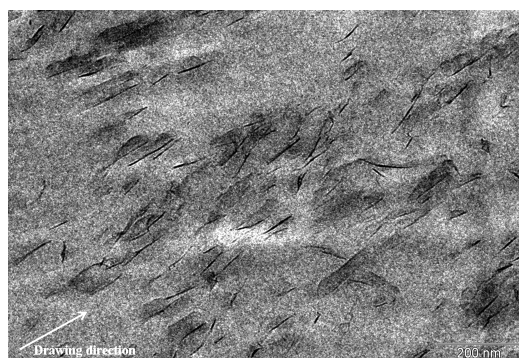


Figure 1

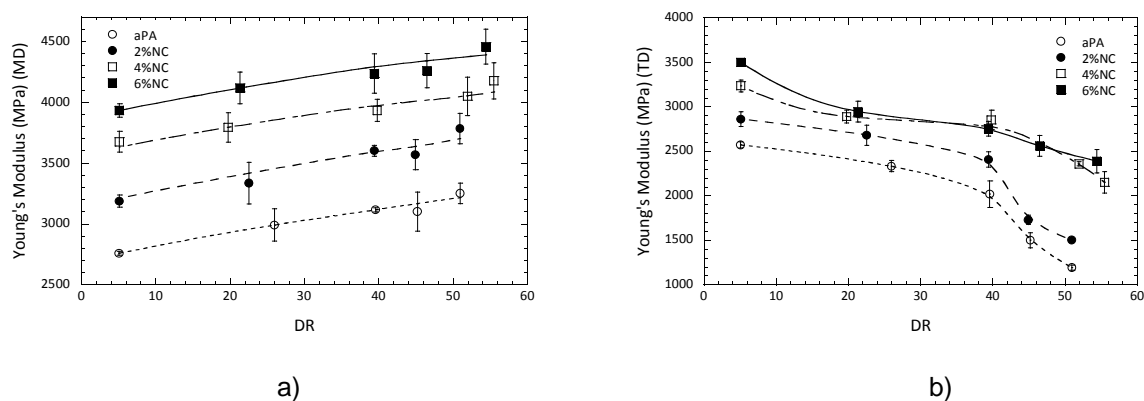


Figure 2

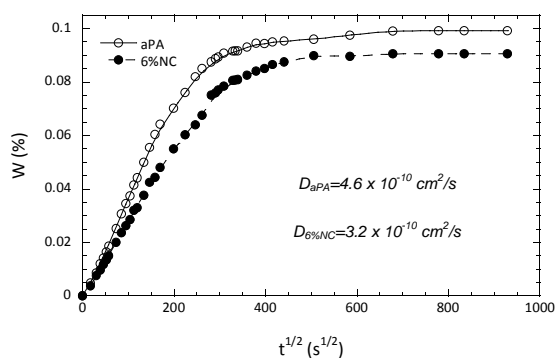


Figure 3