

Crystallization Behavior and Thermal Properties of Montmorillonite/Polyamide-6 Nanocomposites

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INTRODUCTION.

Nanocomposite materials consisting of exfoliated clay nanolayers (usually montmorillonite) in a polymeric matrix show extraordinary physical properties suitable for advanced industrial applications (Wang et al., 2004; Aranda et al., 2006; Ray et al., 2006, Vora and Vora, 2006). The mechanical and thermal properties of the pristine polymers and polymer-clay nanocomposites strongly depend on crystal properties (Yebra et al., 2008).

Polyamide-6 crystallizes in three possible structure types: α , γ , or β . The stable monoclinic α organizes in planar zigzag chains, whereas the metastable pseudo-hexagonal γ is arranged within a twisted chain. The β structure is less well identified and considered to be an intermediate stage between the other two forms.

In this work the crystal changes in polyamide-6 crystals in response to temperature are studied with a view to assessing its thermal stability. X-ray thermodiffraction is a functional and powerful tool used in many researches related to material science as well as geology, archeometry, chemistry and metallurgy among others (Barre et al., 2006; Cardell et al., 2007). One of the major objectives of this research is to evaluate the potential of the combined use of X-ray thermodiffraction (XRTD), thermogravimetry (TG) and differential scanning calorimetry (DSC) to study the mechanism of crystallization on polyamide-6 and montmorillonite/polyamide-6 nanocomposite due to temperature transitions. For this purpose, injection molded samples of polyamide-6 (PA6) and montmorillonite reinforced

polyamide-6 nanocomposites (PA6-MMT) were used.

MATERIALS AND METHODS.

Injection molded plates of polyamide-6 (PA6) and polyamide-6/montmorillonite nanocomposites (PA6 MMT) were manufactured with commercial polyamide-6 (Ultramid®) and a montmorillonite modified with methyl tallow bis-2-hydroxyethyl quaternary ammonium chloride (Southern Clay Products, Inc.). The nanocomposites were obtained by melt intercalation of the montmorillonite in the polyamide-6 matrix using a double screw extruder (250 rpm, 250 °C). The pure polyamide was also extruded to guarantee identical preparation conditions (stress and temperature treatment during processing) as in the PA6 MMT plates. PA6 and PA6 MMT were then processed in an injection molding machine (Krauss Maffei KM 250/900B) at 280 °C in the cylinder of the extruder and 60 °C tool temperature into plates with 2 mm thickness.

In situ XRD data were acquired on a Philips PW1710/00 X-ray diffractometer with PW1712 communication card via RS232 serial port and controlled by the X Powder PLUS software (<http://www.xpowder.com/>). The heating device was equipped with a Pt temperature probe, a precision T controller and a power regulator firing a halogen lamp (Philips Capsule-line Pro 75 W, 220 V) that provides up to 210 °C into the X-ray diffraction chamber. A detailed description of the heating system is described elsewhere (Correcher et al 2006). The X-ray diffraction patterns were scanned over $3^\circ < 2\theta < 30^\circ$ range, with 0.1 goniometric rate and 0.4 s. integration

time. Background of diffraction patterns was subtracted. Scan mode was continuous using Cu $K\alpha_1$ radiation ($\lambda = 1.5406 \text{ \AA}$). Voltage was 40 kV, and tube current 40mA.

Thermal analysis were performed by DSC and TG (Mettler TA-3000 system) after drying by vacuum heating at 80 °C during 48 h (heating rate: 20 °C/min over a temperature range of 25 - 270 °C).

RESULTS AND DISCUSSION.

The X-Ray thermodiffraction results indicate that the polyamide-6 crystal structure is largely dependent on the montmorillonite attendance. The thermodynamically more stable α structure is prominent in the PA6 sample (Fig. 1), whereas PA6 MMT exhibits only the peak of the less stable γ structure (Fig. 2). The analyses show a solid-state reaction at ca. 90 °C for PA6, which corresponds to a Brill transition. From this temperature the amount of α form decreased gradually in favour of γ form during heating to later on stabilized up to 210 °C. In this manner, the introduction of montmorillonite into the polymer matrix causes an increase in the thermal stability of nanocomposites, mainly composed of γ form crystals.

DSC analyses reveal similar crystal structures, with melting temperatures (T_m) of ca. 212 and 222 °C for γ and α structures, respectively. Nanocomposite sample shows a melting peak with a bimodal shape, suggesting the occurrence of both α and γ crystals. PA6 sample also exhibit a melting peak at ca. 210 °C. On the basis of these results, we found that the γ crystals grow preferentially near the surface of the montmorillonite layers, while the α

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develop where the nanolayers do not influence the chain conformation and folding of the polyamide-6. The α diffraction peaks of the PA6 MMT sample are masked by a sharp, intensive peak resulting from a nucleation effect of the nanolayers, while the double-peak of the α structure masks the underlying small peak corresponding to a scarce amount of γ crystals. Moreover, the heating process for PA6 displays a third endothermic peak at around 215 °C, most likely due to the occurrence of the β structure, as a transition between the α and the γ structure.

The DSC cooling process reveals that the crystallization temperature shifts from

ca. 187 °C for the neat polymer to ca. 179 °C for the nanocomposite. Taking into account the nucleating effect of the montmorillonite it is suggested that the strong interaction with the polyamide-6 molecules slow down the organization of the crystallites.

Thermogravimetric analyses prove that organic modified montmorillonite slightly enhances the thermal stability of the polyamide-6 by decreasing the rate of mass loss at high temperature, as a result from the shielding effect of the montmorillonite and the strong interaction between the organoclay and polyamide-6 γ crystals.

CONCLUSIONS.

Organic modified montmorillonite included into the polymer matrix, composed of polyamide-6, increases the thermal stability of the nanocomposite. The montmorillonite enhances the occurrence of γ crystals form, being the α structure the more thermodynamically stable crystal form in the absence of clay modified.

The singularity of the structural characteristics, chemistry, mechanics, dynamics and response of nanomaterials, comprising nanocomposites, constitutes a fitting experimental and conceptual background for the development and improve of emergent nanosciences.

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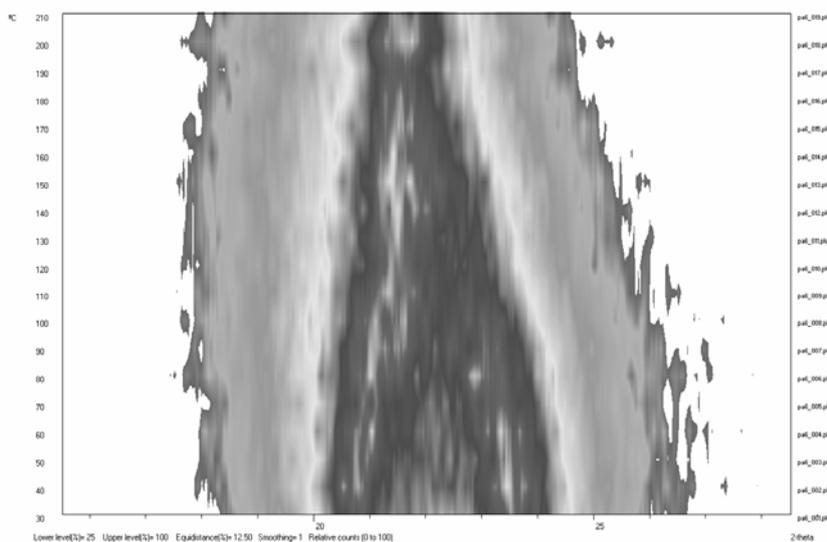


fig 1. XRTD mapping for polyamide-6 heating.

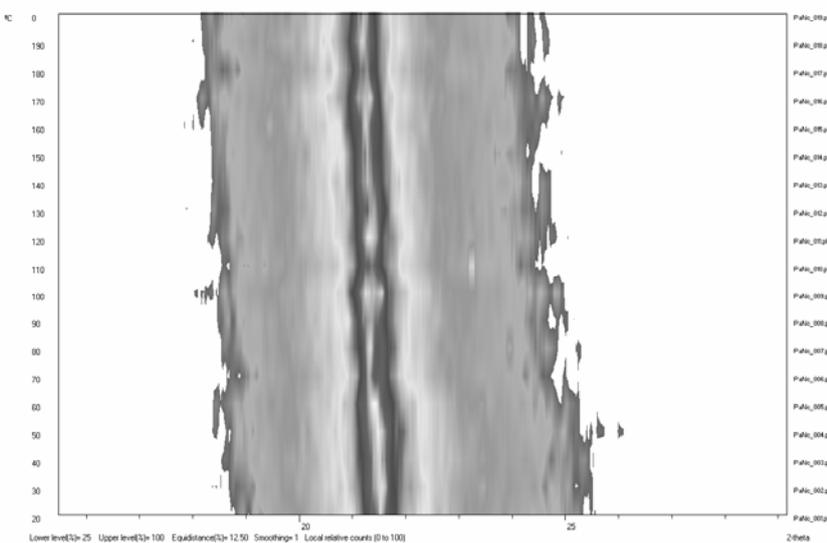


fig 2. XRTD mapping for montmorillonite/polyamide-6 nanocomposite heating.