Review

Short review on the crystallization behavior of PET/clay nanocomposites

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In recent years, the area of polymer nanocomposites based on organically modified clay has attracted much interest in academia and industry because of their peculiar and fascinating properties. Nanomaterials are presently considered to be high potential filler material, with high aspect ratio and extremely large surface area. They improve mechanical and physical properties of polymers. Lighter, thinner, stronger and cheaper structures are the goals of materials science and engineering applications nowadays. Appropriate addition of nanoparticles to a polymer matrix can enhance its performance by simply focussing on the nature and properties of the nanoscale filler. So, the properties of polymer nanocomposites depend greatly on the chemistry of polymer matrix, nature of nanofillers and the way in which they are prepared. Various analysis techniques were used to characterize the dispersion and the properties of the nanocomposites, using XRD, TGA, SEM, DSC, TEM, DMTA, etc. Several polymers such as polypropylene, polyamide 6, polyethylene, polyethylene terephthalate (PET), polybutylene terephthalate (PBT), polylactic acid (PLA), etc., have been tested as matrices. This paper emphasises on the overview of the crystallization properties of PET/clay nanocomposites by different authors. It has been reported that nanoparticles of clay dispersed in PET polymer matrix act as nucleating agent. In this way, they enhance the crystallization rates of PET/clay nanocomposites.

Key words: Nanocomposites, polyethylene terephthalate (PET), clay, crystallization.

INTRODUCTION

The reinforcement of polymers using fillers is common in the production and processing of polymeric materials. Fillers play important roles in modifying the desirable properties of polymers and reducing the cost of their composites (Tjong, 2006; Pettrain et al., 2008). The interest in new nanoscale fillers has grown rapidly in the last two decades. This interest arises from the fact that when these nanoscopic fillers are used instead of conventional reinforcing material, the composite materials exhibit better performances, such as, mechanical, thermal stability, dimensional stability, flame retardant and gas barrier properties etc., at relatively small loadings (Gonzalez et al., 2006; Kusmono et al., 2008; Roohollah and Ahmad, 2008; Nirukhe and Shertukde, 2009).

Polymer nanocomposite is a new class of composite materials derived from nanoparticles and it is a two phase material where one of the phases is in the nanometer range in at least one dimension being less than 100 nm (Giannelis, 1996; Wang et al., 2004; Lei et al., 2006; Manias, 2007).

The most common filler used in nanocomposites is nanoclay, other fillers like carbon nanofibers, carbon nanotubes, graphene, and core shell materials are also found very commonly in polymer nanocomposites. In recent years, polymer/clay nanocomposites have emerged as one of the most promising nanocomposites. They have attracted great academic and industrial interest because of enhancement in properties. These composites offer better mechanical, thermal, barrier and chemical resistance properties as compared to conventional composites. Nanocomposites have high potential for applications in many fields such as automative and packaging industries. With relatively low

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loading of nanometer-sized particles, they show dramatically increased stiffness, heat distortion temperature (HDT), dimensional stability, gas barrier properties, electrical conductivity and flame retardancy (Suprakas and Musami, 2003; Ahmadi et al., 2004; Lei et al., 2006; Hong et al., 2008; Miray and Ulku, 2008; Baniasadi et al., 2010).

The concept of polymer/clay nanocomposites systems were first introduced by researchers from Toyota who discovered the possibility of building exfoliated nanocomposites from nylon 6 and organophilic clay, known as nylon 6-clay hybrid (NCH) via in situ polymerization. The NCH exhibits various superior properties such as high strength, high modulus, and high heat resistance compared to nylon 6 (Naoki et al., 1996, 2000). In addition to this, another observation was proposed by Vaia et al. (2003) to represent the possibility of the making melt-mix polymers with layered silicates, without the use of organic solvents. Today, efforts are being conducted globally, using almost all types of polymer matrices. Until now, many kinds of polymer/clay nanocomposites have been researched upon using polycarbonate, polystyrene, polyimide, epoxy, polymethyl methacrylate (PMMA), polyethylene, polypropylene, polyamide, polyurethane, polyethylene oxide, polyethylene terephalate, polybutylene terephalate, and so on, as matrices (Naoki et al., 2000; Li et al., 2001; Suprakas and Musami, 2003; Ahmadi et al., 2004; Defeng et al., 2006; Quang and Donald, 2006).

Polymer-clay nanocomposites use smectite type clays as fillers such as hectorite, montmorillonite (MMT) or synthetic mica and all minerals with layered structures. Among various kinds of natural and synthetic clays, the most common nanoscopic filler is derived from MMT clay. It was found naturally in layered silicate structure with high surface area, about 750 m^2/gm and high aspect ratio and have a cross sectional area of 100 m^2 which is very small compared to conventional fillers (Akane and Arimitsu, 2006; Clois and Gary, 2006). The properties of clay based nanocomposites polymers are influenced by the type of clay, choice of clay pre-treatment, the selection of polymer component and the way in which the polymer is incorporated into the nanocomposites (Yeh et al., 2004; Tjong, 2006). In general, the improvements in the properties may be attributed to the following factors: Large surface area; High aspect ratio; Submicroscobic dispersion of the clay in the polymeric matrix (Young-Wook et al., 2005); Ionic bond between organic polymer and inorganic clay (Mahmood and Musa, 2002; Nicolas et al., 2007).

The performance of polymer-clay nanocomposites strongly depends on the breaking up of clay particles in the polymer matrix. The dispersion of nanofillers, that is, clay in the polymers, is rather poor due to their incompatibility with polymers. Therefore, organic surfactant and compatibilizer additions are required to improve the dispersion of these nanofillers in polymeric matrices. In order to obtain good interfacial adhesions and mechanical properties, the hydrophilic clay needs to be modified prior to introduce in most polymer matrices which are organophilic (Garcia-Lopez et al., 2003; Suprakas and Musami, 2003; Benetti et al., 2005).

Recently, a new class of materials, PET/clay nanocomposites, has been developed successfully. PET is an engineering semi crystalline thermoplastic polymer with low cost and high performance, which has wide applications in the form of films, fibres and non- fibres. Film applications mainly include food and beverage bottles (In Yee et al., 2004; Mazeyar et al., 2010). PET is intrinsically a polymer with slow crystallization rate and high melting temperature. So, it has not been considered for applications involving high speed processing, such as injection moulding. To accommodate typical industrial injection moulding process, additives (most often nucleating agents) are introduced to enhance the PET crystallization (Cheng et al., 2003, 2004; Yaming et al., 2004; Tong et al., 2004; Yee et al., 2004).

PET/clay nanocomposites have attracted much attention because of its superior thermal resistance, mechanical properties, low permeability, chemical resistance and mechanical performance. The studies on PET/clay nanocomposites are mainly focused on its synthesis, effect of organoclay content on crystallization behavior, nanoscale morphology, thermal behavior and melting behavior. The presence of nanometer sized clay layers in a PET polymer matrix not only creates an enormous interfacial area but also increases crystallization rate, O_2 permeability, wear resistance, flexural, tribological, thermal and mechanical behaviour of PET (Mazeyar et al., 2010). Because of the complexity of the PET/clay system, the effect of clay on the crystallization performance of PET has not been properly addressed (Yaming et al., 2004; Tong et al., 2004; Guohu et al., 2004; Ali et al., 2010). In this article, PET/clay nanocomposites have been studied with regard to their crystallization properties by different authors.

CRYSTALLIZATION BEHAVIOR OF PET/ORGANOCLAY NANOCOMPOSITES

Studies on semi crystalline polymer-clay nanocomposites describe that the nanosized clay particles affect the crystallization behavior and the crystal structure of the matrix polymer (Young-Wook et al., 2005). Qi et al. (1999) reported that PET/clay nanocomposites had a three times faster crystallization rate than that of pure PET. This indicates that nanoparticles of clay dispersed in matrix acted as nucleating agent. Crystallization behavior of PET/clay nanocomposites is of great importance from both a theoretical and industrial standpoints. Many authors studied the effect of the presence of clay on the isothermal and non-isothermal crystallization behavior of PET/clay nanocomposites. Non-isothermal crystallization

can broaden and supplement the knowledge of the crystallization behavior of polymers.

Cheng et al. (2003) studied the nucleating effect of montmorillonite on crystallization of PET nanocomposite by solution intercalation method. They prepared four compositions with varying amount of organoclay (wt %) and neat PET and carried out a comparative study. Layered silicate used in this study was sodium MMT with cationic exchange capacity (CEC) of 114 mEq/100 g (abbreviated as 11 K). Clay was organo-modified with intercalation agent cetyltrimethylammonium chloride (CMC). Nucleating effect of organoclay is investigated using DSC analysis. The crystallization rate of PET in the PET/11 K-M (organoclay) nanocomposites increases with the organoclay loadings from 1 to 10 wt %. Maximum increase in crystallization rate was observed in the 10 wt % organoclay. Further increases in the content of organoclay lead to decrease in crystallization rate. It is due to the agglomeration of organoclay in the PET matrix.

The degree of super cooling ($\Delta T = T_m - T_c$) may be a measurement of a polymer's crystallinity. ΔT is proportional to the free energy of melting, which is thermodynamic driving force of crystallization (Seung et al., 2000). The smaller the value of ΔT, the higher the overall crystallization rate. The ΔT values for the PET/11 K-M nanocomposites are smaller than that of neat PET and 90/10 PET/11 K-M exhibits the smallest ΔT. These findings indicate that 11 K-M based PET nanocomposites have heterogeneous nucleation which offers enormous surface area and hence accelerate the crystallization rate of PET during nucleation.

Cheng et al. (2004) studied the effects of organoclay loading on the crystallization behavior and thermal stability of PET/clay nanocomposites. In their study, layers of sodium MMT with cationic exchange capacity (CEC) value of 87 mEq/100 g (abbreviated as 8 K) were intercalated by cetylpyridinium chloride (CPC) instead of CMC. Again, DSC analysis showed that clay behaves as nucleating agent and enhances the crystallization rate of PET. They calculated half crystallization time ($t_{1/2}$) using equation:

$$t_{1/2} = (T_{on} - T_c)/\chi$$

where, T_{on} is the crystallization onset temperature, T_c is temperature where the exothermal shows a peak and χ is the cooling rate (°C/min). $t_{1/2}$ represents the time for the system to reach 50% of relative degree of crystallinity and it is used to evaluate the rate of crystallization of different systems (Calcagno et al., 2007; Jiann-Wen, 2008).

The $t_{1/2}$ values of nanocomposites are smaller than that of neat PET. The 90/10 PET/8 K-P (organoclay) exhibits the smallest $t_{1/2}$ (1.45 min) and its crystallization rate is 1.55 times than that of pure PET. On the other hand 90/10 PET/11K-M (organoclay) exhibits the smallest $t_{1/2}$ (1.35 min) and its crystallization rate is 1.67 times than

that of pure PET.

Wang et al. (2004) studied the non-isothermal melt crystallization behavior of pristine PET and PET/clay nanocomposites of different viscosities by using DSC, according to different kinetic models namely, Avrami analysis modified by Jeziorny, the Ozawa model and method developed by Mo. Non- isothermal crysatllization dynamics show that the nanocomposites of PET have greater crystallization rates than that of pure PET.

Crystallization morphology and isothermal crystallization kinetics of PET/clay naocomposites were studied by Wan et al. (2004). In an isothermal crystallization process, initially, some crystallites in the nanocomposite are rod shaped and later, exhibited three dimensional growths. Neat PET has typical spherulitic superstructure with a spherulitic size of about 20 μm, whereas, nanocomposites are irregularly shaped with a size of 5 μm, and they interlock with others, without clear boundaries. Avrami equation was used in a kinetic analysis of the isothermal crystallization process, that is:

$$X_c(t) = 1 - \exp(-kt)^n$$

where $X_c(t)$ is the weight fraction of the crystallites at time t, k is the crystallization rate constant; and n is the Avrami exponent. k and n are very useful for determining the crystallization mechanism.

Phang et al. (2004) studied the heterogeneous nucleation effects of clay layers on cold and melt crystallization and melting behavior of PET. They prepared PET/clay nanocomposites by simple melt compounding with different clay loadings. DSC heating-cooling cycles showed that the cold and melt crystallization enthalpies of the nanocomposites increase with increasing clay content. This indicates that, the nanoclay fillers induce the formation of crystals as heterogeneous nucleation sites, thus, promoting the crystallization rate and degree of crystallinity in the nanocomposites.

Calcagno et al. (2007) prepared PET nanocomposites using montmorillonite with different organic modifiers (cloisite 15A, 30B, and 10A) in order to evaluate the effect of clay organic modifies on the morphology and crystallization properties of the nanocomposites. The T_c of the PET nanocomposites was higher than that of pure PET. Higher T_c of the PET nanocomposites indicated that the clay nucleated the PET crystallization process, and the nucleating effect was higher when cloisite 10A was used. This is due to the presence of the aromatic ring in the modifier as in the PET chain, which favours the diffusion process, resulting in more sheets of the clay and more crystallization nuclei. The morphology of crystallization was observed by POM.

Calcagno et al. (2008) studied PP/PET blends system based on nanocomposites. They studied the crystallization behaviour and morphology of nanocomposites based on PP/PET blends. For this

purpose, blend containing PP, PET and MMT were prepared in a twin screw extruder. Polymer blending is a convenient route for the development of new polymeric materials with excellent properties of more than one polymer. The PP/PET blend has importance due to some engineering applications. Several studies have been demonstrated that, clay, acting as a nucleating agent in the nanocomposites, increases the crystallization rate of PP/PET. However, the presence of clay in both blends (with and without compatibilizer, (PP-g-MA)) resulted in a decrease of crystallization rate of the PET phase. The crystallinity degree of PP was higher in the blends when the start point to PP crystallization.

Guan et al. (2004) studied the crystallization behavior of PET/clay nanocomposites, prepared through in situ polymerization method by using techniques DSC, POM and SEM. They concluded that different surface modification of MMT resulted in variation in crystallization behavior. Discrepant crystallization behavior was due to morphology of clay into the matrix, surface shielding effect of small organic surfactant molecule and the nucleating affects of metallic derivative released from MMT. So, the surface modification of clay affects the crystallization rate of PET nanocomposites.

After Phang et al. (2004), Ali et al. (2010) studied the cold and melt crystallization behaviours of PET/clay nanocomposites, using natural MMT (Na MMT) and organo-modified montmorillonite (org-MMT) with the same amount of inorganic content. Two nanocomposites samples were prepared by melt processing. DSC analysis revealed that dispersed clay layers enhanced nucleation by increasing the interfacial surface energy. From the kinetics study, it was reported that the melt crystallization rate of the sample containing Na-MMT was higher than org-MMT at cooling rate. On the basis of their results, they have concluded that the organic ammonium groups in the org-MMT decrease the crystallization rate of PET chains possibly by affecting the chain diffusion and folding.

Conclusion

In the PET/clay nanocomposites, clay particles play a nucleating role and have strong interactions with PET molecular chains. Nanoclays enhance the nucleation, possibly by decreasing the interfacial surface energy. Higher clay contents in PET phase retard the crystallization rate of PET due to the agglomeration of the organoclay in the PET matrix.

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