



# Temperature and Time Effects on Crystallization of Nylon 6 Nanoclay Hybrids

S.M. Vega-Díaz and F.J. Medellín-Rodríguez\*

Centro de Investigación y Estudios de Posgrado, Facultad de Ciencias Químicas,  
Universidad Autónoma de San Luis Potosí, Av. Manuel Nava No. 6, Zona Universitaria, San Luis Potosí, S. L. P.,  
México

## 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  $\alpha$  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,  $\alpha$ -monoclinic and  $\gamma$ -pseudo-hexagonal (Holmes et al., 1955)

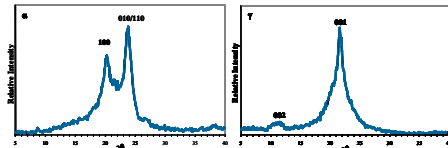


Fig. 1 X-Ray diffraction patterns of Nylon 6 crystalline structures:  $\alpha$  and  $\gamma$  (Holmes et al., 1955)

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)

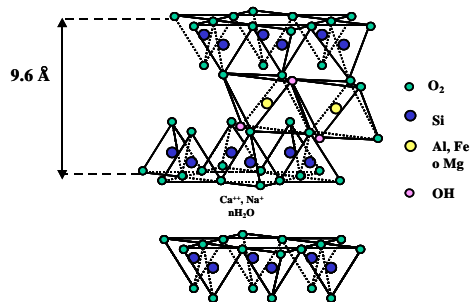


Fig. 2 Montmorillonite structure (Giannelis et al., 1999).

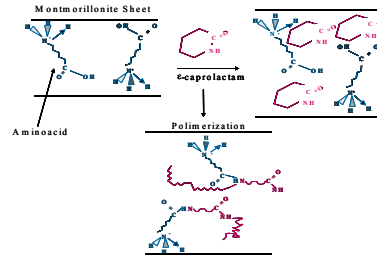


Fig. 3 Scheme for the Nylon 6 nanoclay hybrid polymerization reaction (Liang et al., 2003).

The reaction mechanism involves cations from the Montmorillonite structure which are easily exchanged by surfactants, the *in-situ* polymerization reaction follows by adding  $\epsilon$ -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  $2.17 \times 10^4$  and the clay-hybrids N6NCH2 and N6NCH5 had average-molecular-weights of  $2.22 \times 10^4$  and  $1.97 \times 10^4$  respectively (Krishnamoorti, et al., 1997).

## Effect Of Crystallization Temperature

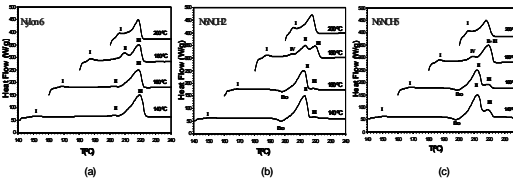


Fig. 4 Melting of (a) Nylon 6, (b) N6NCH2 and (c) N6NCH5 isothermally crystallized at different crystallization temperatures for 60 min.

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

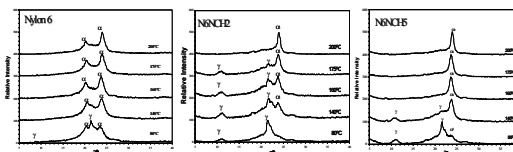


Fig. 5 X-Ray diffraction patterns of: (a) Nylon 6 homopolymer, (b) N6NCH2 and (c) N6NCH5, isothermally crystallized for 1 hr at the indicated temperatures.

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

## POM During Isothermal Crystallization

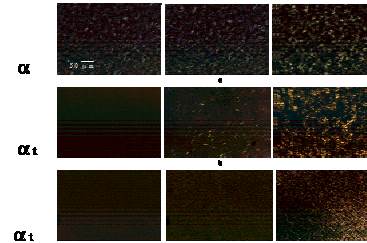


Fig. 6 Morphological evolution of: (a) Nylon 6, (b) N6NCH2, (c) N6NCH5, isothermally crystallized at 206 °C at the indicated time ( $T_m=230$  °C).

## SAXS Behavior

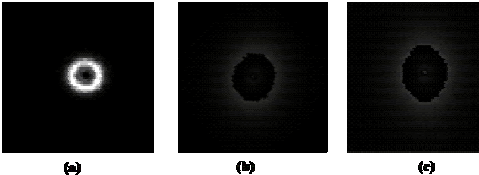


Fig. 7 SAXS images of: (a) Nylon 6, (b) N6NCH2, (c) N6NCH5 isothermally crystallized at 160 °C, for 60 min ( $T_m=260$  °C)

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

## Effect of Crystallization Time

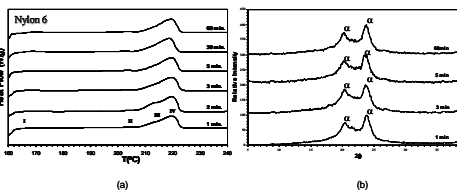


Fig. 8. (a) DSC linear heating traces after isothermal crystallization at 160 °C and different crystallization times. (b) WAXD patterns for the corresponding crystallization times.

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

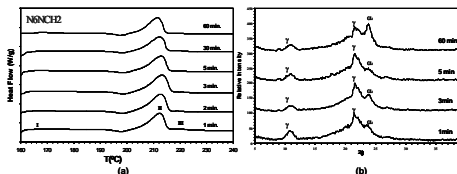


Fig. 9. Nylon 6 with 2% w/w nanoclay (N6NCH2) isothermally crystallized at 160 °C at different crystallization times (a) Melting traces and (b) Diffraction patterns

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  $\gamma$  and not well defined  $\alpha$  and then there is an evolution  $\gamma/\alpha/\gamma$

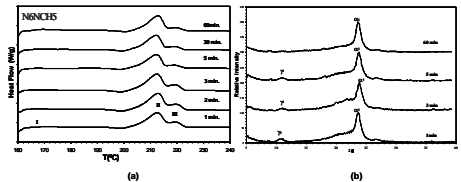


Fig. 10. Nylon 6 with 5% w/w of nanoclay (N6NCH5) isothermally crystallized at 160 °C at different crystallization times (a) Melting traces and (b) Diffraction patterns

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  $\alpha/\gamma$  and the development of truncated  $\alpha$  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  $\gamma$  in the hybrids. However, as crystallization temperature increases, there is the tendency to formation of the stable although truncated  $\alpha$  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  $\gamma$  and a not well defined  $\alpha$  and then there is an evolution  $\gamma/\alpha/\gamma$ . As for N6NCH5 the behavior indicates however a mixture of truncated  $\alpha/\gamma$  and the development of truncated  $\alpha$  at high crystallization times

## References

- >Kyotani, M., Mitsuhashi, S, J. Polym. Sci. A-2,10,1497-1508 (1972)
- >Giannelis, E.P., Krishnamoorti, R., Manias, E., Adv. In Polym. Sci., 138, 108(1999)
- >Liang, Y., Omachinski, S., Logsdon, J., Whan Cho J., Lan T., Technical information, Nanocor Inc. (2003) (www.nanocor.com)
- >Krishnamoorti, Giannelis, Macromolecules, 30,4097-4102. (1997)
- >Medellin-Rodríguez, F. J. Phillips, P.J, Polym. Eng. Sci. 36, 703(1996)
- >Usuki, A., Kawasumi, M., Kojima, Y., Okada, A., Kurauchi, O., J. Mater. Res., 8, 1179-1184 (1993)
- >Wu, T.Z., Chen, E.C., Liao, C.S, Polymer Engineering and Science,42,6, 1141-1150 (2002)

## Acknowledgements

> This work was supported by CONACyT, México through grants 39638-Y and U40177-Y. S. M. Vega-Díaz thanks CONACyT the scholarship 165314. The support of CAS/FCQ is greatly appreciated.

\*E-mail: francmr@uaslp.mx