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Sofia Vega

Abstract

Presentation

Poster

CRYSTALLIZATION AND MELTING MECHANISMS OF NYLON 6-NANOCLAY HYBRIDS

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Abstract

A study on the crystallization and melting mechanisms of poly (ϵ -caprolactam) [Nylon 6] nanoclay-hybrids is presented, using as a reference homopolymer Nylon 6. The effect of crystallization time was first studied, at constant crystallization temperature, in order to determine the most stable conditions before attempting melting studies after isothermal crystallization. After selecting the most stable isothermal crystallization conditions, unusual asymmetrical and truncated crystalline structures were observed in the case of the hybrids. Simulated melting diffraction patterns indicated the gradual evolution of truncated crystal structures. Optical observations under melting indicated step-like melting mechanisms in the hybrids similar to those of the reference homopolymer as an indication of similarities in both types of samples. Morphological characteristics and calculations indicated the typical evolution of Nylon 6 on melting and practically no change for the hybrids. The results allowed to conclude that nanoclay layers mainly influence crystal habits. An explanation is given for the development of truncated crystalline structures on the basis of the observed results.

Introduction

Polymeric nanocomposites are important because the introduction of nanometric particles causes a significant improvement in the overall properties of the polymer. Poly (ϵ -caprolactam) [Nylon 6] is an engineering polymer able to crystallize in at least two crystal habits, α and γ (Holmes *et al.*, 1955). It can be nanostructured with silicate layers through exchange chemical reactions, which render end-tethered polymer macromolecules to the substrate. It is therefore expected that the neat quiescent crystallization process be affected compared with the tethered system. The previous effects have both scientific and practical interests and will ultimately lead to understand and optimize the property-structure relationship in these systems.

In the present study, the crystallization and melting mechanisms of hybrid Nylon 6 were studied and compared with those of homopolymer Nylon 6. The main purpose was to understand the mechanisms involved on the crystallization and melting processes between both types of samples after isothermal crystallization under quiescent condition and linear heating.

Methodology

Nylon 6 homopolymer and Nylon 6 nanoclay-hybrids with 2 wt % (N6NCH2) and 5 wt % (N6NCH5) montmorillonite content were synthesized by Ube Industries, Japan, using ϵ -caprolactam and a modified montmorillonite. This last was prepared through cation exchange with 12-aminolauric acid (Usuki *et al.*, 1993). Nylon 6 homopolymer had an average-molecular-weight of 2.17×10^4 and the clay-hybrids N6NCH2 and N6NCH5 had average-molecular-weights of 2.22×10^4 and 1.97×10^4 respectively (Giannelis, *et al.*, 1999). All samples were originally in film form with an average thickness of 700 μm .

Differential scanning calorimetry (DSC) traces were obtained in a Perkin Elmer DSC-7 calorimeter. Calibrations were made with indium and lead standards covering all the thermal range of the studies before collecting thermal traces. Nylon 6 and the hybrids had an average weight of 8 mg. Samples were placed in aluminum sample holders, heated at 260 °C for 3 min under nitrogen atmosphere, and fast cooled at nominal cooling rate of 500 °C/min to the isothermal crystallization temperature (T_c) where they were maintained for 60 min. After this crystallization time, samples were linearly heated at 10°C /min until the equilibrium melting temperature (260 °C).

Wide Angle X-ray Diffraction (WAXD) patterns were obtained in a Siemens D-500 diffraction equipment. WAXD was used to identify crystalline structures of samples crystallized under identical conditions as in DSC, both before and after heating at specific temperatures. In this last case, samples were fast cooled after introducing the desired thermal history and some were heated up to specific temperatures before the quenching process took place.

Small Angle X-ray Scattering (SAXS) experiments were made in the in the X27C beamline at the National Synchrotron Light Source, Brookhaven National Laboratory, USA. The wavelength was 1.37 Å and a 3 pinhole collimation system was used to reduce the beam size to 0.6 mm in diameter. The 2D SAXS

patterns were taken on Fuji[®] imaging plates which were individually digitized. The sample to detector distance was 1400 mm.

Polarized Optic Microscopy (POM) was made in an Olympus BX60 optical microscope. This was used to register the morphology of the melting process after isothermal crystallization. The microscope was coupled with an Olympus PM-20 photographic system and two Mettler FP82HT hot stages with automatic control.

Results and Discussion

In the present study, the view is adopted that understanding melting after isothermal crystallization will lead to understanding the crystallization process of hybrids as long as there are enough complementary crystallization experiments. The DSC results in Figure 1 indicate that after isothermal crystallization at the selected temperature of 160 °C Nylon 6 and nanoclay hybrids develop different melting traces, which are affected by the crystallization time. In the homopolymer case in Figure 1(a) there is the typical multiple melting behavior. It starts with an apparent double melting and ends up with single melting after 1 hr of crystallization. The hybrid N6NCH2 in Figure 1(b) behaves different and develops a recrystallization exotherm and an almost imperceptible melting endotherm in all the range of crystallization time. As for the hybrid N6NCH5, Figure 1(c) shows a similar thermal behavior, there is the recrystallization exotherm and slightly better defined double melting behavior. Overall, the crystallization and melting process was time dependent in all three samples although it was rather similar in both hybrids. The different proportion in melting endotherms in Nylon 6 has been reported before (Medellín, *et al.*, 2004) as molecular weight dependent although in terms of crystallization temperature. The results in Figure 1 (d-f) also indicate that perfecting (higher peak intensity and truncation process (lack of a family of diffracting planes) and evolution between crystal structures (disappearance of reflections) were present, or took place, as a function of crystallization time. This was an indication of the unstable complex nature of the Nylon 6 hybrids so the highest crystallization time was selected in order to have the most stable morphology at the selected temperature to *in-situ* characterize the melting process.

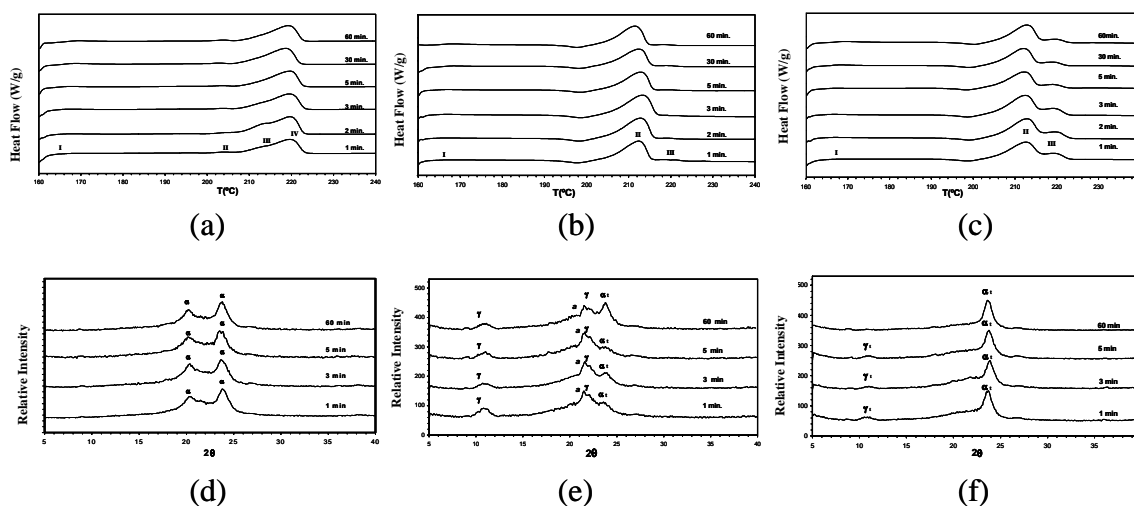


Figure 1. Melting behavior in terms of time of: (a) Nylon 6, (b) N6NCH2 and (c) N6NCH5. Diffraction patterns as a function of crystallization time of: (d) Nylon 6, (e) N6NCH2, (f) N6NCH5. The crystallization temperature was 160 °C

The *in-situ* melting process in terms of WAXD is shown in Figure 2. Other than a slight perfecting process on heating, the Nylon 6 homopolymer develops the typical α crystalline structure (Holmes, *et al.*, 1955). Both Nylon 6 hybrids on the other hand developed different behavior on heating, N6NCH2 started with a mixture of asymmetrical and a complex mixture of truncated crystal habits. These evolved with heating until the final formation of a single α_2 truncated crystal habit. N6NCH5 developed a single reflection

associated with the truncated α crystal structure which preserved characteristics on melting until the final recovery of a single truncated structure before melting, the molten state in these last two cases was highly oriented due to the presence of montmorillonite.

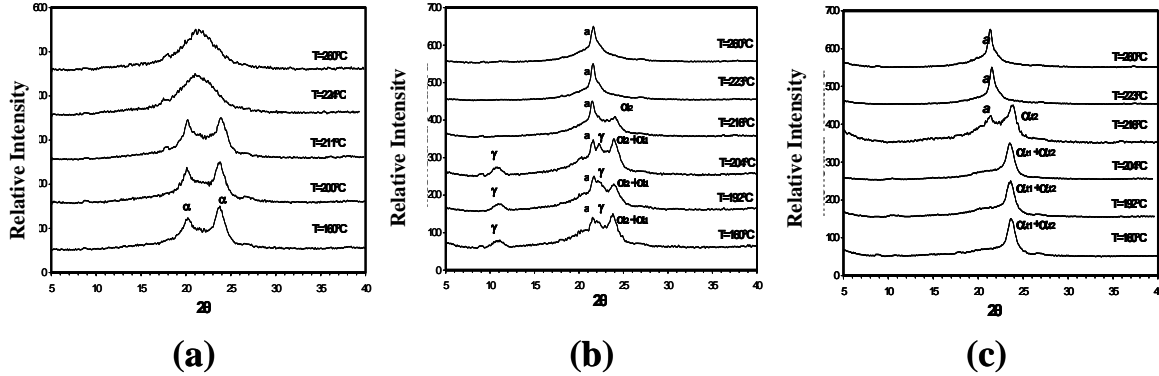


Figure 2. Diffraction patterns along the heating process of: (a)Nylon 6, (b) N6NCH2, (c)N6NCH5. The isothermal crystallization temperature and time were 160 °C and 60 min respectively.

The POM results in Figure 3 indicate that the melting process followed up step-like melting mechanisms such as in other polymeric systems (Medellín, *et al.*, 1996). This was the case both with the homopolymer and with the hybrids and was an indication that, in spite of the nanoclay presence, the crystallization process preserves the general morphological characteristics of homopolymers.

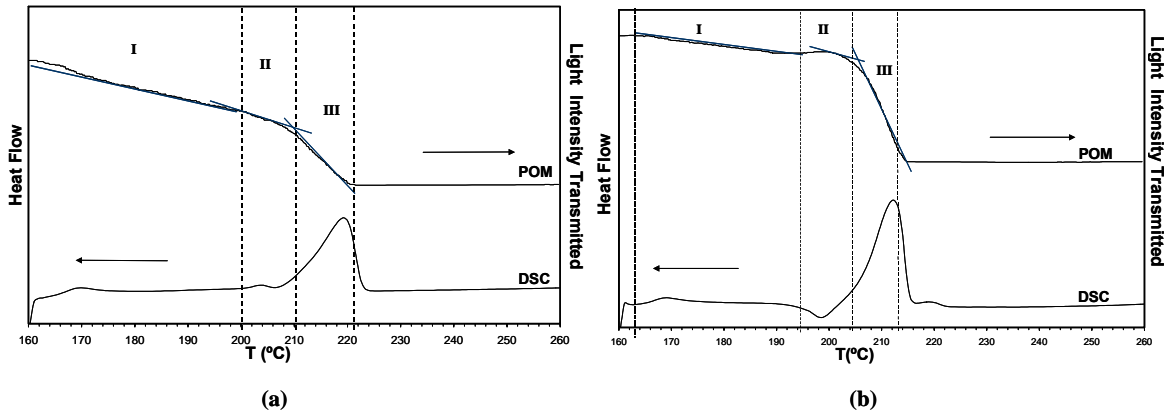


Figure 3. POM/DSC melting results after isothermal crystallization at 160 °C of: (a) Nylon 6 and (b) NCH2

The complex hybrid systems under study indicated that the observed effects could have intrinsically morphological features involved. Therefore, SAXS experiments were used in order to generate information regarding the morphological evolution on melting. It is well known (Liberti, *et al.*, 1968) that Nylon 6 is able to recrystallize to thicker crystals (and also perfect, as shown before) on heating. The recrystallization process on heating is observed as a decrease in the position of the scattering maximum and the perfecting process can be considered related to an increase of the SAXS invariant. The results in Figure 4 (a) and independent calculations, not shown here, indicated the typical evolution of Nylon 6. However, in the case of the hybrids Figures 4 (b-c) only show a decay of the scattering function as an indication of the lack of formation of periodical structures involving a correlation distance.

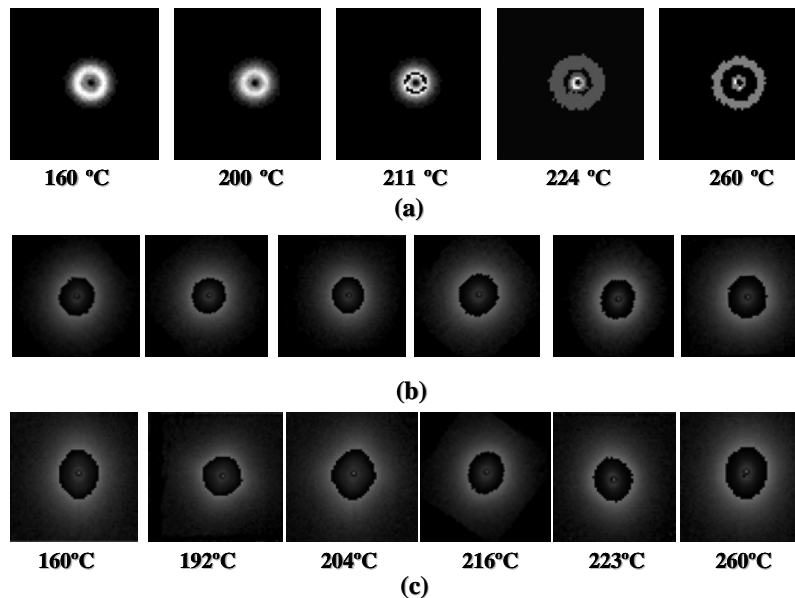


Figure 4. SAXS images corresponding to melting of: (a) Nylon 6, (b) N6NCH2 and (c)N6NCH5, isothermally crystallized at $T_c=160$ °C for 60 min.

On the basis of the previous results a crystallization mechanism for both hybrids can be proposed. Figure 5(a) illustrates the crystallization of hybrids with low nanoclay content. Step I shows the interaction between a montmorillonite layer and the polymeric chains. Step II indicates the beginning of the crystallization process under isothermal conditions. Step III shows the crystallization process where the formation of two crystal habits is involved asymmetrical γ , and a mixture of truncated α . The first structure must be formed by the vicinity of the polymeric chains attached to the montmorillonite layers, motivating hydrogen bonds between neighbor fully extended chains (Kyotani *et al.*, 1972). However if the crystallization time, or melting temperature, increase, the hydrogen bonds will break promoting the formation of folded-chain-like α_t crystal structures, which are thermodynamically more stable. Figure 5(b) shows the crystallization and evolution of the high montmorillonite content hybrids. In this case, the higher nanoclay content must decrease the number of tethered polymeric molecules per unit surface increasing as a consequence the space between molecules and promoting the folded-chain-like, although truncated, α crystals. Regarding the truncation process, it must be originated by the tethering process which impedes diffraction along specific planes such as the (100) of the α structure.

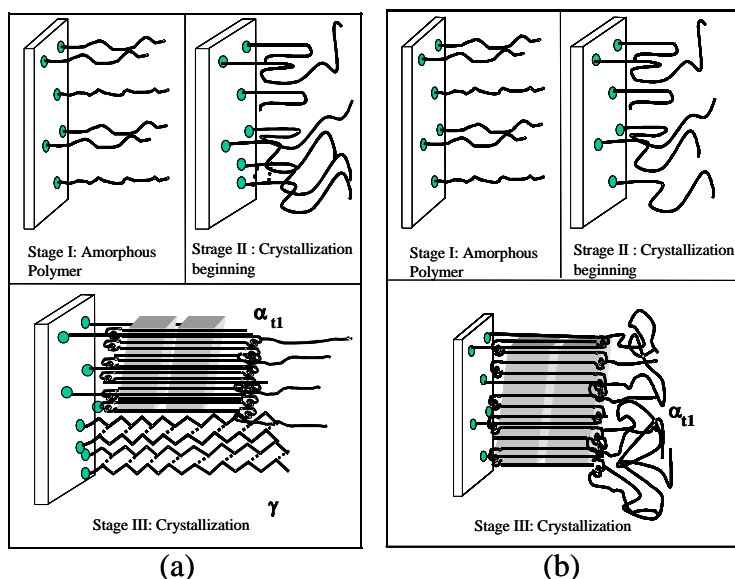


Figure 5. Crystallization Model of: (a) Nylon 6 with low and (b) Nylon 6 with high nanoclay content

Conclusions

The thermal crystallization and melting behavior of Nylon 6 homopolymers and end-tethered Nylon 6 nanoclay hybrids was modified by the nanoclay presence although only small differences were observed in thermal traces after increasing the nanoclay content.

On crystallization conditions there was the formation of atypical asymmetrical and truncated crystal structures. On melting such structures were relatively stable.

Hybrid crystals followed up step-like melting mechanisms as an indication of overall similarities with neat nylon 6 and the behavior of other macromolecules.

There was not apparent lamellar periodicity in the hybrids compared with neat Nylon 6.

The results allowed to propose a crystallization and melting mechanism for the hybrid complex systems

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Acknowledgements

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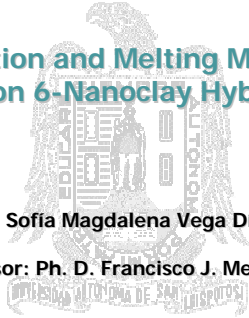
Universidad Autónoma de San Luis Potosí

Centro de Investigación y Estudios de Posgrado

“Crystallization and Melting Mechanisms of Nylon 6-Nanoclay Hybrids”

Sofía Magdalena Vega Díaz

Advisor: Ph. D. Francisco J. Medellín R.



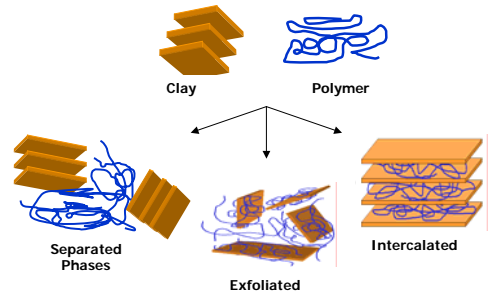
Outline

- ◆ Introduction
- ◆ Objective
- ◆ Methodology
- ◆ Results and Discussion
- ◆ Conclusions

Introduction

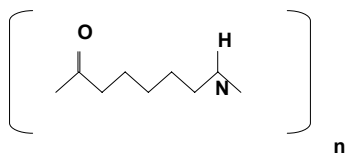
- ◆ Hybrid polymers, nanostructured materials with better physicochemical and mechanical properties
 - ◆ Reduce gas permeability (80 %)
 - ◆ Increase resistance to solvent attack
 - ◆ Decrease flame propagation (175 %)
 - ◆ Increase flexion and stress modules (110 %)
- ◆ Nanostructured polymers pose questions related to their behavior

Different Polymer-Clay Structures

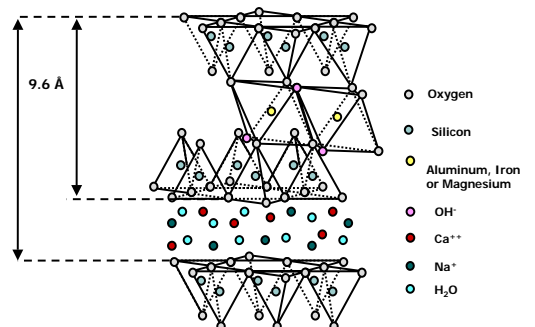


Nylon 6-Hybrid

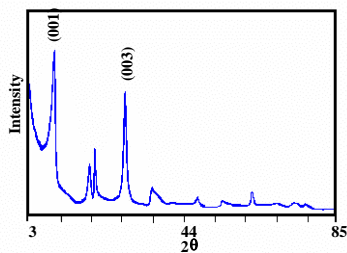
- ◆ Hybrid polymers: chemically bonded to the substrate
- ◆ Nylon 6-hybrid was developed in 1988 by Toyota
- ◆ Nylon 6 is an aliphatic polyamide which contains carboxyl and amide groups forming bifunctional monomers



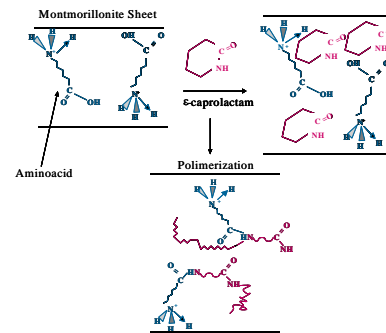
Montmorillonite Structure



Montmorillonite X-Ray Diffraction Pattern

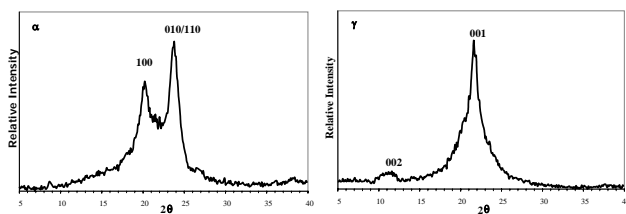


Scheme for the Nylon 6-Hybrid Polymerization Reaction



Nylon 6 Structures Without Additives

- ◆ Nylon 6 can form different crystalline structures because it has flexible chains



X-Ray diffraction patterns for the α and γ structures

Previous Results

- ◆ Kojima and Usuky (1994) determined the preferential orientation to γ form showing that the presence of anisotropic clay sheets made with silica are determinant on the orientation of Nylon 6-hybrid chains.
- ◆ Kojima (1995) proposed that the γ crystalline form has a planar orientation and this orientation increases with the clay content.

Objective

- ◆ Mathias and Davis (1999) and Medellín et al. (2001) reported that the presence of clay in Nylon tends to produce orientation in the polymer chains forming the γ crystalline structure in a preferential pathway
- ◆ Wu et al. (2002) found in Nylon 6-hybrid only one diffraction peak for the α structure in one plane

- ◆ Analyze the crystallization and melting mechanisms of Nylon 6 in the presence of nanoclay

Materials

- Materials: Nylon 6 homopolymer, Nylon 6-hybrid with 2% and 5% w/w montmorillonite content from Ube Industries, Japan

Montmorillonite content (%)	Average Molecular Weight (g/mol)	Code Name
0	2.17×10^4	Nylon 6
2	2.22×10^4	N6NCH2
5	1.97×10^4	N6NCH5

Methods

- DSC: Perkin Elmer 7 equipment
- WAXD: Siemens modelo D-500 equipment
- POM: Olympus model BX60 equipment, Hitachi digital camera model KP-D50, Mettler ZUFP82HT photomonitor, Mettler FP82HT heating platines
- SAXS: Center for Small Angle Reserch at the National Laboratory in Oak Ridge, Oak Ridge TN. USA.

Results and Discussion

Finding optimal conditions for characterization

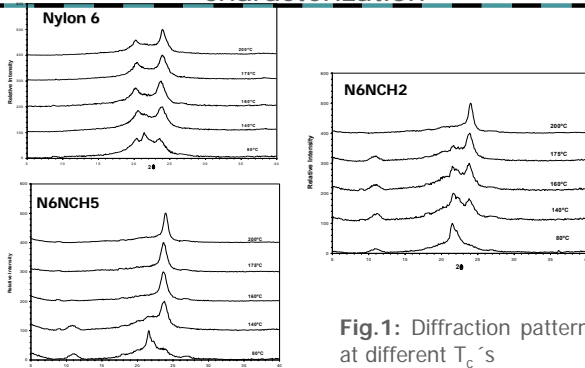


Fig. 1: Diffraction patterns at different T_c 's

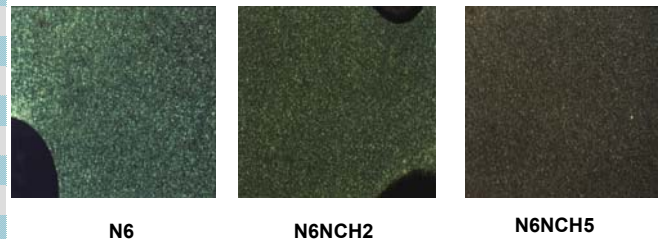


Fig. 2: Morphology for all the samples during isothermic crystallization at 160 °C

Systematic Analysis of Melting Process

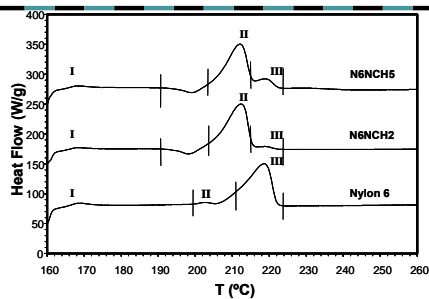


Fig. 3: Melting process for all the samples isothermally crystallized at 160 °C

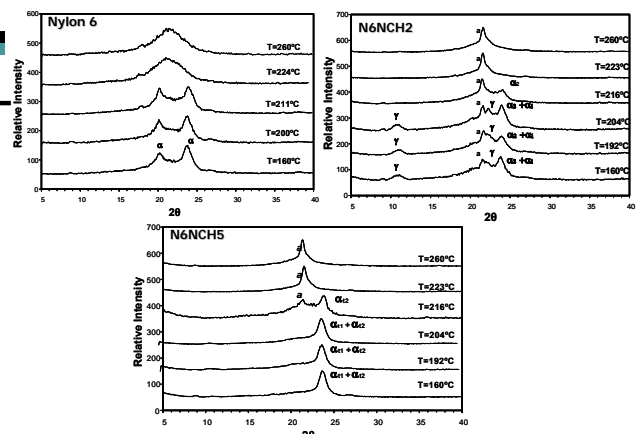


Fig. 4: Diffraction Patterns

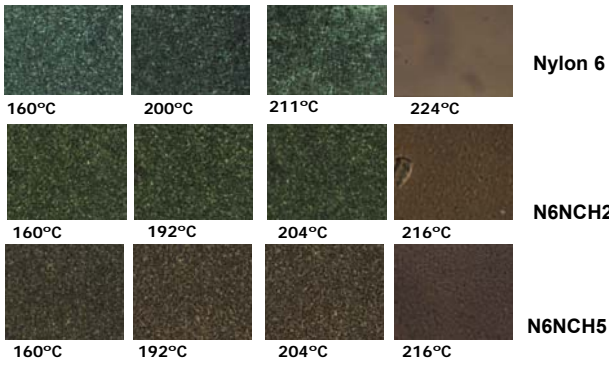


Fig. 6: Melting of the samples isothermally crystallized at 160 °C

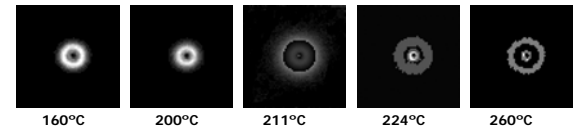
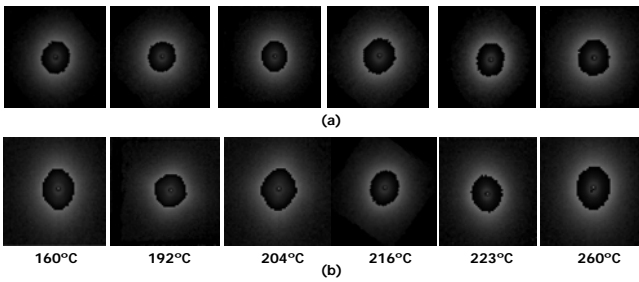


Fig. 7: SAXS images corresponding to the Nylon 6 melting after isothermic crystallization

Fig. 8: SAXS images corresponding to the (a) N6NCH2 and (b) N6NCH5 melting after isothermic crystallization at 160 °C



Recrystallization Hypothesis Analysis

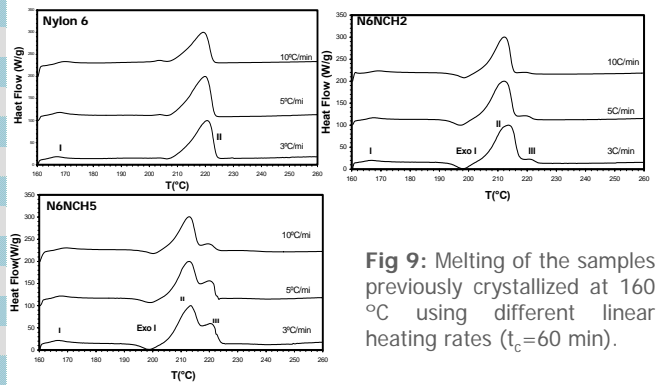


Fig 9: Melting of the samples previously crystallized at 160 °C using different linear heating rates ($t_c=60$ min).

Models

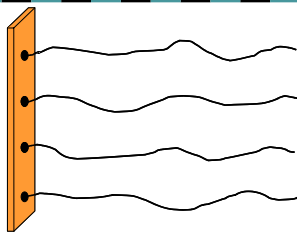


Fig 10. Schematic representation of a nanoclay sheet chemically bonded to polymer chains

Fig 11. Schematic Representation of the unit cell for the α Structure

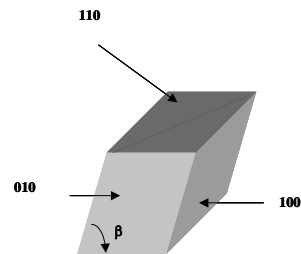


Fig. 12 Crystallization Model for N6NCH2

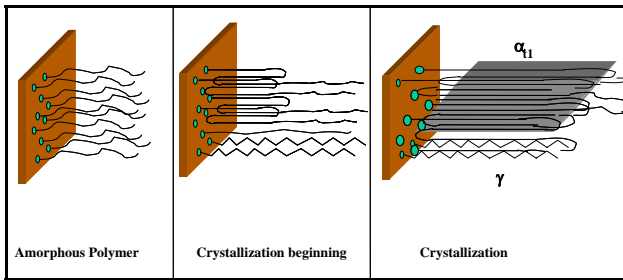


Fig. 13 N6NCH2 Melting

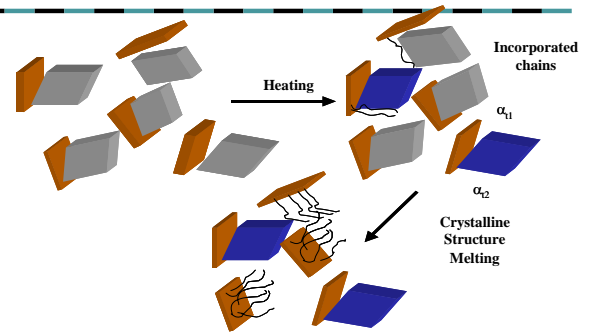


Fig. 14 Crystallization Model for N6NCH5

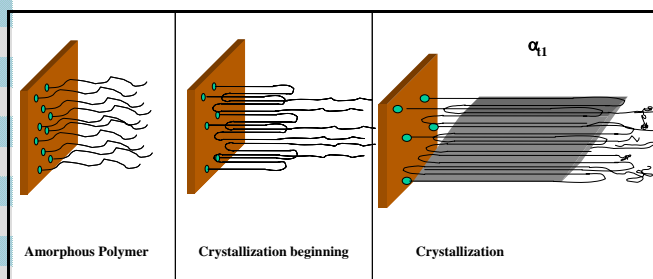
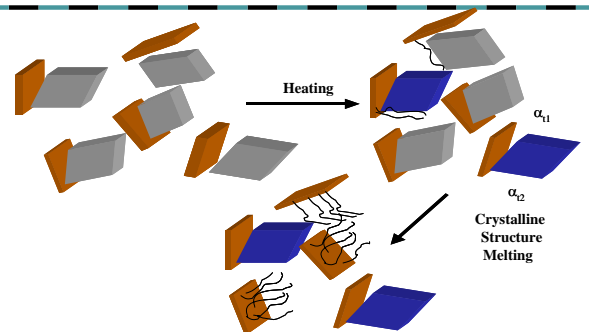


Fig. 15 N6NCH5 Melting



Conclusions

- ◆ Adding anisotropic montmorillonite modifies the crystallization and melting mechanisms
- ◆ Presence of montmorillonite promotes formation of truncated crystalline structures.
- ◆ Low clay content promotes formation of α_{t1} , α_{t2} and γ structures
- ◆ High clay content promotes formation of α_{t1} and α_{t2} structures

Conclusions

- ◆ Crystalline structure named α_{t2} may have its origin due to recrystallization processes
- ◆ The presence of clay promotes high crystallinity
- ◆ Melting process can be described as a combined mechanism involving melting and recrystallization



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- ◆ **Consejo Nacional de Ciencia y Tecnología:**
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Temperature and Time Effects on Crystallization of Nylon 6 Nanoclay Hybrids

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Abstract

Studies on the crystallization and melting mechanisms of Nylon 6 nanoclay hybrids are presented where Nylon 6 homopolymer was used as reference. Both time and temperature after isothermal crystallization were studied in terms of differential scanning calorimetry (DSC) and the results were complemented with several experimental techniques. X-ray diffraction patterns displayed unusual asymmetrical and truncated crystalline structures depending on isothermal crystallization of the hybrids. Optical microscopy showed a complex nucleated morphology when crystallization habits were in the α form. X-rays dispersion indicated diffuse scattering in the hybrids. The amount and type type of crystalline structures in the hybrids were also found to depend on crystallization time. Overall, nanoclays were determined as influencing morphological characteristics of hybrids.

Introduction

Nanostructured polymers contain nanometric size particles as fillers. The addition of such particles to a polymeric matrix strongly affects its properties and so the challenge exists of optimizing such effects. Nylon 6 nanoclay-hybrids were first developed by Toyota Inc. research laboratories and their development has motivated a number of studies. In the present, we are concerned with the thermal behavior and morphological characteristics being the main motivation to understand the evolution of a Nylon 6 when the macromolecules are end-tethered to a substrate such as montmorillonite.

Nylon 6 is a linear semi-rigid polymer with amide and carboxylic groups resulting in a polar behavior of the molecule. These characteristics allow Nylon 6 to develop two different crystalline structures, α -monoclinic and γ -pseudo-hexagonal (Holmes et al., 1955)

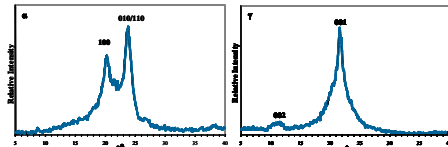


Fig. 1 X-Ray diffraction patterns of Nylon 6 crystalline structures: α and γ (Holmes et al., 1955)

Nylon 6 nanoclay hybrids are obtained end-tethering the Nylon 6 macromolecules to montmorillonite. This last is a natural clay of the smectite family with a crystallographic model proposed by Hoffman (Giannelis et al., 1999)

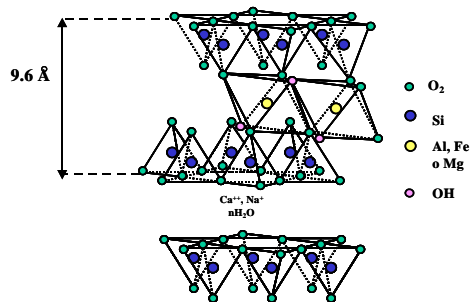


Fig. 2 Montmorillonite structure (Giannelis et al., 1999).

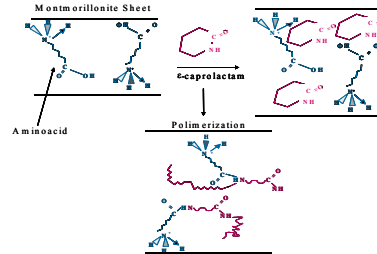


Fig. 3 Scheme for the Nylon 6 nanoclay hybrid polymerization reaction (Liang et al., 2003).

The reaction mechanism involves cations from the Montmorillonite structure which are easily exchanged by surfactants, the *in-situ* polymerization reaction follows by adding ϵ -caprolactam.

Experimental Section

Nylon 6 homopolymer and Nylon 6 nanoclay-hybrids with 2 wt % (N6NCH2) and 5 wt % (N6NCH5) montmorillonite content were synthesized by Ube Industries, Japan by *in situ* polymerization. Nylon 6 homopolymer had an average-molecular-weight of 2.17×10^4 and the clay-hybrids N6NCH2 and N6NCH5 had average-molecular-weights of 2.22×10^4 and 1.97×10^4 respectively (Krishnamoorti, et al., 1997).

Effect Of Crystallization Temperature

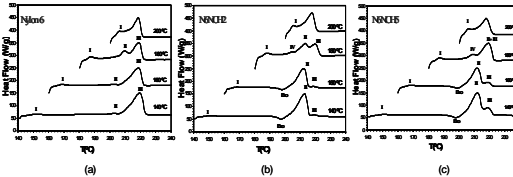


Fig. 4 Melting of (a) Nylon 6, (b) N6NCH2 and (c) N6NCH5 isothermally crystallized at different crystallization temperatures for 60 min.

The results show that all three samples have different behavior depending on crystallization temperature. However, at low crystallization temperatures the behavior is rather similar, particularly in the hybrids.

WAXD Characteristics

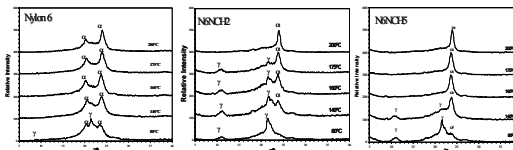


Fig. 5 X-Ray diffraction patterns of: (a) Nylon 6 homopolymer, (b) N6NCH2 and (c) N6NCH5, isothermally crystallized for 1 hr at the indicated temperatures.

At low crystallization temperatures there is asymmetrical γ in the hybrids. However, as crystallization temperature increases, there is a tendency to formation of the stable although truncated α form.

POM During Isothermal Crystallization

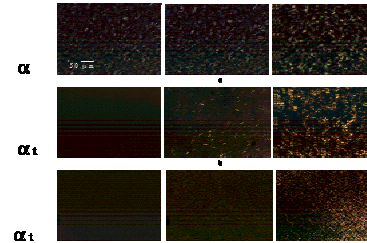


Fig. 6 Morphological evolution of: (a) Nylon 6, (b) N6NCH2, (c) N6NCH5, isothermally crystallized at 206 °C at the indicated time ($T_m=230$ °C).

SAXS Behavior

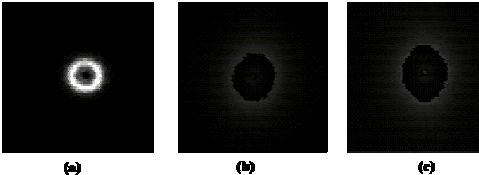


Fig. 7 SAXS images of: (a) Nylon 6, (b) N6NCH2, (c) N6NCH5 isothermally crystallized at 160 °C, for 60 min ($T_m=260$ °C)

Nylon 6 shows two-phase behavior whereas the hybrid materials show diffuse patterns.

Effect of Crystallization Time

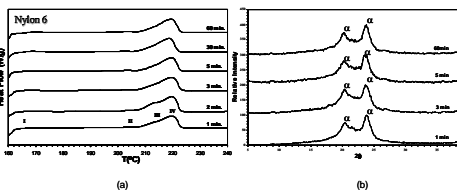


Fig. 8. (a) DSC linear heating traces after isothermal crystallization at 160 °C and different crystallization times. (b) WAXD patterns for the corresponding crystallization times.

The DSC behavior of Nylon 6 does not show important changes. The WAXD behavior indicates the formation of the stable α crystalline structure

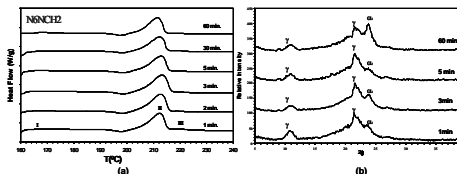


Fig. 9. Nylon 6 with 2% w/w nanoclay (N6NCH2) isothermally crystallized at 160 °C at different crystallization times (a) Melting traces and (b) Diffraction patterns

N6NCH2 shows triple melting although the first and third endotherms are only slightly defined. There is also a crystallization exotherm. The WAXD patterns start with a mixture of asymmetrical γ and not well defined α and then there is an evolution $\gamma/\alpha/\gamma$

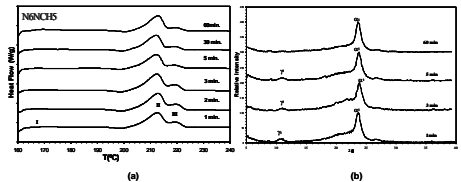


Fig. 10. Nylon 6 with 5% w/w of nanoclay (N6NCH5) isothermally crystallized at 160 °C at different crystallization times (a) Melting traces and (b) Diffraction patterns

N6NCH5 shows a better defined triple melting behavior which stays basically the same as a function of crystallization time. The WAXD behavior indicates however a mixture of truncated α/γ and the development of truncated α at high crystallization times

Conclusions

> Nylon 6 nanoclay hybrids have complex crystallization and melting mechanisms.

> In both hybrids, the thermal behavior is similar at low crystallization temperatures although it is very different at intermediate temperatures becoming again similar at high crystallization temperatures.

> At low crystallization temperatures there is asymmetrical γ in the hybrids. However, as crystallization temperature increases, there is the tendency to formation of the stable although truncated α form.

> Nylon 6 shows two-phase behavior whereas the hybrid materials show diffuse patterns.

> In terms of time, the N6NCH2 WAXD patterns start with a mixture of asymmetrical γ and a not well defined α and then there is an evolution $\gamma/\alpha/\gamma$. As for N6NCH5 the behavior indicates however a mixture of truncated α/γ and the development of truncated α at high crystallization times

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