

# Effect of Inorganic Additive on the Chain Crystallization in Polymer / Layered Silicate Nanohybrids

K. Chrissopoulou<sup>1\*</sup>, E. Pavlopoulou<sup>1,2</sup>, H. Papananou<sup>1,3</sup>, S. Fotiadou<sup>1,3</sup>, G. Portale<sup>4</sup>, W. Bras<sup>4</sup> and S. H. Anastasiadis<sup>1,3,5</sup>

<sup>1</sup> Institute of Electronic Structure and Laser, Foundation for Research and Technology-Hellas P. O. Box 1527, 711 10 Heraklion, Crete, Greece

<sup>2</sup> Department of Materials Science and Technology, University of Crete, Heraklion, Crete, Greece

<sup>3</sup> Department of Chemical Engineering, Aristotle University of Thessaloniki, 54124 Thessaloniki, Greece

<sup>4</sup> DUBBLE CRG, European Synchrotron Radiation Facility, Grenoble, France

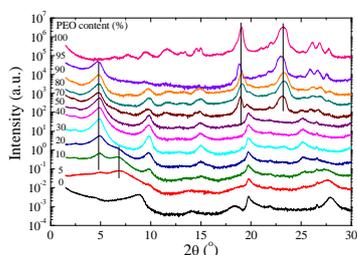
<sup>5</sup> Department of Chemistry, University of Crete, Heraklion, Crete, Greece

\*kiki@iesl.forth.gr

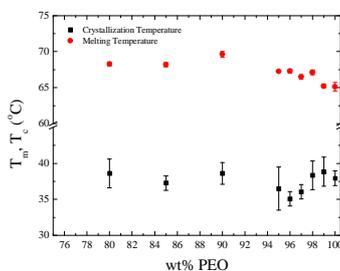
Polymer / layered silicate nanocomposites constitute an interesting class of materials which allow the investigation of basic scientific problems and at the same time are utilized in many technological applications. Mixing polymers with layered silicates leads to three different micro- or nanostructures depending on the interactions between the chains and the inorganic surfaces: the phase separated, where the two materials are immiscible, the intercalated that the polymer chains reside in the interlayer galleries of the silicates forming 0.8-2.5nm films and the exfoliated, in which the structure of the inorganic material is destroyed and the platelets are dispersed in the polymeric matrix. [1,2] A reason that these materials have attracted the scientific interest is related with their unique properties that render them candidates for numerous technological applications. In the case of crystalline polymers, the improvement in the properties can be attributed further than the reinforcing contribution of the inorganic additives and the formation of different nanostructures, to the alteration of the crystalline behaviour and characteristics of the polymer chains due to the presence of the inorganic material.

In this work we investigate the structure, morphology and crystallization behavior of a hydrophilic, semi-crystalline polymer, poly(ethylene oxide), PEO, ( $M_n=100000$ ,  $T_g=-67^\circ\text{C}$ ,  $T_m=65^\circ\text{C}$ ) when mixed with natural montmorillonite ( $\text{Na}^+$ -MMT) in a range of compositions that covers the whole regime from pure polymer to pure clay. The structure of the hybrids was investigated by X-ray diffraction, Polarizing Optical Microscopy (POM), Differential Scanning Calorimetry (DSC) and Small Angle X-ray Scattering (SAXS).

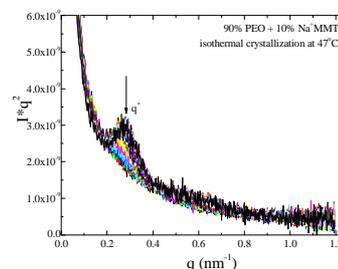
Figure 1 shows the X-ray diffraction patterns for the pure components and the nanohybrids. [3] The pure  $\text{Na}^+$ MMT shows a main (001) diffraction peak at  $2\theta=8.8^\circ$ , which corresponds to an interlayer spacing of 1.0 nm. As the PEO concentration increases, the  $\text{Na}^+$ MMT diffraction peak disappears and two other peaks emerge at  $6.8^\circ$  and  $4.8^\circ$  that correspond to interlayer distances of 1.30 and 1.85 nm and whose relative intensities depend on the PEO content. At concentrations up to 20 wt%, the PEO chains within the galleries form either a single- or a double-layer structure of disordered liquid-like chains. Further increase of the PEO concentration reveals only double-layers of intercalated PEO chains. Moreover, for PEO content below 70 wt% no peaks are observed that can be assigned to the crystalline structure of PEO. It is only for PEO concentrations higher than 70 wt% that two peaks at  $18.9^\circ$  and  $23.2^\circ$  emerge, which agree with the diffraction peaks of bulk PEO due to its monoclinic crystal structure (with a unit cell parameter of 1.93 nm along the helix axis). This indicates crystallization of the excess polymer outside the completely full galleries.



**Figure 1:** X-ray diffraction spectra of PEO/  $\text{Na}^+$ MMT nanocomposites.



**Figure 2:** Composition dependence of the melting and crystallization temperatures.

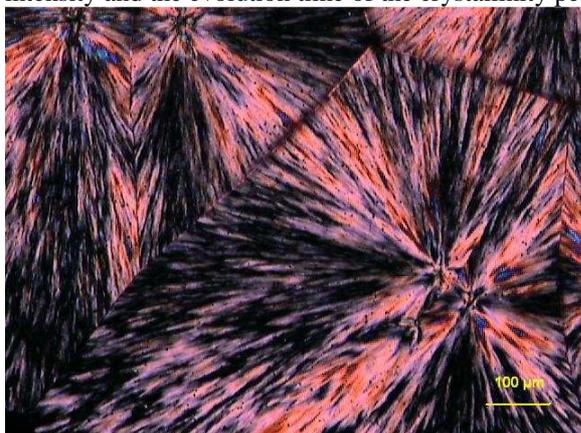


**Figure 3:** Wavevector dependence of the scattered SAXS intensity for the 90wt%PEO+10wt% $\text{Na}^+$ MMT hybrid

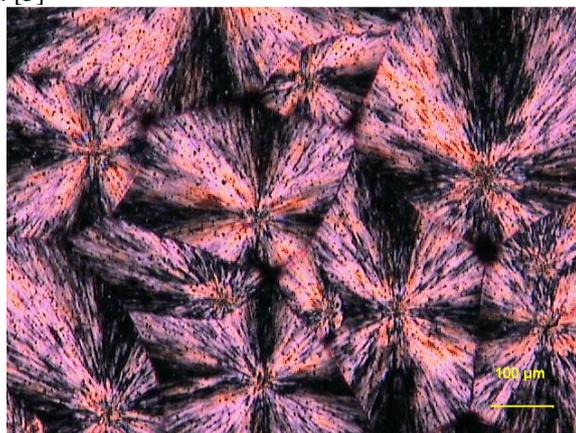
Indeed DSC measurements on hybrids with low polymer content [4] reveal that the PEO chains remain

amorphous and it is only for composites with 70wt% PEO and more that the characteristic melting and crystallization transitions appear in agreement with the XRD data. In the latter cases, a small effect of the inorganic additive on the melting and crystallization temperatures is observed (Figure 2). Furthermore, the polymer crystallinity resulting from both the XRD and the DSC analysis show a small increase for low inorganic content. Moreover, these results are verified by independent FT-IR and Raman Spectroscopy measurements in which the sharp peaks that correspond to the crystalline PEO are observed only in nanohybrids with high polymer content. [4]

In the case of hybrids with high polymer content, where the chains are able to crystallize, the kinetics of crystallization along with the crystalline characteristics were recorded utilizing time resolved Small Angle X-ray Scattering (SAXS) measurements carried out at the Dutch-Belgian Beamline (DUBBLE) at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France, in the scattering vector range  $0.06 < q < 1.2 \text{ nm}^{-1}$ . The samples were annealed above the melting temperature,  $T_m$ , and then quenched at different isothermal crystallization temperatures,  $T_{IC}$ . Sequential SAXS patterns were acquired, following the isothermal crystallization at the respective temperatures. Figure 3 shows the scattering patterns (after utilization of the Lorentz correction) of the nanocomposite with 90% PEO + 10%  $\text{Na}^+$ -MMT collected during isothermal crystallization at  $47^\circ\text{C}$ . The initial scattering curves correspond to those of the melt state of the amorphous polymer. After a while, a peak appears at approximately  $q=0.27\text{nm}^{-1}$ , corresponding to a lamellar period of 23nm. The intensity of the peak increases until the end of the crystallization process, and then remains constant. The patterns of all the nanocomposites at various  $T_{IC}$  were similar, however differences were observed in the intensity and the evolution time of the crystallinity peak. [5]



**Figure 4:** POM image of PEO obtained during isothermal crystallization at  $53^\circ\text{C}$ .



**Figure 5:** POM image of 99wt%PEO + 1wt%  $\text{Na}^+$ MMT obtained during isothermal crystallization at  $53^\circ\text{C}$ .

Polarized Optical Microscopy images were recorded for pure PEO and nanohybrids with low amount of additive (Figures 4 and 5) as well. [5] The samples were placed in a heating stage, melted at  $120^\circ\text{C}$  for 5min and then cooled down either to room temperature or to selected crystallization temperatures. The images reveal that even the presence of very small amount of the inorganic material results in an important decrease of the spherulite size accompanied with an increase in the spherulite number. In all cases, increase of the spherulite size was observed with the increase of the crystallization temperature as well. It is noted that for each system, the ideal melting temperature was estimated and its dependence on the inorganic content was examined.

Furthermore, results from both SAXS and DSC kinetic experiments indicate that the crystallization mechanism is altered due to the silicate from that of homogeneous nucleation for the pure polymer to heterogeneous and epitaxial nucleation with the increase of the inorganic material.

[1] Giannelis E. P., Krishnamoorti R., Manias E., *Adv. Polym. Sci.* 138, 107 (1999)

[2] Alexandre M., Dubois P., *Materials Science and Engineering* 28, 1 (2000)

[3] Elmahdy M. M., Chrissopoulou K., Afratis A., Floudas G., Anastasiadis S. H., *Macromolecules* 39, 5170 (2006)

[5]. Fotiadou, S., Chrissopoulou, K., Andrikopoulos, K., Anastasiadis, S. H. *In preparation* (2009)

[6]. Chrissopoulou, K., Papananou, H., Pavlopoulou, E., Portale, G., Bras, W., Anastasiadis, S. H. *In preparation* (2009)

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