

Effect of nm-thin inorganic layered fillers on the crystallization of polymer nanocomposites

H. Nakajima^{1,2}, and E. Manias^{*1}

¹Pennsylvania State University, Materials Science & Engineering Department, 325-D Building, University Park, PA 16801

²Sumitomo Chemical Co., Ltd., Petrochemicals Research Laboratory 2-1 Kitasode, Sodegaura, Chiba, 299-0295, Japan

INTRODUCTION

Polymer nanocomposites have attracted a lot of interest in academic and industrial materials research^{1,2}. The vast majority of the research effort in polymer/clay nanocomposites has been focused on the dispersion of clays in polymers, usually expecting that complete exfoliation of the clays in the polymer would yield the best performing composite systems². However, for semi-crystalline polymers, the effect of the inorganic filler on the crystallization of the organic matrix becomes extremely important for the properties of the composite.

For example, nylon-6/montmorillonite³ studies have shown a nucleating and epitaxial effect of the inorganic surfaces, which stabilizes a surface-induced crystalline phase³ (γ phase), that is rarely found in the bulk polymer. This effect results in impressive enhancements of the mechanical and thermal properties in the nanocomposite, since the surface nucleated crystalline phase has better mechanical and thermal characteristics than the bulk crystal phase (α phase). For the nylon-6 case, the current opinion is that the origin of this substantial effect on the polymer crystallization lies in the manner that amide interact with the inorganic aluminosilicates, through strong hydrogen-bonding interactions.

In order to investigate the effect of nano-layered fillers (esp. montmorillonite) on polymer crystallization, we compare the crystallization behavior of polymer/montmorillonite nanocomposites, across a number of different polymers; namely, poly(vinyl alcohol) [PVA⁴], polypropylene [PP⁵], poly(ethylene terephthalate) [PET], syndiotactic-polystyrene [sPS⁶], and poly(ethylene oxide) [PEO⁷].

EXPERIMENTAL

Materials. Sodium montmorillonite (mmt) and its organically modified variants (ommt) were obtained from Southern Clay Products and Nanacor. Organophilic clays used in this study were I44PA (Nanacor) and alkyl-imidazolium modified montmorillonite (Imm-mmt). Maleic anhydride modified polypropylene (PP-MA) was obtained from Sumitomo Chemical Co., Ltd. Poly(ethylene oxide) (PEO) was purchased from PolySciences and Alfa Aesar. Poly(ethylene terephthalate) (PET) was purchased from KoSA. Detailed information for the polymers are provided somewhere else^{6,7}.

Characterization. Differential scanning calorimetry (DSC) was performed in a Perkin-Elmer DSC7 and a TA Q100. Cross-polarization optical microscopy (CPOM) was carried out in a Olympus BH-2 optical microscope, equipped with a Mettler hot-stage, and a video camera connected to a VCR. Atomic force microscopy (AFM) was performed using a Digital Instruments Multimode AFM, controlled by the Nanoscope IIIa scanning probe microscope controller with a Nanoscope Extender.

Preparation of polymer/clay nanocomposites. PP-MA/ommt nanocomposites were prepared in a Brabender Plasticoder at 200 °C for 10min. PET/Imm-mmt nanocomposites were prepared by a twin-screw extruder. PEO/mmt nanocomposites were prepared by solution casting⁷.

RESULTS and DISCUSSION

The equilibrium melting temperature (T_m^0) of various polymers in the presence of mmt fillers was studied by standard DSC approaches and was compared to that of the neat (unfilled) polymer. As shown in Figure 1, T_m^0 of PP-MA, PET, and PEO were estimated based on Hoffman-Weeks plots, and it is clear that when mmt content is less than

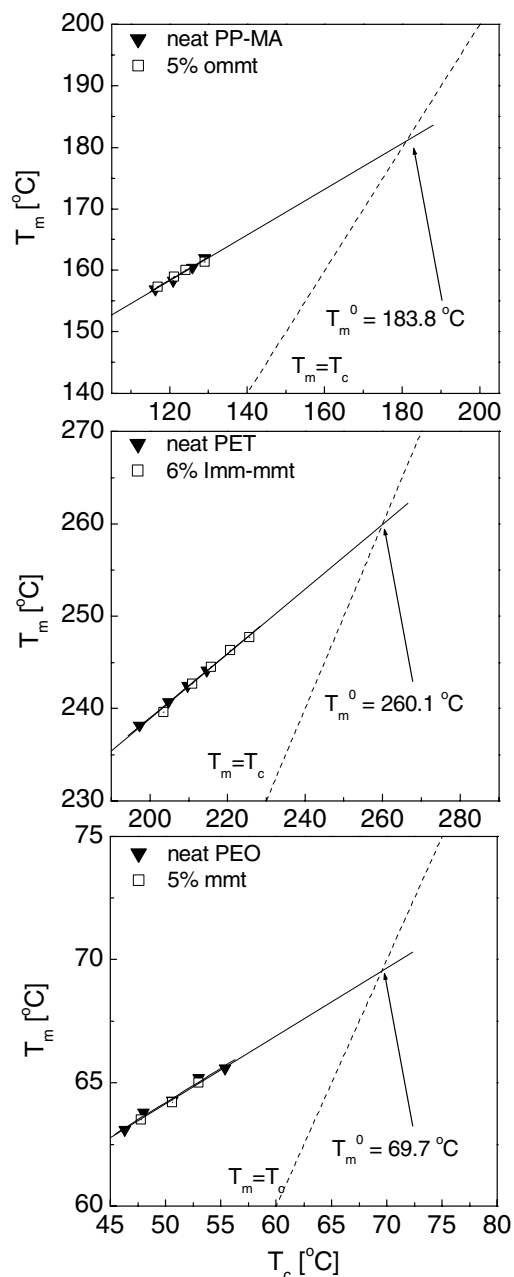


Figure 1. Hoffman-Weeks plots of neat polymers and their nanocomposites: [top] PP-MA, [middle] PET, [bottom] PEO.

10wt%, the mmt addition does not change T_m^0 [T_m^0 (PP-MA) = 183.8 °C, T_m^0 (PET) = 260.1 °C, T_m^0 (PEO) = 69.7 °C]. These results are consistent with the literature reported before^{8,9}, and allows for comparing the crystallization kinetics of neat polymers and their nanocomposites at the same isothermal crystallization temperature.

To understand the effect of mmt on the crystallization kinetics of these polymers, isothermal crystallization measurements were carried out with DSC, and complemented by direct imaging (CPOM and AFM) for systems crystallized under the same conditions. Initially (crystals grow in 3-D and the crystallites have not yet impinged), crystallization kinetics can be expressed by the following equation:

$$V_f^c = \frac{4}{3} \pi \rho_n G_R^3 t^3$$

where, V_f^c is the total crystal volume (crystallinity), ρ_n is nuclei density, G_R is the linear crystal growth rate, and t is the crystallization time.

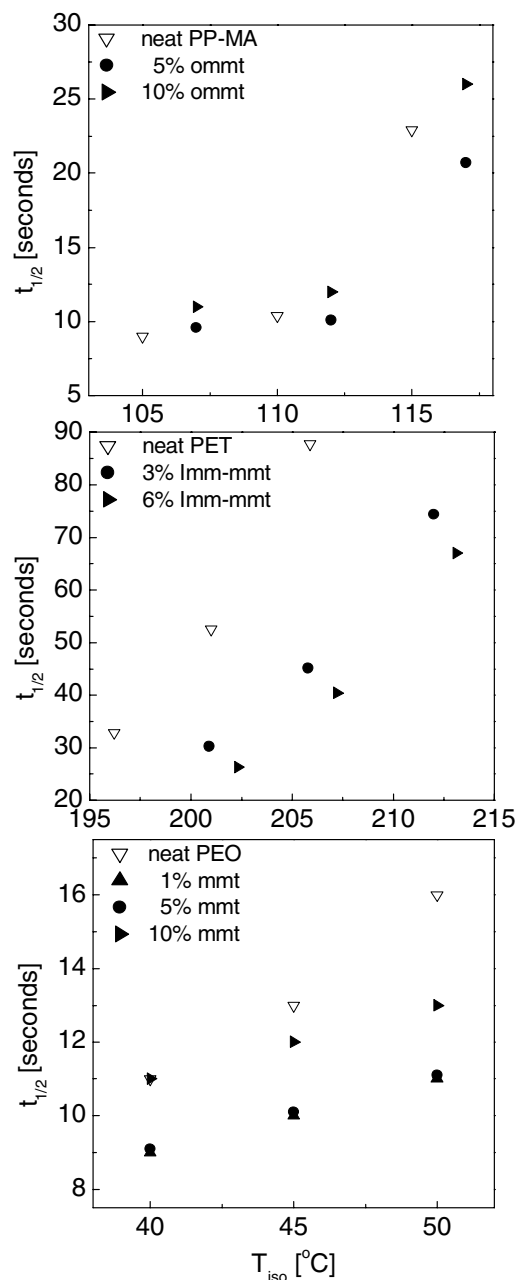


Figure 2. Half time of crystallization for neat polymers and their nanocomposites: [top] PP-MA, [middle] PET, [bottom]

When V_f^c is 50%, the crystallization time t is defined as the half time of crystallization ($t_{1/2}$), and corresponds to the time necessary to reach 50% of total enthalpy of crystallization under isothermal DSC conditions (figure 2). When ρ_n is measured by CPOM and/or AFM, G_R can be eventually estimated.

Figure 2 shows the half times of crystallization ($t_{1/2}$) for various isothermal crystallization temperatures (T_{iso}) for neat polymers and their nanocomposites. As expected, $t_{1/2}$ decreased as T_{iso} decreased and the clay content increased. However, for PP-MA, there was no distinct effect of clay on $t_{1/2}$ below $T_{iso} = 115$ °C. Thus, the overall crystallization rate increases with the clay addition in the polymer.

The effect of clay on the nuclei density of polymer was evaluated by CPOM and AFM. There is a general trend that the nuclei density of

polymer increases as the clay content increases¹¹, independent of the polymer/clay interactions. For both PP-MA and PET, the crystal growth starts near the montmorillonite surface, which indicates that the clay act as a nucleating agent and promotes the heterogeneous nucleation. These results are consistent with the scanning DSC studies, which exhibit an increase of the crystallization temperature by adding mmt¹⁰. As for PEO, a similar significant increase of nuclei density (more than an order of magnitude) was also observed after montmorillonite addition⁷, however, in this case, the crystal nuclei initiate in the bulk PEO, indicating that there is no heterogeneous nucleation as for the previous systems, i.e. PP-MA and PET. In this last case, the strong coordination of PEO to small cations (e.g. Na^+) on the mmt surface, highly suppresses the crystallization of PEO next to the inorganic fillers⁷.

Despite the qualitative differences between PEO and PP, PET crystallization when reinforced by mmt, and despite the quantitative differences in $t_{1/2}$ (figure 2), when the increase of nuclei density is accounted for, the linear crystal growth is slowed down due to the introduction of clay across all systems. Namely, $G_R^{(PP-MA/ommt)} \cong 1/2 G_R^{(PP-MA)}$ for PP-MA, $G_R^{(PET/lmm-mmt)} \cong 1/4 G_R^{(PET)}$ for PET, and $G_R^{(PEO/mmt)} \cong 1/3 G_R^{(PEO)}$ for PEO, i.e. for all systems that G_R decreases 2-4 fold by the addition of mmt. This agreement between such different systems strongly indicates that the geometric constraints associated with the dispersion of mmt fillers is determining the effect (decrease) on the linear crystal growth rate in these systems, rather than the polymer/mmt interactions. In this latter case, one would expect a qualitatively different effect in PET/PP compared to PEO, and also substantial quantitative differences between PET and PP as well.

CONCLUSIONS

A comparative study of the effect of nm-thin layered filler (mmt) on the crystallization kinetics of semi-crystalline polymers (i.e. PP-MA, PET, PEO) was carried out. The introduction of mmt fillers results in an increase of the overall crystallization rate, as well as an increase of nuclei density, across all three polymers; the enumeration of these properties reveals quantitative differences between these three systems that span two orders of magnitude. Despite these quantitative differences, the linear crystal growth rate (G_R) is slowed down due to the introduction of clay by 2-4 fold, reflecting a much stronger effect of the geometric constraints associated with the dispersion of mmt fillers, rather than the polymer/mmt interactions, on the G_R .

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- For PP-MA, the crystal nuclei density increased by ca. 6-8 fold, at 5-10wt% ommt content; whereas for PET, the increase of nuclei density was more than 500 fold, at 3-6wt% lmm-mmt.