Influence of processing conditions on the optical and crystallographic properties of injection molded polyamide-6 and polyamide-6/montmorillonite nanocomposites

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This paper presents a study of the crystallographic and optical properties of injection molded samples of neat polyamide-6 (NPA6) and polyamide-6/montmorillonite nanocomposites (PA6-Mt) cooled at different temperatures (40, 60, 80 and 100 °C). Montmorillonite filler prevents the solid-to-solid phase transition \(\alpha \rightarrow \gamma\) of polyamide-6 crystals at -90 °C by stabilizing the metastable \(\gamma\) structure. This \(\gamma\) structure presents higher crystal symmetry (pseudo-hexagonal) favoring epitaxy with the montmorillonite nanoplatelets, which also display hexagonal morphology. Moreover, the montmorillonite does not affect the optical clarity of the reinforced polymer since its thorough exfoliation promotes smaller crystallite size.

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1. Introduction

Clay polymer nanocomposites (CPN) have been widely used for industrial applications since Toyota introduced the first polymer/clay auto parts in the 1980s (Okada et al., 1987). The enhancement of mechanical (Hong et al., 2005), thermal (Chung et al., 2008), barrier (Vora and Vora, 2006; Xu et al., 2006) and other properties of nanocomposites compared to neat polymer has been related to the close interaction between the polymer matrix and the organically modified clay minerals. Moreover, it is also related to the level of exfoliation of the clay in the matrix (Mohanthy and Nayak, 2007; Wang et al., 2008). In terms of scratch resistance, the presence of clay promotes the formation of brittle cracks. However, with no clay filler, plastic flow controls the scratch damage in neat polyamide-6 with large residual depths (Dasari et al., 2008).

In the case of injection molded semi-crystalline polymers, crystal properties are highly influenced by processing conditions (Van der Beek, 2005). With increasing cooling rate and constant pressure, the transition from melt shifts towards lower temperature. Furthermore, an increasing cooling rate augments the specific volume and consequently decreases the degree of crystallinity. On the other hand, Kamal et al. (2002) reported that the compression heating is significant at higher crystallization pressures, so that crystallization begins at higher temperature than the experimental crystallization temperature. Additionally, the presence of clay in nanocomposites induces the crystallization of \(\gamma\) phase of polyamide-6 preferentially over the more stable \(\alpha\) phase, which also partially modifies the mechanical properties of the material (Fornes et al., 2002). Moreover, the literature reports that the epitaxial nucleation of the polymer on the clay surface (i.e. montmorillonite) induces the formation of the less stable \(\gamma\) structure. The explanation for the epitaxial mechanism is the good correspondence between the disposition of the amide groups in the polyamide-6 and the OH groups in the basal plane of the montmorillonite along its [001] direction. In fact, epitaxy triggers the formation of H-bonds between amide and OH ions and further stabilizes the CPN structure (Yebra-Rodriguez et al., 2009b).

Recent literature reports the benefits of such materials also in optical devices (De Paiva et al., 2007; Kelarakis and Yoon, 2008; Ritzhaupt-Kleissl et al., 2006). Indeed for some industrial applications, it is crucial to improve toughness without diminishing optical clarity. For high translucency, the filler should have an average size smaller than the wavelength of visible light (i.e. 400–800 nm). Translucency is associated with a good level of exfoliation of the clay fillers in the polymer matrix; indeed light is not deflected due to the small size of...
clays. Nanocomposites manufactured with clay nanoparticles are usually transparent up to a certain weight percent even though a similar matrix with similar weight percent of larger particles (not clays or clay minerals) can be less transparent (Park and Chang, 2009). Moreover, the level of translucency in polyamide thin films is not affected significantly by increasing the organoclay content up to 1.0 wt % (Jin and Chang, 2008).

In this paper, the crystallographic properties of neat polyamide-6 and polyamide-6/montmorillonite nanocomposites were evaluated. Samples were injection molded and afterwards cooled at different cooling temperatures to simulate industrial manufacture. We also examined their translucency to establish the dependence on the cooling temperature after injection molding. To avoid skin-core effects (Yebra-Rodríguez et al., 2009a), plates of 1 mm thickness were investigated.

2. Experimental

2.1. Materials

The samples of neat polyamide-6 (NPA6 samples) and polyamide-6/montmorillonite nanocomposites (PA6-Mt samples) were manufactured with commercial unreinforced polyamide-6 (Ultradur® BASF A.G.) and an organically modified montmorillonite (Cloisite 30B®, Southern Clay Products, Inc.).

The nanocomposites (polyamide-6 with 5% wt. organically modified montmorillonite) were obtained by melt intercalation in a double screw extruder (250 rpm, 250 °C), and afterwards injection molded in a Krauss Maffei KM 250/900B with a flow velocity of 95 mm/s at a pressure of 170 MPa and 280 °C in the cylinder of the extruder. Samples of NPA6 and PA6-Mt were injected into plates with 1 mm thickness at 40, 60, 80 and 100 °C tool temperatures. The pure polyamide was also extruded prior to injection in order to guarantee identical preparation conditions (stress and temperature treatment during processing) as in the PA6-Mt plates.

2.2. Characterization

Differential Scanning Calorimetry (DSC) analyses were carried out with 10 mg samples after drying by vacuum heating at 80 °C during 48 h in a DSC 822e (Mettler Toledo). The heating rate was 20 °C/min over a temperature range of 25–270 °C. Crystallinity indices (Wc) were calculated from the ratio between the enthalpy of melting (ΔHm) and that of a fully crystalline sample, as described in Mehta (1999).

The orientation study of polyamide-6 crystals in the plates was performed in a single-crystal diffractometer SC-XRD Smart APEX D-8 Bruker (Karlsruhe, Germany). Samples were aligned perpendicular to the incident X-ray beam and parallel to the CCD area detector. For each sample, a transmission diffraction pattern was recorded using MoKα radiation and the following experimental conditions: 50 kV acceleration voltage, 30 mA filament current, 0.5 mm collimator diameter, 30 s exposure time and 60 mm distance to detector. The two dimensional X-ray diffraction (2D-XRD) patterns were analyzed using the XRD2D Scan Software (Rodriguez-Navarro, 2006). This software was also used to convert the 2D patterns into the equivalent 1D powder diffractograms (e.g. 2θ scans). Information regarding the crystalline phase composition of the polyamide-6 crystals, and degree of preferential orientation was inferred from the 2D patterns and the calculated powder diffraction patterns. The orientation and delamination of the montmorillonite nanoplatelets were observed in a Transmission Electron Microscopy (TEM) Zeiss EM 902 operating at 80 kV. For that purpose, ultra-thin sections (ca. 50 nm) were obtained at cryo-temperature (-80 °C) using a Leica Ultracut E microtome equipped with a diamond knife. The sections were placed in a formvar/carbon-coated copper grid and stained with osmium tetroxide (OsO₄) to enhance phase contrast.

Color measurements were made using a spectroradiometer SpectraScan PR-704, Photo Research Inc. (Chatsworth, USA), with a 4% measurement accuracy and standard deviation of repeat measurements over a 15-minute period less than 0.1% (Pérez et al., 2000). Samples were located in a color assessment cabinet (CAC portable, Verivive Limited, Leicester LE3 5AG, England), and irradiated with a source simulating the relative spectral irradiance of CIE standard illuminant D65. Illuminating/viewing configuration was CIE d/0° geometry, and the CIE 1964 10° supplementary standard colorimetric observer was employed. Three sets of L*, a*, b* values (color coordinates in CIELAB) of each sample were obtained, and then averaged to establish a single set of values for each sample. The resulting standard deviations were lower than the instrumental accuracy (4%).

3. Results and discussion

The X-ray Diffraction (XRD) results are shown in Fig. 1. In agreement with the literature, the thermodynamically more stable α structure is prominent in the NPA6 samples, whereas the Mt-PA6N samples show the less stable γ, irrespective of the tool temperature after the molding process (Forne et al., 2002; Giannelis, 1996; Kojima et al., 1993; Liu et al., 1999; Wang et al., 2007; Yebra-Rodríguez et al., 2009a and references therein). The crystallinity index related to the full width at half maximum (FWHM) was obtained from (001) reflections for the polyamide-6 crystals (002) reflection for the

![Fig. 1. Diffractograms of NPA6 and PA6-Mt samples. Note that stable polyamide-6 α structure is noticeable in NPA6 samples and less stable γ is prominent in Mt-PA6N samples.](Image)
polyamide-6 α crystals in NPA6 samples and (001) reflection for the polyamide-6 γ crystals in PA6-Mt samples (Table 1). In both NPA6 and PA6-Mt samples crystallinity enlarged with increasing temperature for the (001) reflection. However, PA6-Mt samples present higher crystallinity than NPA6 samples (i.e. lower FWHM index values), irrespectively of the processing conditions (i.e. cooling temperature after injection molding). Therefore α and γ crystals enhanced their crystallinity as the temperature increased. The crystallization process consists of two steps: nucleation and crystal growth. Nucleation occurs in the melt or in solution, when the molecule is transformed to a compact chain-folded state. During the crystal growth, the polymer chains approach the nuclei and partially attach to the crystal surface where they reorganize by chain-folding (Mandelkern, 2002). Considering that the polymer chains are continuously adsorbed to the growth surfaces during the growing process, the crystallinity values will be enhanced by: (1) longer time in the melting state, or (2) reduced differences between the melting and moulding temperature. By contrast, rapid cooling from the melt leads to either a fully amorphous or a poorly crystallized state.

Similar results were obtained on the basis of DSC. Fig. 2 displays one melting peak during the heating process for the NPA6 samples (α structure at ca. 222 °C) and two for the PA6-Mt samples (at ca. 210 and 222 °C, respectively corresponding to the γ and α structures). Table 1 shows that the crystallinity values (Wc) calculated from DSC improve with increasing injection molding temperature in the neat polymer, and slightly in the nanocomposite samples. As revealed in Fig. 2, NPA6 samples show a shoulder in the DSC melting plot starting at around 90 °C, corresponding to a solid-state reaction α → γ. Previous work in this laboratory demonstrated a non isothermal transformation of the polyamide-6 crystals in absence of montmorillonite filler, taking place at around 90 °C, with no amorphization process before the melting T is achieved (Yebra-Rodríguez et al, 2009b). The H-bond angle in the α structure (173°, Malta et al., 1979) is closer to linearity than in the γ structure, where the H-bonds are formed between parallel chains as a consequence of contraction of the c axis during the α → γ transition (Bradbury et al., 1965). We can assume that the H-bonds in the polyamide-6 α structure are weaker than those of the γ structure and therefore relax at the onset of mobility of the chain segments in the amorphous and the crystalline regions occurring at ca. 90 °C. On the other hand, the shoulder at around 90 °C is less evident in the PA6-Mt samples (even absent at the highest tool temperature). This should be attributed to the montmorillonite that impedes the shifting of H-bonds associated with the crystallization of the thermodynamically more stable α structure, especially in the samples with the lowest cooling rate after the injection molding process. The organized layered montmorillonite nanoplatelets impose some spatial confinement on the crystalline nucleation which produces a defined polyamide-6 crystal structure.

Additionally, Fig. 1 reveals that only in NPA6 samples the (00L) reflections did 2θ values shift to lower 2θ values (i.e. higher dhkl) with increasing cooling temperature and crystallinity, due to a dilatation of the lattice parameters. On the contrary, in PA6-Mt samples, the polyamide-6 crystals fit the montmorillonite through an epitaxy phenomenon, implying a residual stress in the crystal structure (Yebra-Rodríguez et al., 2009b). Dilatation of the lattice in NPA6 samples makes possible the reorganization of the polyamide-6 into crystals with higher symmetry, i.e. from polyamide-6 monoclinic (lower symmetry) α crystals towards polyamide-6 pseudo-hexagonal (higher symmetry) γ crystals, even though the γ structure is thermodynamically less stable. A heterogeneous nucleation of polyamide-6 crystals on the montmorillonite in PA6-Mt samples should stabilize the crystal structure of the polyamide-6-γ even with varying processing temperatures. Additionally, the increase in crystallinity observed in the PA6-Mt samples must be due to the nucleation of polyamide-6 crystals on the clay surfaces which facilitates the development of a higher degree of crystalline ordering. More importantly, it should be remarked that the basal planes of montmorillonite show a pseudo-hexagonal symmetry which could trigger the nucleation of pseudo-hexagonal γ crystals by epitaxy. Montmorillonite platelets also have a great influence on the orientation of polyamide-6 crystals subjected to an injection molding process. The 2DXRD pattern for all NPA6 samples exhibit only one Debye–Scherrer ring resulting from a homogeneous intensity produced by randomly orientated polyamide-6 crystals. As an example, Fig. 3 shows the ring corresponding to a 40 °C tool temperature. On the contrary the PA6-Mt samples exhibit two Debye-Scherrer incomplete rings (arcs). The disposition of these arcs indicates that polyamide-6 crystals have a preferential orientation defined by the flow direction. As the degree of preferred orientation of crystals increases, the reflections are concentrated in smaller arcs. These results suggest that the preferential orientation in PA6-Mt samples should be caused by the presence of montmorillonite. Presumably during the molding process the montmorillonite platelets aligned parallel to the (h00) planes of the polyamide-6 crystals, thus inducing the occurrence of the γ structure. Similar behavior was observed when examining the nanocomposite samples on the basis of TEM. The

Table 1
Calculated crystallinity index on the basis of XRD data (FWHM index) and DSC data (Wc index, according to Mehta, 1999). 2θ position corresponds to the (002) reflection for the polyamide-6 α crystals in NPA6 samples and to the (001) reflection for the polyamide-6 γ crystals in PA6-Mt samples.

<table>
<thead>
<tr>
<th></th>
<th>2θ (00L)</th>
<th>FWHM index</th>
<th>Melting peak (°C)</th>
<th>Wc index (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NPA6 40 °C</td>
<td>10.73</td>
<td>6.10</td>
<td>224.25</td>
<td>27.19</td>
</tr>
<tr>
<td>NPA6 60 °C</td>
<td>10.35</td>
<td>5.80</td>
<td>222.74</td>
<td>28.34</td>
</tr>
<tr>
<td>NPA6 80 °C</td>
<td>10.19</td>
<td>5.40</td>
<td>222.08</td>
<td>29.09</td>
</tr>
<tr>
<td>NPA6 100 °C</td>
<td>9.27</td>
<td>5.30</td>
<td>222.86</td>
<td>29.86</td>
</tr>
<tr>
<td>PA6-Mt 40 °C</td>
<td>9.88</td>
<td>4.80</td>
<td>221.20</td>
<td>28.03</td>
</tr>
<tr>
<td>PA6-Mt 60 °C</td>
<td>9.88</td>
<td>4.66</td>
<td>221.00</td>
<td>28.16</td>
</tr>
<tr>
<td>PA6-Mt 80 °C</td>
<td>9.81</td>
<td>4.55</td>
<td>223.08</td>
<td>28.57</td>
</tr>
<tr>
<td>PA6-Mt 100 °C</td>
<td>9.88</td>
<td>4.44</td>
<td>222.52</td>
<td>28.18</td>
</tr>
</tbody>
</table>
images of PA6-Mt samples are displayed in Fig. 4, where preferential orientation (not completely but highly oriented) can be observed. However, the complete exfoliation of the montmorillonite can be assumed due to the absence of montmorillonite stacks in the TEM images, as well as the lack of XRD peaks in the 2theta region below the diagnostic peaks of the polyamide-6 (corresponding to the organically modified montmorillonite).

Regarding optical properties, in this work we are particularly interested in translucency. Two parameters are usually employed to specify translucency: the contrast-ratio (Kim et al., 2006; Patton, 1961) and the translucency parameter (TP). This latter is more employed to specify the translucency of all types of composites (Ahn and Lee, 2008; Woo et al., 2008). This parameter is defined as the color-difference between the measured colors when the sample is placed on two neutral backgrounds, i.e. black and white. Fig. 5 shows the TP% values of both sets of samples. TP values are systematically higher for the NPA6 samples than for PA6-Mt samples, due to the presence of montmorillonite as reinforcing filler (5% wt.). In the pristine polymer translucency diminished with increasing cooling temperature (20.13 CIELAB units at 100 °C up to 44.02 CIELAB units at 40 °C), whereas no significant variation was observed in the nanocomposite samples (18.26 CIELAB units at 40 °C up to 21.21 CIELAB units at 100 °C). Nonetheless beginning at around 100 °C it is observed that the optical clarity of the polymer matrix is not sacrificed in spite of the presence of the montmorillonite filler. Translucency is correlated to the crystallite size of materials (Asuka et al., 2006). Since crystallite size of the polyamide-6 crystals can be related to the cooling temperature (higher temperature implies bigger crystallite size, Lisbão Simal and Regina Martin, 1998), it appears that the montmorillonite stabilizes the crystallite size (and thus optical properties), irrespective of the processing conditions.

4. Conclusions

This study provides useful insights into the mechanisms controlling the degree of crystallinity, preferred orientation of crystals, and optical properties in polyamide-6 and polyamide-6/montmorillonite nanocomposites. In contrast to NPA6 samples, the crystallinity degree of PA6-Mt increases with rising tool temperature after the injection molding process. Moreover, the presence of montmorillonite in the nanocomposites triggers the crystallization of the metastable γ phase – instead of the α phase – thus avoiding a non desirable solid-to-solid phase transition α → γ at around 90 °C. In NPA6 samples, the lattice of the polyamide-6 dilates with increasing cooling temperature. These data corroborate the conversion of α to γ structure in the pristine polymer at temperatures below melting by switching into a higher symmetry class. In the nanocomposites the montmorillonite nanoparticles yield to a better orientation of the polyamide-6 crystals, which it is known to be directly related to enhancement of mechanical properties.
Our results reveal that translucency of the nanocomposite samples is connected to the good exfoliation of the montmorillonite. Indeed this fact biases the clay to work as nucleating agent and thus stabilizes the crystallite size, irrespective of the cooling temperature after the injection molding process.

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