Crystallization, Properties, and Crystal and Nanoscale Morphology of PET–Clay Nanocomposites

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ABSTRACT: The crystallization process and crystal morphology of poly(ethylene terephathalate) (PET)–clay nanoscale composites prepared by intercalation, followed by *in-situ* polymerization, have been investigated by scanning electronic microscopy (SEM), transmission electronic microscopy (TEM), dynamic scanning calorimetry (DSC), and X-ray techniques, together with mechanical methods. Results of the noniso-thermal crystallization dynamics show that the nanocomposites of PET (Nano-PET) have 3 times greater crystallization rate than that of pure PET. The thermal properties of Nano-PET showed heat distortion temperature (HDT) 20–50°C higher than the pure PET, while with a clay content of 5%, the modulus of Nano-PET is as much as 3 times that of pure PET. Statistical results of particle distribution show that the average nanoscale size ranges from 10 to 100 nm. The particles are homogenously distributed with their size percentages in normal distribution. The agglomerated particles are 4% or so with some particles size in the micrometer scale. The morphology of exfoliated clay particles are in a diordered state, in which the morphology of the PET spherulitics are not easy to detect in most of microdomains compared with the pure PET. The molecular chains intercalated in the interlamellae of clay are confined to some extent, which will explain the narrow distribution of the Nano-PET molecular weight. The stripe-belt morphology of the intercalated clay show that polymer PET molecular chains are intercalated into the enlarged interlamellar space. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 1139–1146, 1999

Key words: PET–clay; nanoscale composites; morphology

INTRODUCTION

Poly(ethylene terephathalate) (PET) is a polymer material with low cost and high performance, which has found wide applications to fields of fibers and nonfibers. The statistical reports show that the overall output of PET in the world in 1995 has surpassed 16 million tons, in which fiber usage accounts for approximately 71% and the nonfiber usage accounts for only a lower percentage,[1] showing the great potential grown for PET in nonfiber applications. The nonfiber usages of PET mainly include its applications to bottles, films, and engineering plastics. These nonfibers applications stimulate research on the development of PET. Patents concerning PET or overall polyesters are numerous,[2] in which some patents cover a variety of fields, and other patterns concerning PET are dealt with blends and/or composites of PET with inorganic particles.[3,4] Macro-blending of PET with an inorganic phase, such as $CaCO_3$, carbon fiber, and glass fiber has also produced many high-performance PET-based blending composites. By means of different surface modifications, such as reversing the wettability of the inorganic particles surface, grafting hydro-

philic, and/or hydrophobic group into polymer chains, the properties of PET based composites are improved a lot. These improvements have provided PET-based blending and/or composites with higher mechanical and thermal performance than pure PET.[1–6] However, the phase separation resulting from the difference of the surface tension force between the filler and polymer matrix is usually obvious, which has produced an obstacle on the ultimate dispersion and adhersion of particles to the polymer matrix.

The nanoparticles are often used to directly blend with polymer resins but have also achieved some successful results.[7] These direct blending method cannot avoid the particle clustering tendency. Thus, the advantages of nanoscale particles have been limited.

Recently, Usuki et al.[8–10] and Qi et al.[11–13] have reported the preparations of nylon 6–clay nanocomposites, which adopted the lamellar clay as an inorganic phase, and the clay is intercalated by organic compounds, such as ε-caprolactum, by which the intercalated clay can react with nylon 6 monomers to give the nano-nylon 6 with heat distortion temperature enhanced 100°C or so, compared with nylon 6 itself.

By means of the intercalated chemistry, the clay can be exfoliated into different sized sheets and be reacted *in-situ* with the monomers, which formed a hybride composites of clay–organic polymers.

Design of such kinds of hybrid nanocomposites not only provides a way to homogeneously disperse the nanoscale clay particles into polymer matrixes but also stimulates the development of new materials with high strength, high modulus, high heat distortion temperature (HDT), and low gas permeability.

In this article, the crystallization behavior, the properties, and the crystal and nanoscale morphology are investigated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) methods.

MATERIALS AND EXPERIMENTS

Sample Preparation

The original clay is made from Xuanhua, Hebei, China. The raw ores of clay have an approximately 80% content of montmorrilonite ore. The raw clay is refined and made into particles with diameters of 40 μm or so and with cation ion exchange capacity ranging from 70 to 110 meq/100 g. This kind of refined clay is made into slurry first, forming solution with intercalated reagent,[11,14] through which the obtained clay is called treated clay, which directly reacts with PET monomers in an autoclave (for example, 151). This preparation of Nano-PET still deals with some additives, which have been patented in China.[11,14]

The obtained melted Nano-PET is cut into pellets through the cutting machine with the water as cooling media, and then these pellets are used to compress into film with thickness from 1–2 mm at 270°C. The pellets should dry for 4 h at 120°C before use.

The samples for mechanical measurement are made according to the standard of GB1447-83, GB1449-83, GB1843-80, and GB 1634-79, which refer to the corresponding international standard of ASTM.

Samples for SEM are films cracked in cold liquid N_2, or the samples with fresh face are produced by Noched Izod impact and/or tensile breaking. The fresh face samples are coated with metal of Au for SEM observation.

The super thin films for TEM are obtained by a steel knife blade to give film thicknesses below 100 nm. Some film samples are cut with original samples in the capsule.

Characterization

Sample viscosity is measured under such conditions such that Nano-PET pellet is solved in solvents of 50/50 (w/w) of 1,1,2,2-tetrachloro ethane–phenol and is measured with Ulman viscometry with a concentration of 0.1 g/100 mL.

The above solution is diluted into 1/10 of the concentrations in solvent of $CHCl_3$ (chloroform) and then are measured on Shimidazu GPC for measurement of molecular weight.

Nano-PET samples go through the DSC scanning with scanning rate from 10 to 20°C/min and a scanning scope from 50 to 300°C.

X-ray patterns of Nano-PET are measured on Regaku/D-Max RA 12 kv with scanning rate of 2°/min and scanning scope from 1.0 to 40.0°.

RESULTS AND DISCUSSIONS

The samples obtained have intrinsic viscosity from 0.56 (pure PET) to 0.68 (Nano-PET with a clay weight content of 5%). These samples are

Table I   Results of Nano-PET Under Nonisothermal Crystallization Process

Sample No.	Clay Content (wt %)	$T_{m.c}$ (°C)	$T_{g.c}$ (°C)	T_c (°C)	$t_{1/2}$ (min)
1	0.0	174.0	134	194	1.80
2	0.5	201.0	—	—	—
3	1.5	206.0	126.0	194	0.72
4	2.5	209.0	127.0	194	0.80
5	5.0	208.0	122.0	194	0.60

$T_{m.c}$ is the crystallization temperature from the melt state; $T_{g.c}$ is the crystallization temperature from the glassy state; T_c is the crystallization temperature from the melt.

adopted to go through a nonisothermal crystallization process, which is described by Avrami equations.[15,16] By means of Avrami equations, the Avrami number (n) and crystallization dynamics constant (k) are obtained, which will be used to get crystallization rate ($t_{1/2}$) shown below:

$$t_{1/2} = (\ln 2/k)^{1/n} \qquad (1)$$

The obtained results of $t_{1/2}$ and the thermal dynamics parameters for Nano-PET are listed in Table I.

From the different values between T_m and $T_{g.c.}$, it is seen that the clay content affect the crystallinity and take the role of nucleating reagent. When annealing at 194°C, the crystallization half-time of $t_{1/2}$ is decreased with the clay content, and thus the crystallization rate for sample no. 5 is three times or so greater than that of the pure PET, demonstrating that the clay plays a nucleating role to some extent.

The thermal properties and mechanical properties of Nano-PET are shown in Table II.

In Table II, the heat of fusion for nano-PET samples is calibrated by formula (2), as follows:

$$\Delta H_m = \Delta H_0/(1 - \text{k.x}) \qquad (2)$$

where $\text{k} = \Delta H_0/\Delta H_t$, ΔH_t is the total heat of fusion (J), ΔH_0 is the heat of fusion per gram of sample of Nano-PET (J/g), ΔHm is the corrected value of heat of fusion, and x is the absolute weight of clay in the Nano-PET samples (g). When the clay content is low, the k.x will be approximately substituted by the percentage of clay content. The heat of fusion in Table II are corrected by formula (2) with the clay weight percentage as values of kx.

From Table II, it is seen that the heat of fusion decreases with the content of clay, and the heat distorsion temperature (HDT) increases with the content of clay. Thus, it seems obvious that the introduction of nanoscale of clay produced an obstacle on the molecular chains movement; that is, the lamellar space of clay confines the molecular chains movement, which will reduce the tendency for molecular chains to be crystallized, though the confined molecular chains may be well ordered in the lamellar space. Similarly, the nanoscale clay does exert shielding effect on molecular chains subjected to external heat, and this shielding effect will keep until the external temperature is high up to the melting point of the polymer matrixes. There exists a critical temperature for nanoscale particles; when the external temperature overpasses the critical temperature, the nanoscale particles will be self-ordered very well and give a high heat distortion temperature, seen in Table II. In the case of Table II, the external temperature is the polymerization heat and external temperature.

In Table II, the melting points of Nano-PET slightly decreases with the content of clay; these results are not the errors of the DSC experiments but are related with the size reduction of nanoscale particles. It is well known that the nanoscale particles have a much lower melting point than the block ones, which has brought

Table II   Thermal Properties and Mechanical Properties of Nano-PET

No.	Clay (wt %)	H_m (J/g)	HDT (°C)	σ_b (MPa)	E_b (MPa)	$T_{m.p}$ (°C)	T_d (°C)
1	0.0	50.0	75	108	1400	259.0	410
2	0.5	—	83	110	2070	258.0	—
3	1.5	43.5	95	97	2700	257.0	416
4	3.0	44.0	101	88	3620	254.0	413
5	5.0	45.2	115	82	3800	252.0	429

Figure 1 Thermal degradation behaviors of PET–clay nanocomposites: (no. 1) pure PET; (no. 2) 0.5 wt % clay; (no. 3) 1.5 wt % clay; (no. 5) 5.0 wt % clay.

some advantages in processing, such as in porcelain, for which the cacination temperature will be quite low for nanoscale particles.[17]

It will be seen that the difference between the nanoscale particles and macroparticles in that the nanoscale particle will help to increase the interface properties of polymer composites, but macroparticles will not do and will even decrease some properties under some cases. For example, PET, blending materials with macroparticles of clay (with diameters of over 2 μm) have their processing properties reduced greatly compared to pure PET due to the weak or bad interface interaction, but the processing properties of PET–clay nanocomposites enhanced due to good or strong interface interaction.

When the external temperature approach the degradation temperature, the nanoscale particles will show more strong interaction with the matrixes of PET, which explains the results of Nano-PET degradation temperature enhanced, shown in Table II. The degradation behaviors of Nano-PET are shown in Figure 1.

The enhancement of modulus for the Nano-PET can be explained by Halpin–Tsai equations.[18] According to the Halpin–Tsai equation, the hard particles have a much higher modulus than the polymer matrices, which will increase the composite modulus.

In fact, the obtained Nano-PET samples are very hard compared with the original PET. According to Hall–Petch relation[18] of formula (3), when the particle size becomes smaller and smaller, the hardness of obtained composites materials will become harder and harder until the condition of $d < dc$ (critical size) is reached, and the materials will become soft compared with the block ones:

$$H = H_0 + kd^{-1/2} \qquad (3)$$

where H_0 is hardness of the original scale of particles and H is the hardness of average scale of particles.

The critical size of PET–clay nanocomposites do not appear to have been reached as no soft samples are obtained in our preparations. Thus, this phenomenon will need further investigating.

The interaction between clay and PET matrix can also be relatively demonstrated by the enlargement degree of interlamellar distance. The interlamellar distances can be decided by the diffraction peak and the position of d_{001} in the X-ray method, the values of which are decided by Bragg equation shown as below:

$$2d_{001}\sin \theta = \lambda \qquad (4)$$

Figure 2 X-ray patterns of clay, treated clay, and PET–clay nanocomposites: (1) PET–clay; (2) intercalated clay in a dry state; (3) clay in a dry state; (4) intercalated clay in a moist state.

where d_{001} is the interplanar distance of (001) diffraction face, θ is the diffraction position, and λ is the wavelength.

In our practice, it is believed that the greater the interlamellar distance, the greater the interaction of PET molecular chains with clay sheets. That is to say, the interaction of PET molecular chains with clay lamellar sheets can be expressed relatively by the interlamellar distance of d_{001}. Figure 2 has shown the X-ray patterns of Nano-PET, original clay, and treated clay.

It is seen that the interlamellar distance of Nano-PET can reach 1.4 to 3.5 nm, and the lamelar distance is enlarged from 0.3 to 2.5 nm compared with the lamellar distance of 1.12 nm of original clay, which show that the clay interlamellar distance is enlarged by both water and intercalated molecules (reagents). The interlamellar distance shown in Figure 2 is calculated by formula (4).

The exfoliated silicates sheets can reduce the surface potentials of the microsize of particles, which increases with the degree of the particles exfoliated. The cluster of the particles is reduced depending on these interactions.

Figure 3 shows the SEM results for sample no. 3, whose particle distribution morphology includes overall projection and microdomain. The morphology in the overall projection in Figure 3 shows that, in different project positions of the matrices of Nano-PET, nanoscale particles are homogeneously dispersed with the matrices,

which are characterized with some toughness. In different microdomains, the existence of the nanoscale is diverse. The statistical results from Figure 3 shows that the particle sizes ranging from 30 to 100 nm.

Figure 4 shows the particles distributions morphology of sample no. 4 with statistical results shown in Table III. Figure 4(a) and (b) show the morphology of PET–clay with different preparation method. Both show that the particles are homogenously dispersed, but in Figure 4(a), the agglomerated particles are detected; the same is true for Figure 4(b), in which the treated clay

Figure 3 SEM morphology of the overall project of fracture surface and the particles distribution in microdomains for the PET–clay nanocomposite (no. 3).

Table III   The Nanoscale Particles of Nano-PET in Normal Distribution

Size (nm)	Distribution (%)
1000	<·1
500	1
300	4
200	5
100	12
80	25
60	21
50	13
40	10
30	7
10	<3

strongly interacts with the matrix compared with the weak interaction in Figure 4(b).

It is seen that the particle size of nanoscale lies in the scope from 30 to 100 nm. The particle size

Figure 4 SEM morphologies of PET–clay nanocomposites (no. 4) under the conditions of (a) weak interaction and (b) strong interaction between treated clay and the matrix, which are prepared by different methods.

Figure 5 TEM morphologies of the PET–clay nanocomposite (no. 4) with the sample (a) not dyed by RuO4 and (b) dyed by RuO4.

greater than 300 nm is thought of as agglomerated particles, which account for 4% or so in sample no. 4. Seen in Figure 3, it can also obtain the similar results of particle distributions.

The morphological results as above are called the first-level structure of nanoscale particles, especially for Nano-PET by SEM. Similarly, TEM techniques can also be applied to investigation of the first-level structure. By means of TEM, the electron will penetrate the film detected. Thus, the cubic structure of clay particles will probably be detected, the result of which has been demonstrated in Figure 5.

Due to the electronic transmission effect, the cubic structure of the particles appear with exfoliated sheet morphology of clay particles shown there. When clay is exfoliated, the particles oriented in disorder, among which the fibular structure shows their veins in the picture and the matrices there. In fact, the particles with different sheet morphologies are overlapped together there in Figure 5(a), which is not dyed, and Figure 5(b), which is dyed by RuO4.

The secondary level structure of the nano-PET can also be demonstrated by the TEM technique,

Figure 6 The second level of lamellar structure morphology of PET–clay nanocomposites with the possible intercalation direction from left to right.

Figure 7 The possible clusters and/or agglomerated particles detected in PET/clay nanocomposites.

which reflects the morphological structure with stripe-belt characteristics. The interlamellar distances of the lamella obtained by TEM method can be compared with those from X-ray method. And, both of them often give agreeable results with each other. Figure 6 has shown that the veins of the interlamellar distances are clearly seen; specifically, the distances in the left end of the lamella space seems larger than that in the left end shown in Figure 6, probably showing that polymer molecular chains are intercalated into the lamellae space in the left end while stopped intercalating in the right end of the lamella space. The degree of the enlarged space in the left end is greater than that in the right end, which shows the process of both the intercalation and the formation of exfoliated sheets of clay.

The interlamellar distances obtained from TEM method can be compared with these from X-ray method, the results of which are shown in Table IV.

The intercalated molecular chains are called polymer brushes, showing the degree of the poly-

mer molecular chains intercalated into the clay lamellar space. As a matter of fact, in Nano-PET, the PET molecular chain order are reduced or even lost due to the effect of clay exfoliation, which will be seen in our further report by the atomic force microscopy (AFM) method.

Besides, the clusters or agglomerated particles are also detected by the TEM method with its result shown in Figure 7; from the scale, the micrometer particles detected, which is common in nearly all the samples in the paper with agglomerated particles, the percentage of 4% or so are calculated.

CONCLUSIONS

In PET–clay nanoscale composites, the nanoscale ranges from 30 to 100 nm. The exfoliated clay particles play a nucleating role and have strong interactions with PET molecular chains. Thus, the Nano-PET properties are enhanced a lot compared with the PET itself, but it seems that the nanoparticle potentials do not demonstrate to the greatest degree, which probably either resulted from the relative low content of clay (for example, 5% in the paper) or from the agglomerated particles. The other reason may possibly be the relatively weak interface formed between clay particle and the matrices of PET resulting from the agglomerated particles.

Table IV   The Nanometer Size Distribution and Interlamellar Distances Obtained by Both TEM and X-ray Methods

No.	Clay Content (%)	d_{001} by TEM (nm)	d_{001} by X-ray (nm)	Size to Percentage (nm to %)
4	3.0	3.0	3.5	10–100 (96)
5	5.0	2.2	2.4	10–70 (92)

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