

THE EFFECT OF CLAY DISPERSION ON THE CRYSTALLIZATION AND MORPHOLOGY OF POLYPROPYLENE/CLAY COMPOSITES*

Qin Zhang, Xiao-lin Gao, Ke Wang and Qiang Fu**

Department of Polymer Science & Materials, Sichuan University, State Key Laboratory of Polymer Materials Engineering, Chengdu 610065, China

Abstract PP/clay composites with different dispersions, namely, exfoliated dispersion, intercalated dispersion and agglomerates and particle-like dispersion, were prepared by direct melt intercalation or compounding. The effect of clay dispersion on the crystallization and morphology of PP was investigated via PLM, SAXS and DSC. Experimental results show that exfoliated clay layers are much more efficient than intercalated clay and agglomerates of clay in serving as nucleation agent due to the nano-scale dispersion of clay, resulting in a dramatic decrease in crystal size (lamellar thickness and spherulites) and an increase of crystallization temperature and crystallization rate. On the other hand, a decrease of melting temperature and crystallinity was also observed in PP/clay composites with exfoliated dispersion, due to the strong interaction between PP and clay. Compared with exfoliated clay layers, the intercalated clay layers have a less important effect on the crystallization and crystal morphology. No effect is seen for samples with agglomerates and particle-like dispersion, in regard to melting temperature, crystallization temperature, crystal thickness and crystallinity.

Keywords PP/clay, Dispersion, Crystallization, Morphology

INTRODUCTION

Since the first report^[1] by researchers at Toyota has demonstrated a 168% increase in room temperature tensile modulus, an 87°C increase in heat distortion temperature, and a 40% decrease in water permeability of PA6/clay nanocomposites over unmodified PA6, polymer layered silicate nanocomposites have been intensely investigated because of their potential excellent properties. Many polymers were shown to make nanocomposites successfully and some advantages have been reported, such as improved modulus, decreased thermal expansion coefficient, reduced gas permeability, increased solvent resistance, and enhanced ionic conductivity when compared to the pristine polymers. The enhanced properties are presumably due to the synergistic effects of nanoscale structure and improved interaction between filler and polymer.

Polypropylene (PP) is one of the most widely used polyolefin polymers. Since it does not contain any polar group in its backbone, the homogeneous dispersion of the hydrophilic clay layers in polypropylene is very difficult. PP/montmorillonite (MMT) nanocomposites was first reported by Kato *et al.* in 1997^[2–5]. Since then, many research groups have investigated PP/layered silicate nanocomposites^[6–13] due to their promising applications. We have also successfully prepared well-ordered intercalated polypropylene/MMT nanocomposites via direct melt intercalation in a twin-screw extruder^[8]. Compared with Nylon 6/MMT nanocomposites, PP/MMT nanocomposites show much less enhanced mechanical property. For example, less than 10% increase of tensile strength was noted^[2, 6, 8]. It is not clear so far why the mechanical properties of PP/MMT nanocomposites are much poorer than what is expected from the concept and idea of nanoscale reinforcement.

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** Corresponding author: Qiang Fu (傅 强), E-mail: fuqiang1963@yahoo.com

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This may be attributed to the different matrix and the dispersion of silicate layers in matrix.

So far most of work was focused on the preparation and characterization of different polymer nanocomposites. Little work was focused on the morphology and crystallization of polymer between confined layered silicates. As we know, layered silicate is a kind of particular inorganic filler, which shows one dimension on the nano-scale. The layers have a thickness of 1 nm and the aspect ratios (defined as diameter/thickness) range from 10 to 1000. It was reported that polymer chain motions were confined between silicate layers, causing disappearance of glass transition temperature and change of rheological behavior^[14–18]. However, the effect of the dispersion of layered silicate on the crystallization of PP received less attention.

Since the morphology and crystallization behavior are directly related to the properties of PP layered silicate nanocomposites, in this work we concentrated our attention on the effect of the dispersion of silicate layers on the crystallization and morphology of PP, in order to understand the mechanical properties of PP/MMT nanocomposites better. Four samples were chosen: (1) PP nanocomposites with 1 wt% MMT content (PP-1), representing the completely exfoliated dispersion, (2) PP nanocomposites with 5 wt% MMT content (PP-5), representing the intercalated (incompletely exfoliated) dispersion, (3) PP compounded directly with pure MMT (PP-A), representing agglomerates and particle-like dispersion, and (4) pure PP for comparison.

EXPERIMENTAL

Materials

The materials used for the preparation of the PP/MMT nanocomposites are listed in Table 1. Dioctadecyl dimethylammonium bromide is an alkylammonium salt used for cation exchange. PP-MA in which maleic anhydride group is randomly grafted on a PP backbone was used as a “compatibilizer”.

Table 1. Raw materials used in the experiment

Name	Characterization	Supplier
Sodium montmorillonite	Cation exchange capacity: 68.6 mmol/100 g MMT	Renshou, Sichuan, China
Dioctadecyl dimethylammonium bromide (C-18)		Zhongli Co., China
Polypropylene 1300	Melt index: 1.0 g/10 min	Yan Shan Co., China
Maleic anhydride-modified PP (PP-MA)	MA: 0.6wt%	Chengguang Research Institute, China

Preparation of Organically Modified MMT

50 g sodium montmorillonite was dispersed in 1000 mL hot water using a stirrer. The dioctadecyl dimethylammonium bromide (25 g) was dissolved in hot water (300 mL) and then poured into the montmorillonite-water solution under vigorous stirring for 2 h. The product was washed three times and filtered, then dried in vacuum at 100°C for several hours. It is termed OMMT. The interlayer spacing of pure and treated MMT was measured by X-ray diffraction.

Preparation of PP/MMT Composites

PP/MMT nanocomposites with different modified MMT contents (1 wt% and 5 wt%, termed PP-1 and PP-5, respectively) were used. The values (for example 1 wt% and 5 wt%) correspond to the amount of OMMT added to the PP, not the accurate content (which can be obtained by heating and burning the samples). OMMT and PP-MA were melt-mixed with PP at 200°C using a twin screw extruder. The temperature of the extruder was maintained at 160°C, 190°C, 210°C, 210°C, 195°C from hopper to die. The screw speed was 110 r/min. PP compounded directly with pure MMT (PP-A) was obtained under the same processing conditions as used for PP/MMT nanocomposites.

Characterization of the Dispersion of MMT in PP Matrix

The dispersibility of the silicate layers in the composites was evaluated by using X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The XRD analysis was

performed using a Rigaku Denki RAD-B with Cu-K α ($\lambda = 0.154$ nm) radiation at room temperature. The basal spacing of the montmorillonite was estimated from the (001) peak in the XRD pattern. For SEM investigation, the samples were fractured in liquid nitrogen. The fractured surfaces were then gold coated and investigated in an SEM instrument, JEOL JSM-5900LV SEM, using an acceleration voltage of 20 kV. For TEM measurement, ultrathin sections with a thickness of 100 nm were prepared at -80°C using a diamond knife. The measurement was performed on a LEO 912 Omega at 120 kV.

Characterization of Crystallization and Morphology of PP in the Composites

DSC measurements were conducted on a computerized Perkin-Elmer differential scanning calorimeter, Model Pyris 1. The specimens were weighed in the range of 3–5 mg. During the measurement, dried N₂ gas was purged at a constant flow rate. In the case of isothermal crystallization, the sample was kept at 190°C for 5 min to remove residual crystals, which may serve as seeds for the crystallization. Then they were cooled rapidly to the predetermined crystallization temperature T_c at a rate of 100 K/min and the temperature was held constant until the crystallization was completed. Thereafter the specimens were heated again without prior cooling to obtain the DSC endotherms at a rate of 10 K/min. The temperature reading and calorific measurement were calibrated by using standard indium.

Polarized Light Microscopy (PLM), with a camera attached, was used to observe the macroscopic morphology. Thin films were prepared by melt-pressing a small amount of the sample between the cover glass and glass slide at a temperature of 190°C , then quenched to room temperature or annealed at certain temperatures.

The SAXS experiments were carried out with the aid of a Kratky-camera attached to a conventional Cu-K α X-ray source, employing a temperature-controlled sample-holder. Scattering curves were usually registered within ten minutes counting time, with the help of a position-sensitive metal wire detector. The slit-smeared data were deconvoluted by application of an algorithm developed by Strobl^[19]. Evaluation of the SAXS patterns was carried out assuming that the stacked lamellae have large lateral dimensions. Scattering data were analyzed by calculating the one-dimensional autocorrelation function and the second derivative of the autocorrelation function, which gives the interface distance distribution function. Both curves provide information about crystalline and amorphous layers thickness and yield the linear crystallinity.

RESULTS AND DISCUSSION

The Dispersion of MMT in Composites

To obtain an overall macroscopic view of MMT dispersion in PP, we begin with the result of SEM. This is shown in Fig. 1. For PP-1 and PP-5, some primary MMT particles are observed with a size of 100–200 nm. They are quite homogeneously dispersed in PP matrix. For PP-A, however, aggregates with a size of 1 micron are seen. Due to the low resolution of SEM, one does not know whether the observed particles have an intercalated-structure, or an exfoliated structure existing in the remaining area. So other experiments are needed. XRD and TEM are two dominating methods for characterizing the dispersion of MMT in nanocomposites. Both give the information in microscopy. Figure 2(a) shows the XRD profiles of MMT, OMMT. The peaks correspond to the (001) reflections of the clay (the interlayer gallery height). The basal spacing of the OMMT increases, from 1.47 nm for the pure MMT, to 1.9 nm. Figure 2(b) shows the XRD profiles of PP-1, PP-5 and PP-A. One finds the peak of OMMT further expands to 3.3 nm for PP-5, suggesting that the intercalation of PP into the gallery indeed takes place. There exists a clear regular layered structure, demonstrated by the presence of the d_{001} and higher-order diffraction peaks. For PP-1, almost no peak of d_{001} is seen, due to either an exfoliated dispersion of clay sheets in this case, or the content of clay is too low to be detected by XRD. For PP-A, the peak of d_{001} remains the same as for pure MMT, indicating that neither intercalation nor exfoliation occurs.

In order to verify further the dispersion of the silicate layers in PP matrix, a TEM experiment was carried out. Shown in Fig. 3 are the TEM photographs of PP-1, PP-5 and PP-A, where the dark lines are the cross sections of silicate layers. For PP-1, most of the silicate layers are dispersed uniformly in the polypropylene

matrix with sizes of only 5–10 nm, which indicates that most of the silicate layers are exfoliated. For PP-5, most of intercalated layers with size of 50–100 nm are also observed and intercalated dispersion is evident. However, for PP-A there are no intercalated structures but aggregates are formed. Combined together with the results of

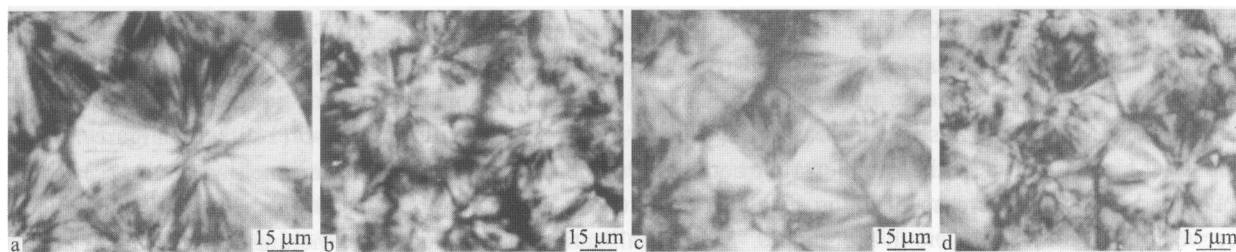


Fig. 4 PLM pictures of samples crystallized at 130°C for 90 min (a) PP, (b) PP-1, (c) PP-5 and (d) PP-A

In contrast, for PP-1, the smallest spherulites among the samples are seen (Fig. 4b), which is certainly caused by the exfoliated dispersion of clay. The boundaries of spherulites are irregular and unclear. They look very open and loosely packed compared with those of pure PP, indicating a strong interaction of PP and clay in this case. PP-5 shows a middle size of spherulite (Fig. 4c) between PP and PP-1, which may be caused by the existence of more intercalated layers in PP-5 than in PP-1. At the same time, we find that PP-A also shows a reduced size of spherulites (Fig. 4d) compared to PP. This result suggests that even macro-aggregates can serve as nucleation agent, and the efficiency of intercalation dispersion as nucleation agent is not very much different from that of macro-aggregates dispersion.

SAXS results

For SAXS data analysis, we are particularly interested in the interface distance distribution $K''(z)$, from which one can get the most probable thickness of the crystals and amorphous layers. Two peaks (one is for crystal thickness and one is for amorphous layers) and a minimum corresponding to long spacing are seen for all the samples. Figure 5 is the second derivative of corresponding normalized one-dimensional correlation function (K'' -curves) of samples obtained by quenching from melt temperature to room temperature. The curves are calculated by the method developed by Strobl^[19]. One can easily read off the lamellar thickness, amorphous layer thickness and long spacing from the curves. From the crystallinity (around 40%) obtained by DSC experiment (see below), the first peak can be assigned as lamellar thickness. Taking SAXS curve of PP as an example, the maximum at 3.4 nm correspond to the crystal thickness d_c and the minimum at 13.9 nm gives the long spacing L . The difference between d_c and L of 11.1 nm is determined to be the amorphous layer thickness d_a ($d_a = L - d_c$). A linear crystallinity can be derived from the SAXS data as: $X_l = d_c/L = 3.4/13.9 = 24.5\%$. Table 2 gives the data of long spacing (L), amorphous layer thickness (d_a) and crystal thickness (d_c) of samples studied. We can find that the crystal thickness of PP-1 and PP-5 decreases from 3.4 nm of pure PP to 2.5 nm, independent of the MMT content (1 wt% and 5 wt%) and state of dispersion (intercalated and exfoliated). This is probably caused by the strong interaction between PP and MMT in the samples, which hinders the motion of PP molecules. The limited molecular motion can be further proved by the reduced linear crystallinity, which shows a decrease from 24.5% for pure PP to 18% for PP-1 and 18.6% for PP-5. Even more, one finds an increase of d_a from 10.5 nm for pure PP to 11.4 nm for PP-1 and 10.9 nm for PP-5 respectively, indicating an insertion of MMT layers between lamellae of PP. For PP-A however, only a small change of d_c , d_a and linear crystallinity is seen, indicating once again that the crystallization and crystal morphology of PP are not very much affected by macro-aggregation of particles. It should also be noted that the long spacing keeps more or less constant for all the samples, and a third peak exists around 6 nm for PP-1. More work is needed to verify the third peak in PP-1, which is most likely due to additional lamellar stacking in the sample.

Crystallization Behavior

Non-isothermal crystallization

The DSC experiment was carried out to study the dispersion of MMT on crystallization and melting of the samples. Figure 6 depicts the DSC crystallization traces of samples recorded during cooling from the isotropic

melt at a cooling rate of 10 K/min. One observes a dominant exothermic peak (T_c) for all the samples, which shifts to high temperatures for PP composites. Compared with the crystallization temperature (T_c) of PP (111.3°C), the highest increase of T_c is seen for PP-1 (123.0°C), which suggests a super nucleation effect of exfoliated MMT layers. A slight increase of T_c is seen for PP-A (119.7°C) and PP-5 (119.7°C). Figure 7 shows the DSC heating curve of the samples after cooling. One observes almost a constant melting peak (T_m) for PP, PP-5 and PP-A. A decrease of T_m is seen for PP-1, which again may be caused by the strongest interaction between PP and MMT layers in the sample. The crystallization temperature (T_c), melting temperature (T_m), heat of fusion (ΔH_f), as well as the crystallinity calculated from the heat of fusion for all the samples are listed in Table 3. There is no difference of crystallinity between PP and PP-A, but an obvious decrease is seen for PP-1 and PP-5. The reduced crystallinity in PP-1 and PP-5 can be understood as an indication of limited molecular motion of PP caused by exfoliated or intercalated MMT layers. The higher crystallinity obtained by DSC than that obtained by SAXS may be caused by the thermal history of the samples. For SAXS experiments, samples were quenched from the melt to room temperature (cooling rate was around 50 K/min), but for DSC experiments, samples were cooled down at a rate of 10 K/min.

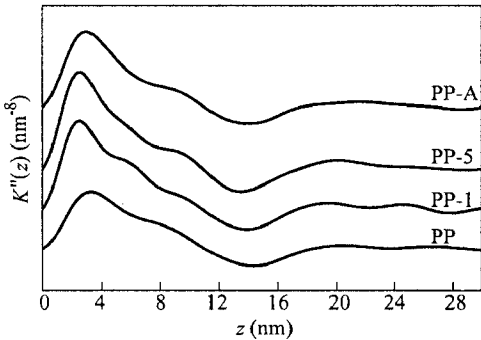


Fig. 5 Interface distance distribution function $K''(z)$ for different samples as derived from SAXS data, samples were quenched from melt to room temperature.

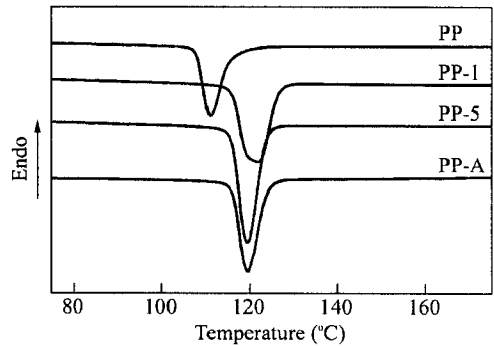


Fig. 6 DSC crystallization traces of samples recorded during cooling from the isotropic melt at a cooling rate of 10 K/min

Table 2. The SAXS results of the samples

Sample	d_c (nm)	L (nm)	d_a (nm)	X_l (%)
PP	3.4	13.9	10.5	24.5
PP-1	2.5	13.9	11.4	18.0
PP-5	2.5	13.4	10.9	18.7
PP-A	3.1	13.3	10.2	23.3

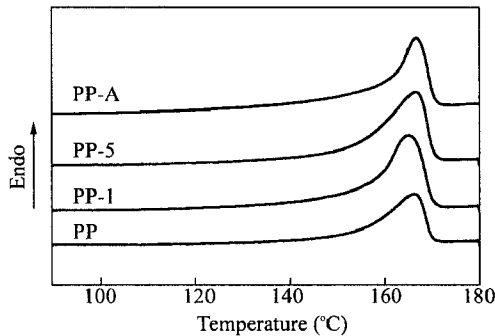


Fig. 7 DSC heating curves of the samples after cooling

Isothermal crystallization

DSC also was used to study the isothermal crystallization of the samples. Figure 8 shows the crystallization

DSC also was used to study the isothermal crystallization of the samples. Figure 8 shows the crystallization exotherms at various crystallization temperatures for PP, PP-1 and PP-5. From these curves, some useful data can be obtained for describing their isothermal crystallization behavior, such as the crystallization peak time, which represents crystallization rate, and relative degree of crystallinity (X_c) as a function of crystallization time. It is clearly seen from the figure that the exothermic peak shifts, as expected, to a longer time and becomes more flat when the crystallization temperature increases, which is attributed to the slower crystallization rate with decreasing super-cooling temperature ($T_m^0 - T_c$). Therefore a longer time is need to complete the crystallization.

Table 3. The DSC results of the samples

Sample	T_c (°C)	T_m (°C)	ΔH_f (J/g)	X_c (%) *
PP	111.3	166.1	85.8	41
PP-1	123.0	164.5	79.8	38
PP-5	119.7	166.4	80.9	39
PP-A	119.7	166.4	84.5	40

* The effect of MMT weight has been deducted.

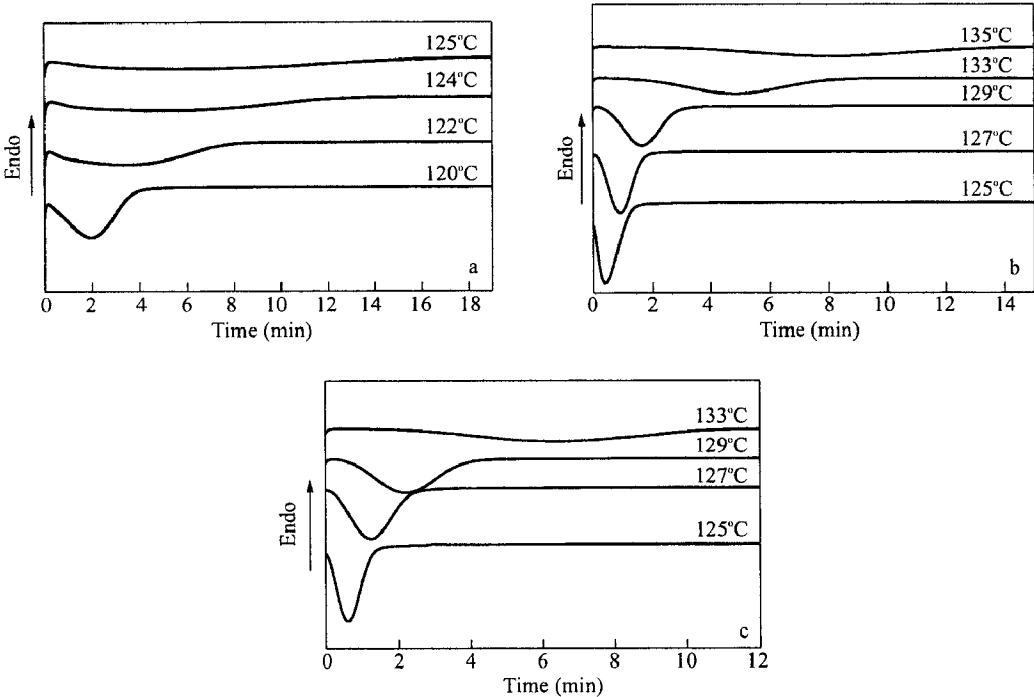


Fig. 8 The crystallization exotherms at various crystallization temperatures for (a) PP, (b) PP-1 and (c) PP-5

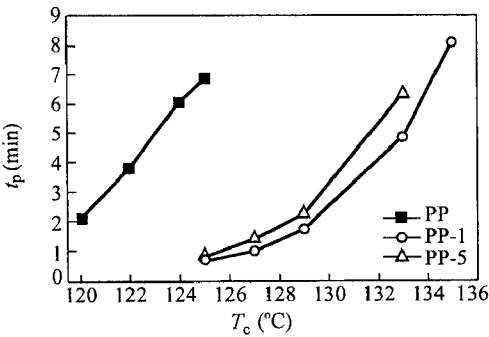


Fig. 9 t_p of the samples at different crystallization temperatures

Comparison of the crystallization rate, crystallization peak time (t_p) as a function of crystallization temperature, is shown in Fig. 9. For a given crystallization temperature, PP-1 has the smallest t_p , thus a fast crystallization rate although it has lower MMT content compared with PP-5. It is evident that exfoliated MMT layers are much more efficient than intercalated MMT in serving as nucleation agent.

CONCLUSION

In summary, the dispersion of clay in PP matrix has a great effect on the crystallization and morphology of PP. The exfoliated clay layers play a dominating role in reducing the crystal size and speed up the crystallization rate due to the nano-scale dispersion. The nano-scale dispersion also results in strongest interaction between PP and clay, which in turn causes a decrease of melting temperature and crystallinity. A sample with intercalated dispersion shows a less significant effect on crystallization behavior and crystal morphology. Our results explain in part the reason why only the exfoliated structure can significantly enhance the tensile modulus of PP nanocomposites^[21]. Since a homogeneous exfoliated dispersion is extremely difficult to achieve for PP/clay composites, particularly at higher clay content (large than 5 wt%), due to the non-polar property of PP, there seems a long way to go for high performance PP/clay nanocomposites.

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