Isothermal Crystallization Behavior of Poly(*p*-dioxanone) Layered Double Hydroxides Nanocomposites

M. Zubitur,[*1] *M. Cortázar,*[2] *A. Mugica*[2]

Summary: Isothermal crystallization of nanocomposites of poly(p-dioxanone) and layered double hydroxides (unmodified or oganically modified) prepared by melt extrusion has been studied by Dynamic Scanning Calorimetry and Optical Microscopy. Although the nanoclay acts as a nucleating agent, the spherulite growth rate of the nanocomposites decreases due to the polymer chain mobility restriction induced by layered double hydroxides. In addition, it has not observed any change on the crystallization mechanism in presence of layered double hydroxides.

Keywords: clay; crystallization; layered double hydroxides; poly(p-dioxanone); nanocomposites

Introduction

The crystallization kinetics of semicrystalline polymers is affected by the presence of the fillers, especially in fillers than can promote high polymer/filler superficial area like exfoliated clays. In many cases, it has been reported that nanoclay particles act as nucleating agent accelerating the crystallization process of the matrix.[1] However, reduction of the crystallization rate as consequence of the nanoclay presence in the polymeric matrix has also been reported.[2]

Poly(p-dioxanone) (PPDO) is a biodegradable and biocompatible poly(ester-alt-ether) that is a good candidate to be used as matrix polymer since its properties, such as mechanical strength, flammability and gas permeability, can be enhanced by clays. Among the different clays layered double hydroxides (LDHs), also known as anionic clays, are of particular interest for biocompatible polymers due to their nontoxic components. The effect of the addition of some fillers like boron nitride, talc and hydroxyapatite on crystallization process of PPDO has been analysed by Müller,[3] concluding that polymer/filler interactions affect the nucleation behavior. However, no reports on the isothermal crystallization of PPDO in presence of LDH have been reported.

In this work the isothermal crystallization behavior of nanocomposites of poly(p-dioxanone) and unmodified or organically modified layered double hydroxides was investigated in order to know the effect of nanoclay on the morphology and crystallization properties of nanocomposites.

Experimental Part

The LDH was organically modified with sodium dodecyl sulphate (DDS) using restacking method. Nanocomposites of PPDO and unmodified LDH (PPDO/LDH) and LDH modified with DDS (PPDO/LDH-DDS) were prepared by melt-extrusion (5 wt% LDH). The obtained nanocomposites have an intercalated-exfoliated morphology as it was

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discussed in a previous paper.[4] Isothermal crystallization behavior of PPDO was analyzed by dynamic scanning calorimetry (DSC). The samples were first heated to 140 °C to erase previous thermal history and then quickly cooled (at 80 °C/min) to the desired crystallization temperature (T_c) where the isothermal DSC scans were registered till apparently the crystallization concluded. Then the samples were heated up to 140 °C at a scan speed of 10 °C/min. Spherulitic morphology of PPDO and its nanocomposites was studied by Polarized Optical Microscopy (POM).

Results and Discussion

Isothermal Crystallization

The effect of LDH on the isothermal crystallization behavior of PPDO was analyzed by DSC. The development of relative crystallinity (X_t) with time during the isothermal crystallization process for neat polymer and both nanocomposites was analyzed using the Avrami equation. It was observed that X_t increased faster for neat PPDO than for nanocomposites, being PPDO/LDH the sample that crystallizes more slowly (Figure 1). The calculated values of the Avrami parameter *n* (from 2 to 3) of the nanocomposites showed similar trends than that of unfilled PPDO. This result points out that the presence of the nanoclay does not induce a significant change on the crystallization mechanism.

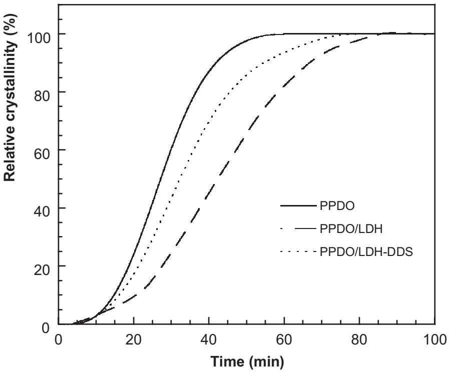

Figure 1.
Variation of relative crystallinity with crystalization time for neat PPDO and its nanocomposites at crystallization temperature of 82 °C.

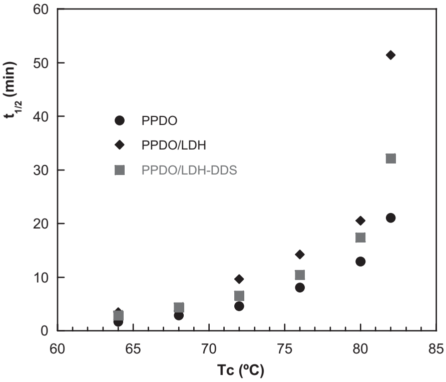

Figure 2.
Temperature dependences of $t_{1/2}$ for neat PPDO and its nanocomposites at various crystallization temperatures.

A parameter that is usually utilized to describe the overall rate of crystallization is the half-crystallization time $t_{1/2}$, defined as the time required to reach 50% of the complete crystallization. The $t_{1/2}$ values obtained from DSC curves recorded during the isothermal crystallization for pure PPDO and its nanocomposites are shown in Figure 2. It can be seen that the crystallization rate was slower in presence of nanoclay in the investigated temperature range. At low crystallization temperatures the nanoclay effect on $t_{1/2}$ is not important, however when T_c increases the difference between pure polymer and nanocomposites increases. These results are in good agreement with those found in nonisothermal crystallization.[4] At a given T_c, the increase in $t_{1/2}$ by LDH addition could result from two possible events: the first is the reduced nucleation while the other is the decrease in the crystal growth rate.

Melting Behavior

DSC melting curves of the samples are shown in Figure 3. PPDO nanocomposites showed a melting behavior similar to neat PPDO[3] with melting-recrystallization mechanism. Two melting endotherms appear, the first one (T_{m1}) changes in

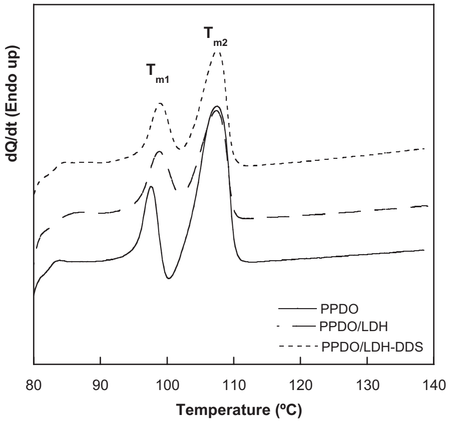

Figure 3.
DSC thermograms of PPDO and its nanocomposites after isothermal crystallization at $T_c = 80\,°C$ at a heating rate of 10 °C/min.

magnitude and position respect to the second one (T_{m2}), shifting to higher temperature with increasing T_c (Figure 4). The second one is practically maintained at a constant temperature.

In the case of the nanocomposites, it was observed (Figure 4) that the melting peaks (T_{m2}) shifted slightly to lower temperatures, indicating than more imperfect crystals are present comparing to neat PPDO. This is probably due to the presence of more heterogeneous nucleation induced by LDHs and more restriction of PPDO polymer chains to pack between LDH, leading to less perfect crystals. Nevertheless, the equilibrium melting temperature T_m^0 which can be estimated extrapolating the linear T_m vs T_c data until intersection with $T_m = T_c$ line, according to Hoffman and Weeks equation (Figure 4)[5] show practically the same value of T_m^0 within the experimental errors for unfilled PPDO and its nanocomposites. This observation can be explained assuming that higher degrees of recrystallization occur in PPDO/LDH nanocomposites.The value obtained for $T_m^0 = 115\,°C$ is in good agreement with that obtained by Pezzin et al.[6]

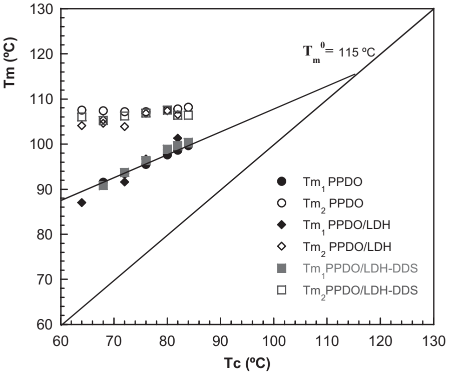

Figure 4.
Hoffmann and Weeks plot for PPDO and its nanocomposites.

Morphology and Spherulite Growth Rate

Optical observations of the crystallization showed that a spherulitic morphology exhibiting the classical Maltese-cross pattern was developed for neat PPDO as its nanocomposites (Figure 5). The concentric bands observed in PPDO spherulites attributed to lamellar crystal twisting are also observed in PPDO nanocomposites. The frequency of these bands is higher in nanocomposites than in neat PPDO, probably as consequence of strong hindrance for spherulite formation. In addition, comparing with the double banding morphology observed in neat PPDO, the nanocomposites showed a single banding.

However, smaller spherulites were observed for PPDO nanocomposites as consequence of an increase in the nucleation density promoted by the well dispersed LDH layers (Figure 6).

A linear increase of spherulite radius with the time of crystallization before impingement of spherulites was observed for all samples. The spherulite growth rate G was measured from the slope of radius vs crystallization time. Figure 7 shows the dependence of G with T_c for neat and PPDO nanocomposites. For both neat and PPDO nanocomposites G decreased when increasing T_c in the temperature range 64–84 °C, suggesting a nucleation-controlled growth. The spherulite growth rate of PPDO decreased approximately 2-fold by the presence of the clay for both nanocomposites. This result indicates that the

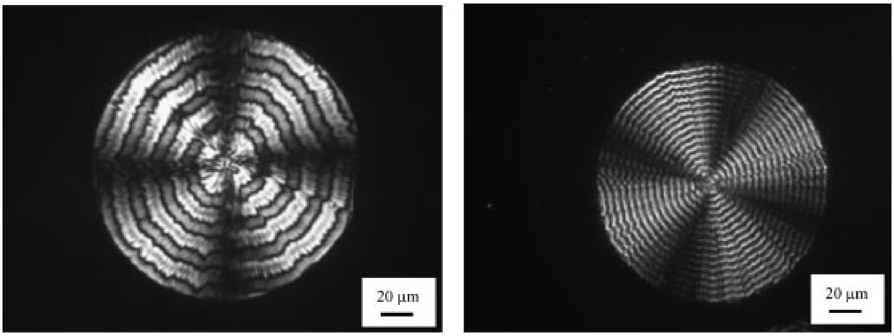

Figure 5.
POM images of neat PPDO (left) and PPDO/LDH nanocomposite (right) (bar = 20 μm).

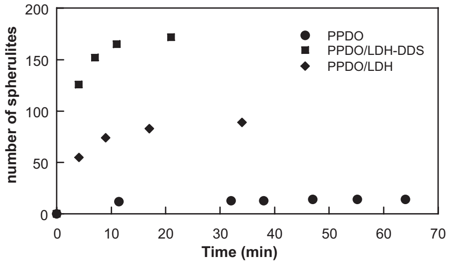

Figure 6.
Number of spherulites at $T_c = 80\,^{\circ}C$ for PPDO and its nanocomposites.

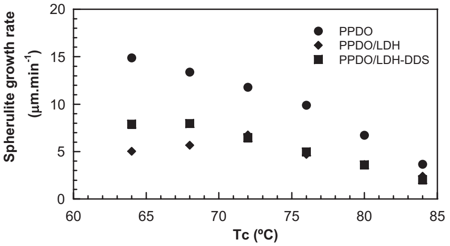

Figure 7.
Spherulite growth rate of PPDO and its nanocomposites.

LDH concentration used (5 wt%) provide restriction to mobility and diffusion of PPDO chains to crystal growth fronts.

Conclusion

Nanocomposites of poly(p-dioxanone) (PPDO) with unmodified and organically modified layered double hydroxide (LDH) have been prepared by melt extrusion method. It has been observed that the presence of unmodified or modified LDH does not induce any change on the crystallization mechanism, whereas it has a significant influence on the spherulitic morphology of PPDO. In addition, although the nanoclays have a nucleation effect a decrease of the spherulite growth rate was observed as consequence of the restriction to the polymer chain movement induced by the nanoclays.

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