

Crystallization Behavior of Poly(ethylene oxide) in the Presence of Na⁺ Montmorillonite Fillers

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The crystallization behavior of poly(ethylene oxide) (PEO) was studied in the presence of an inorganic filler surface (sodium montmorillonite) with DSC, as well as isothermal cross-polarization optical microscopy. Crystallization of PEO is found to be inhibited, exhibiting a decrease of spherulite growth rate and crystallization temperature. However, the overall crystallization rate increases with silicate loading as a result of extra nucleation sites, which occur in the bulk PEO matrix (i.e., far from the silicate surfaces). PEO differs from other systems, where crystallinity is typically enhanced next to such surfaces, in that the polymer is amorphized near the montmorillonite surfaces. This behavior is attributed to the specific way that PEO interacts with Na⁺ montmorillonite, where strong coordination of PEO to the surface Na⁺ cations promotes noncrystalline (ether crown) PEO conformations.

Introduction

Polymer crystallization behavior near an inorganic surface has been the focus of extensive study.¹ In most cases the inorganic surface is shown to produce a nucleating or epitaxial effect,^{2–5} which often stabilizes the bulk crystal phase or, in some cases, it promotes growth of a different crystal phase. The polymer mechanical and thermal properties can be enhanced through this mechanism, where the surface-nucleated crystalline phase has better mechanical and thermal characteristics than the bulk crystal phases.^{3–7} Fillers with large surface areas maximize these filler-induced enhancements of the material properties; a dramatic manifestation of such a response is found in nylon-6/montmorillonite nanocomposites.^{3–5} Less dramatic property enhancements are found in systems where the bulk crystalline phase is simply stabilized via the incorporation of heterogeneous nucleation sites, such as in polypropylene/organo-montmorillonite systems.⁸

The nylon-6/inorganic hybrids show dramatic enhancements in their mechanical and thermal properties upon addition of a minute amount (2–10 wt %) of montmorillonite (MMT),⁴ a nanometer-thin mica-type layered silicate with a surface area of about 750 m²/g. This was later attributed to a filler-stabilized γ crystalline phase of nylon-6 formed at the silicate surface.^{9,5,3} PVA/layered-silicate nanocomposites also possess such filler-induced property enhancements,⁶ which were also attributed to the existence of a non-bulk-like crystalline structure promoted when Na⁺ montmorillonite (MMT) is added to PVA.⁷

The present work is inspired by the unique character of PEO, which exhibits crystallization enhancement in the presence of inorganic fillers, but at the same time, its crystallization is hindered by the addition of alkali cations.^{10,11} These two competing mechanisms are simultaneously present in PEO when Na⁺MMT is added (since the polymer/MMT interactions are favorable to mixing and crystallization, whereas the polymer/Na⁺ interactions are favorable to mixing but not conducive to crystallinity). Thus, we aim to elucidate the crystallization behavior of PEO upon addition of Na⁺MMT, where the general heterogeneous nucleation of polymers competes with the PEO coordination to Na⁺, which is known to destroy PEO crystallinity. We use differential scanning calorimetry (DSC) techniques (isothermal and scanning) as well as cross-polarization optical microscopy (CPOM) to investigate the crystallization behavior of PEO and PEO/Na⁺MMT hybrid materials. We focus on the effect of the inorganic filler on the PEO crystal-

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lization, and specifically on the morphology, nucleation, growth, and overall crystallization rate.

Experimental Section

Materials and Sample Preparation. Sodium montmorillonite (MMT) was obtained from Southern Clay Products (Cloisite Na⁺) with a cation-exchange capacity (CEC) of 0.95 mequiv/g, which corresponds to about one Na⁺ per 70 Å². MMT is a naturally occurring 2:1 phyllo-silicate, capable of forming stable suspensions in water. This hydrophilic character of MMT also promotes dispersion of these inorganic crystalline layers in water-soluble polymers such as poly(vinyl alcohol)^{12,6} and poly(ethylene oxide).^{13–17} Films of neat PEO and PEO/inorganic hybrids were prepared using a film-casting method.⁶ Hybrid films were cast from a MMT/water suspension where PEO was dissolved. Room-temperature distilled water was used to form a suspension of sodium montmorillonite at a concentration of ≤2.5 wt %. The suspension was stirred for 1 h and sonicated for 20 min. PEO (number-average molecular weight 136 000 g/mol, polydispersity 1.2) (PolySciences) was added to the stirring suspensions such that the total solids (silicate plus polymer) concentration was ≤5 wt %. The mixtures were then heated to 50 °C to ensure complete dissolution, again sonicated for 20 min, and finally films were cast from solution on top of glass substrates. Drying was done on a hot plate at 35–40 °C covered, for 24 h, followed by drying under vacuum at 40 °C. Samples were then melted at 100 °C for 30 min and allowed to cool slowly, to ensure good intercalation of the tactoid layers by the PEO. The nominal film thickness for the optical microscopy samples was 10–50 μm. Specimens for XRD and DSC studies of neat PEO and PEO/MMT systems were prepared by the same method.

Characterization. Cross-polarization optical microscopy was carried out in a Olympus BH-2 optical microscope, equipped with a Mettler hot stage (RT-300 °C), and a video camera connected to a VCR. The crystallization behavior of all systems was recorded in real time video, which was used later for analysis. Differential scanning calorimetry (DSC) was performed in a Perkin-Elmer DSC7 at variable heating (or cooling) rates as well as at isothermal conditions under an argon atmosphere. Wide-angle X-ray diffraction (XRD) data were collected in digital form using a Rigaku Geigerflex powder diffractometer with a Dmax-B controller and a vertical goniometer. Operation was in the θ – θ geometry. The instrument uses radiation from a copper target tube (Cu K α radiation λ = 1.541871 Å, including both the K α_1 and K α_2 , whereas K β was eliminated with a graphite monochromator). The PEO molecular weight was characterized by aqueous GPC, bearing PH-aquagel-OH columns (OH 30, 8 μm, Polymer Laboratories), and calibrated with PEO standards.

Results and Discussion

Results. In this work we comparatively study the crystallization behavior of neat—unfilled—PEO and PEO/Na⁺MMT hybrids. The structure of these polymer/inorganic hybrids is well-known (Figure 1), studied extensively both by experiment^{13–15} and by molecular simulations^{16,17} and is markedly independent of the filler loading. When enough PEO exists in the compos-

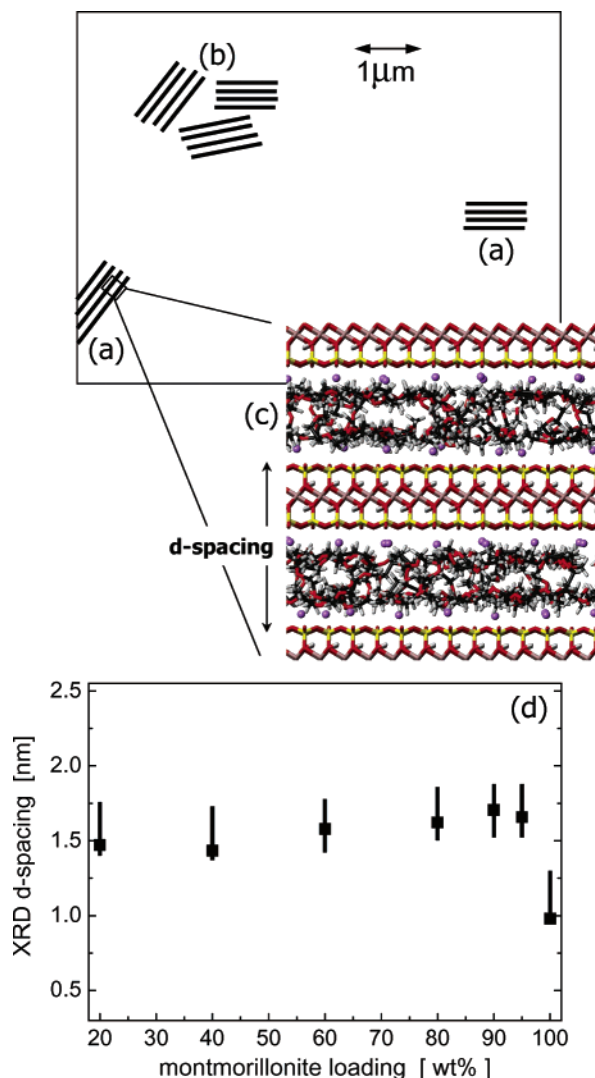


Figure 1. Schematic of the PEO/Na⁺MMT intercalated nanocomposites. The layered inorganic MMT layers assemble in a parallel fashion, creating stacks of layers referred to as tactoids (a), and most times tactoids are found in groups referred to as agglomerates (b), separated by bulklike polymer regions. Within the tactoid, MMT layers are separated by a 0.8-nm film of PEO (c), which is stable through a wide range of MMT loadings as seen in the X-ray diffraction data (d). The MMT layers bear a large number of Na⁺ (one cation per 70 Å²), depicted by purple dots in the simulation snapshot (c, from ref 17).

ite, an intercalated structure is formed (with d spacings distributed around 1.7 nm, which corresponds to a PEO bilayer of about 0.8-nm thickness). For composites with extremely small amounts of PEO ("polymer-starved" composites at montmorillonite loadings of $\phi_{\text{MMT}} > 90\%$), an intercalated monolayer of PEO can also be observed, with an intercalated d spacing of about 1.37 nm. These latter structures are of no interest to this present work. For the montmorillonite loadings of interest here ($\phi_{\text{MMT}} = 1\text{--}10\text{ wt \%}$) the layered silicates retain their pristine parallel registry, but there is an increase in the d spacing (Figure 1d) due to the intercalation of PEO in the interlayer gallery (Figure 1c). Successive single layers self-assemble in stacks (tactoids, Figure 1a), in a highly parallel stacking that can give rise to 001 XRD diffraction peaks up to the 11th order.¹³ These micrometer-size tactoids are dispersed in the PEO matrix—either

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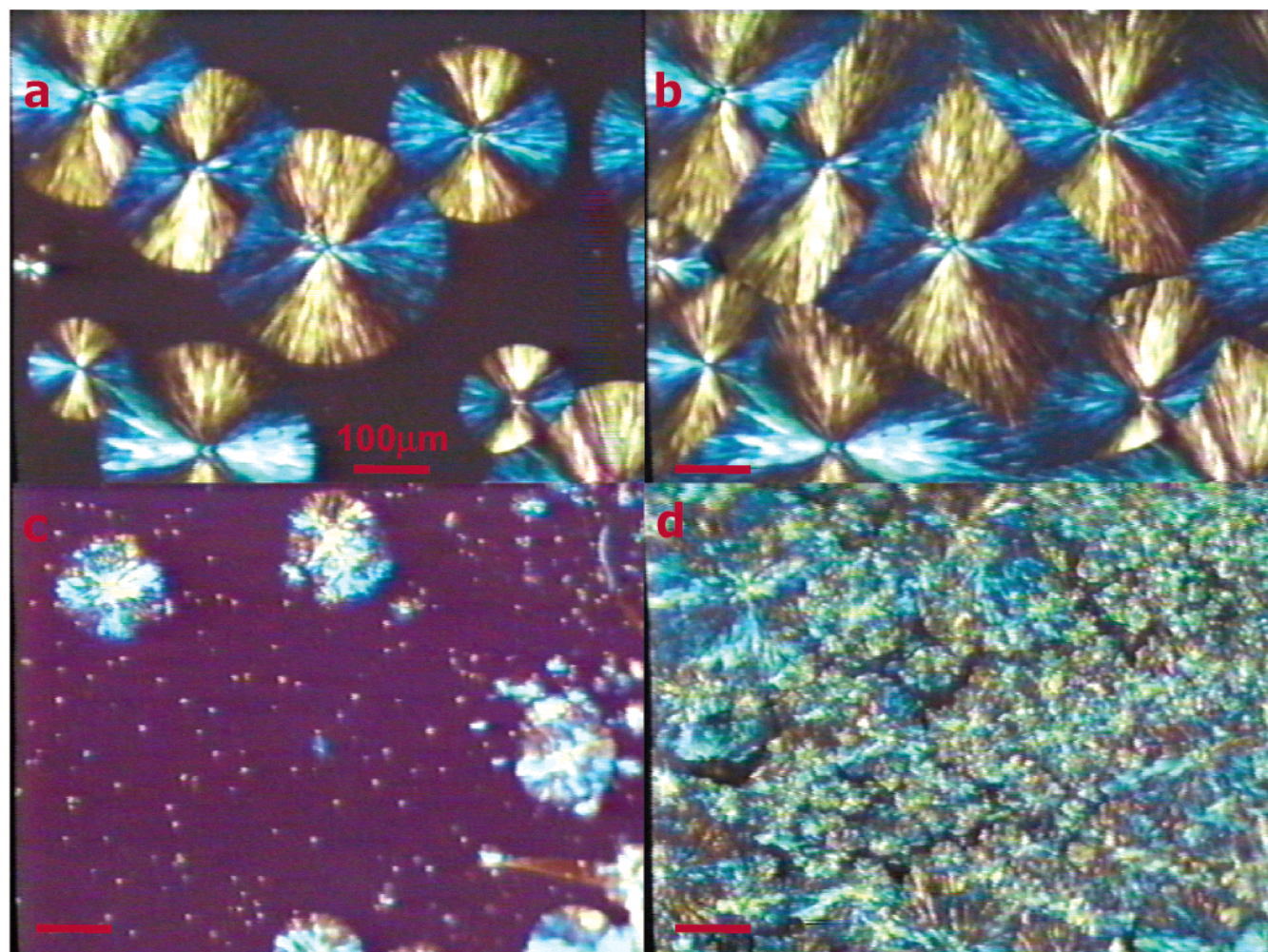


Figure 2. Cross-polarization optical microscope images of neat PEO (a,b) and PEO containing 5 wt % MMT (c,d). Images on the left (a,c) are early in the crystallization process, whereas those on the right (b,d) are the final images. The scale bar is the same for all images (100 μm). White spots in (c) are tactoids found in the nanocomposite system. The (d) image illustrates the fact that later in the process many smaller spherulites grow to fill the space in the composite system. The growth front of the composite system (c) appears highly jagged, in contrast with the very smooth front found in the neat PEO spherulites (a).

in isolation or in groups of tactoids (agglomerates, Figure 1b)—separated by regions of pure polymer (Figure 1).

Cross-polarized optical microscopy (CPOM) was used to compare the crystal morphology between filled and unfilled PEO, and subsequently DSC studies were used to further quantify the relevant crystallization kinetics. We focus on systems with low silicate loadings ranging from neat PEO (0 wt % MMT) to PEO with 10 wt % MMT. In Figure 2 we compare the CPOM images of neat PEO and a PEO/5 wt % MMT intercalate, both crystallized at 45 $^{\circ}\text{C}$. The morphology of the crystals is shown at an early stage (neat, Figure 2a; intercalate, Figure 2c) and at the final stage of crystallization (neat, Figure 2b; intercalate, Figure 2d). For the neat PEO, it can be clearly seen that the spherulites are similar in size, and prior to impinging upon one another, they appear circular, suggesting an isotropic (spherical) three-dimensional shape. For the intercalated system (Figure 2c,d) the spherulite sizes vary a lot, and they are typically much smaller than the ones seen in neat PEO. Moreover, in these systems the spherulites are characterized by very anisotropic, nonspherulitic shapes (Figure 2d) with jagged edges, even before impinging upon one another (Figure 2c).

A CPOM time series, following a crystalline growth front in the same intercalated material, can provide some clues on the origin of these crystal morphologies. In Figure 3 a progression of a growing crystallite is shown for the PEO/5 wt % MMT system. The early and late stages are shown in parts a and f of Figure 3, where silicate tactoids can be seen, manifested as either bright/white features (near the focused plane) or dark features (below and above the focused plane). Parts b–e of Figure 3 are a higher magnification of the selected area (shown as the box in Figure 3a/f) as the spherulite growth-front encounters an MMT agglomerate (or a large tactoid). As the growth proceeds, the lamellar pathways are interrupted and they are forced to grow around the tactoid, breaking the spherical symmetry of the crystallite, and crystallization is delayed in the region downfield from the tactoid. The same behavior is also observed for the smaller tactoids in the image, albeit at smaller scale. At the end of crystallization (Figure 3f), we see that the effect of the MMT on the crystallite growth resulted in “spherulites” grown in a haphazard fashion with tortuous lamellar pathways and jagged edges. Also, the crystallite size is markedly smaller than the spherulites developed in neat PEO (Figure 2b).

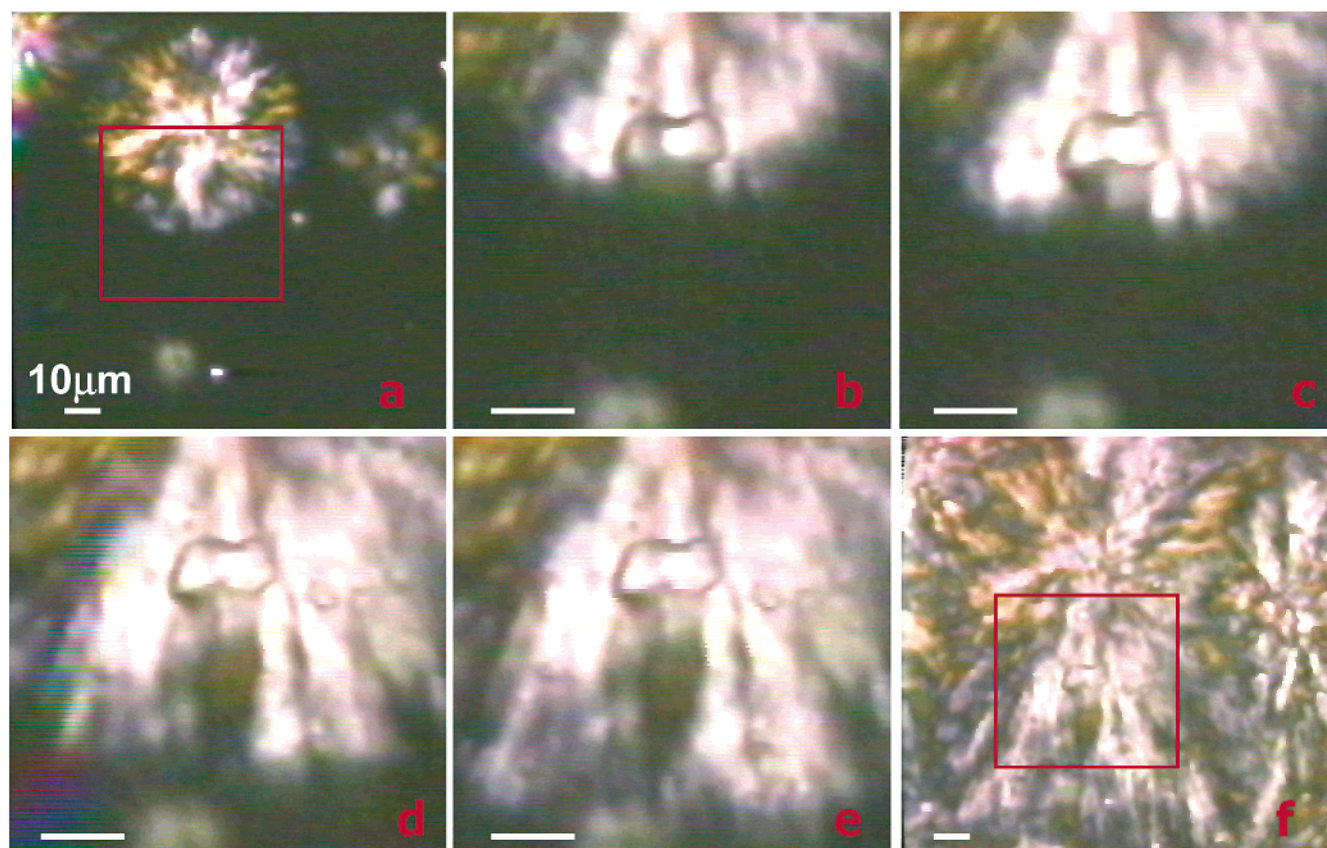


Figure 3. A time series of cross-polarization optical microscopy images of a nanocomposite region from PEO containing 5 wt % MMT. Images (a) and (f) have the same magnification and are at the beginning (a) and the end (f) of the crystallization. The box in (a) and (f) outlines the area shown in (b)–(e) at a higher magnification, which focus on the growth of a spherulite “front” as it encounters an MMT agglomerate. The scale bar in all images is 10 μm .

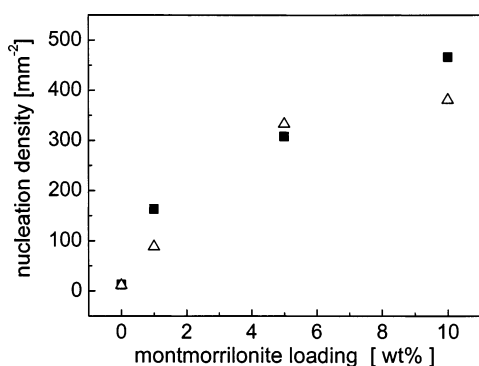


Figure 4. Nucleation density as a function of silicate loading, as measured from cross-polarization optical microscopy. Crystallization is done at 45 °C (squares) and 50 °C (triangles). The number of nucleated spherulites per unit area increases by more than 10-fold, even at low silicate loadings.

This difference in crystallite size can be quantified by enumerating the number of crystallites/spherulites per area. In Figure 4 we show the density of crystallites, as measured in the isothermal crystallization CPOM experiments at temperatures (T_{iso}) of 45 and 50 °C. It is seen that the density of crystallites increases by more than an order of magnitude when MMT layers are introduced in PEO, even at very small silicate loadings. Moreover, CPOM reveals that almost all of the crystal nuclei initiate in the bulk PEO, i.e., far away from the MMT fillers. Albeit this huge difference in the number of crystallites between neat and intercalated PEO, the polymer crystalline fraction—as measured

through DSC experiments—does not show a marked change between these two systems: In Figure 6 we plot the enthalpy of melting (ΔH_m) as measured by DSC, showing no strong effect of the silicate loading and/or the crystallization temperature on the final crystallinity of the systems. One of these DSC experiments is shown in Figure 5a for neat PEO and PEO/5 wt % MMT. The onset and peak crystallization temperatures (T_c) can also be measured from the cooling response (Figure 5b). The addition of MMT fillers in the PEO decreases the polymer T_c for all cooling rates used, suggesting that the MMT hinders the PEO crystallization, a conclusion which is in concert with the behavior seen in Figure 3. As expected, the DSC-observed T_c decreases with cooling rate, and the crystallization temperature of PEO/MMT composite deviates more from the neat polymer's T_c as more MMT filler is added. The fact that the dependence of T_c on the cooling rate is similar for the neat PEO and the filled PEO suggests that these differences are due to genuine changes in the polymer crystallization, rather than changes of the thermal conductivity caused by the incorporation of the inorganic fillers. In the latter case, if the DSC-observed decrease of T_c were actually due to changes in thermal conductivity, the difference in T_c between the neat and filled PEO would have been a strong function of the cooling rate.

Finally, isothermal DSC measurements can be used to quantify the overall crystallization rate, which is the product of the nucleation rate and the crystal growth rate. Namely, in Figure 7 the crystallization half-time ($t_{1/2}$) is plotted against the “undercooling” for various

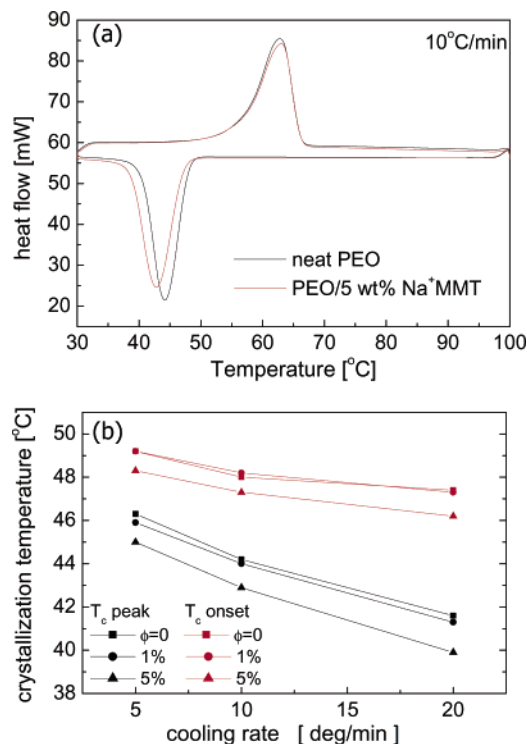


Figure 5. (a) A typical DSC scan for PEO and PEO/5 wt % MMT, at a heating/cooling rate of 10 °C/min. (b) Peak and onset of the crystallization temperature, as a function of DSC cooling rate, for PEO and PEO/MMT nanocomposites. The crystallization temperature is decreasing with silicate loading, showing that a higher degree of undercooling is needed for crystallization of composites.

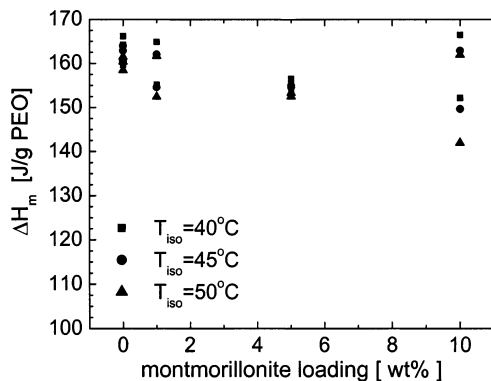


Figure 6. Enthalpy of melting for PEO versus filler loading. The PEO crystallinity does not change markedly with silicate loading, for various isothermal temperatures of crystallization ($T_{iso} = 40, 45$, and 50°C : squares, circles, and triangles, respectively). All samples were melted and then rapidly cooled to the T_{iso} ; after isothermal crystallization in the DSC, samples were heated at 10 °C/min and ΔH_m was measured.

isothermal temperatures (T_{iso}), for neat and filled PEO systems. The half time of crystallization ($t_{1/2}$) was defined as the time necessary to reach 50% of the total polymer crystallization, after the induction period. "Undercooling" is defined as the $T_c - T_{iso}$ temperature difference, where T_{iso} is the temperature that crystallization was studied under isothermal conditions and T_c is the DSC crystallization temperature.¹⁸ Due to the nature of these system's crystallization behavior (Figure 5), different definitions of "undercooling"—or of T_c —will only shift the x-axis of Figure 7, but will not change the relative positions of the data points depicted in it.¹⁸

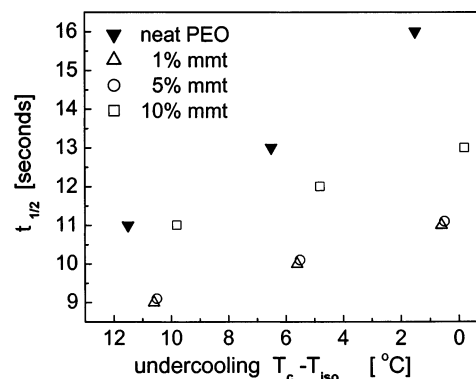


Figure 7. Half-life times of crystallization ($t_{1/2}$) versus undercooling ($T_c - T_{iso}$), for various silicate loadings ($\phi_{\text{MMT}} = 0\%$, 1%, 5%, 10%: down triangles, up triangles, circles, squares). Times decrease when PEO is filled with MMT; that is, crystallization takes longer for the bulk system.

From Figure 7, it is obvious that the half-time of crystallization increases as T_{iso} approaches the crystallization temperature, as expected; that is, crystallization becomes slower as T_{iso} approaches the T_c for each system. Furthermore, when silicate is added to the system, the half-life time is reduced for all undercoolings; thus, the overall crystallization rate increases with the addition of MMT in the polymer.

Discussion. Before we discuss our results, we outline the three main experimental observations to be explained:

1. The introduction of MMT fillers hinders the PEO crystallization, as observed directly by optical microscopy (Figure 3) and manifested in the decrease of the crystallization temperature (Figure 5).

2. The overall PEO crystallinity is not affected by the filler introduction (Figure 6) for small (< 10 wt %) filler loadings, but the crystal morphology is strongly altered by the MMT presence, resulting in more, smaller, and nonisotropic crystallites (Figures 2 and 4).

3. The overall crystallization kinetics becomes faster with the addition of MMT (Figure 7).

At first glance, our first observation seems at odds with the last: Although crystallization is hindered by the introduction of MMT fillers, the overall crystallization kinetics becomes faster. This is a consequence of the much larger number of crystallites created in the presence of MMT compared to the neat PEO system (Figure 4). Because the overall crystallization rate—as measured by $t_{1/2}$ —is the product of the nucleation rate and the crystal growth rate, it is actually possible for the overall kinetics to increase despite a slowing down of the crystal growth rate, when more crystals are nucleated, as is the case here (Figure 4).

The most interesting finding of this work is probably the fact that the introduction of MMT inorganic fillers slows down the polymer crystal growth in the vicinity of the filler. This contrasts the usual behavior of

(18) The crystallization temperature (T_c) used in the definition of undercooling corresponds to the onset of the DSC crystallization peak at the slowest cooling rate used (1 °C/min) and differs between the neat PEO and the nanocomposites (Figure 5). Alternative definitions of T_c , for example, by extrapolating to static conditions (at the cooling rate limit of 0 °C/min), or at any other—higher—cooling rate studied, would only shift the x axis of Figure 7. Defining the undercooling from the melting point of each system—instead of the T_c —would be misleading because the DSC melting points obtained here are insensitive to changes in the crystallization kinetics.

semicrystalline polymers, where fillers normally result in heterogeneous nucleation, promoting crystals in their vicinity. Such crystal nucleating effects are in fact observed also for MMT when incorporated in other semicrystalline polymers, such as poly(vinyl alcohol),⁷ polypropylene,⁸ and nylon-6.⁹ The unusual behavior observed herein for PEO originates from the specific manner that MMT interacts with poly(ethylene oxide): Addition of small cations, in the form of salts, has been shown to reduce or completely destroy the crystallinity of PEO.^{10,11} This behavior is attributed to the strong coordination of PEO to small cations, such as Na⁺ and Li⁺, which promote "crown ether" type of backbone conformations coordinated to the cations.¹⁹ Such crown-ether conformations deviate from the helical PEO conformations—typically found in bulk PEO crystals—and therefore amorphize the PEO. Because the MMT surfaces bear large numbers of cations (approximately one Na⁺ per 70 Å²), PEO chains in their vicinity are highly coordinated to the Na⁺, adopting conformations with many crown-ether arrangements, which are highly amorphous. A similar behavior—with cations promoting an amorphous PEO structure—has also been seen in the interlayer gallery between the MMT layers in PEO/Li⁺-MMT composites by computer simulations,^{16,17} and we herewith find that this is also an important effect on the external surfaces of the tactoids.

We believe that the slowing of the crystal growth rate is due to this amorphization of the polymer in the vicinity of the silicate, which forces the spherulite to grow around the dispersed tactoids, resulting in "broken" lamellar pathways and geometrically anisotropic shapes. Scanning (cooling) DSC further corroborates these optical microscopy observations because it is found that the crystallization temperatures are shifted to lower values with MMT loadings. This T_c reduction is additional evidence that crystallization is inhibited with the addition of silicate fillers, as larger undercoolings are now needed to begin the crystallization process. If this is the case, reducing the surface density of Na⁺ cations on the MMT surfaces should result in enhanced PEO crystallization.²⁰

Finally, putting all these pieces together, we can trace the crystallization behavior of PEO in the presence of Na⁺-MMT fillers: primary nucleation takes place in the bulk—away from the MMT surfaces—and initially spherulites grow normally until they encounter a filler. At this point, because amorphous PEO structures are promoted in the vicinity of the MMT, there is a retardation of the spherulite growth front, resulting in jagged edges and nonspherulitic morphologies. This delay in

covering space allows for the nucleation of other spherulites that grow in the same manner until all volume is filled. These additional nuclei cause the PEO to crystallize faster overall, despite the slower crystal growth rate, and allows for the total volume to crystallize more quickly, albeit with much smaller crystallite sizes than in bulk PEO.

Conclusions

Using scanning and isothermal DSC, and cross-polarization optical microscopy, we have investigated the differences of crystallization behavior in neat PEO films and PEO films filled by MMT inorganic layers. The coordination of PEO to the montmorillonite Na⁺ promotes the polymer–filler miscibility, but renders the PEO/MMT interface not conducive to crystallization because it promotes amorphous polymer conformations in the vicinity of the inorganic fillers. Thus, MMT causes a retardation of the crystal growth front and results in crystal morphologies that are characterized by non-spherical shapes with jagged edges. Moreover, this PEO crystal obstruction by the MMT allows for the "homogeneous" nucleation of large numbers of crystallites, which grow to much smaller sizes than neat PEO spherulites. In the Na⁺-MMT-filled PEO, crystallization nucleation sites occur in the bulk of the PEO matrix, i.e., far from the silicate surfaces, in considerably larger numbers than in unfilled PEO at the same undercooling. This higher nucleation density is a manifestation of two effects: (a) the disruption of the spatial continuity by the inorganic layers, which allows for the independent nucleation of PEO crystallites in the spaces between the fillers, and (b) the characteristic PEO/Na⁺ coordination, which markedly inhibits "heterogeneous" nucleation by the MMT fillers. The absence of marked heterogeneous nucleation contrasts the PEO behavior against most of the other polymer/MMT systems studied, where heterogeneous nucleation and/or epitaxial crystallization are the dominant effects. Despite the different crystal morphologies between neat and filled PEO, there is no marked change in polymer crystal fraction for the small amounts of silicate ($\phi_{\text{MMT}} < 10\%$) studied here. For larger MMT loadings than studied here, the introduction of more PEO/MMT interfaces in the system decreases the PEO crystallinity proportionally to ϕ_{MMT} .^{20,21}

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