Morphology and Mechanical Properties of Polypropylene/Organoclay Nanocomposites

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ABSTRACT: Polypropylene (PP) nanocomposites were prepared by melt intercalation in an intermeshing corotating twin-screw extruder. The effect of molecular weight of PP-MA (maleic anhydride-modified polypropylene) on clay dispersion and mechanical properties of nanocomposites was investigated. After injection molding, the tensile properties and impact strength were measured. The best overall mechanical properties were found for composites containing PP-MA having the highest molecular weight. The basal spacing of clay in the composites was measured by X-ray diffraction (XRD). Nanoscale morphology of the samples was observed by transmission electron microscopy (TEM). The crystallization kinetics was measured by differential scanning calorimetry (DSC) and optical microscopy at a fixed crystallization temperature. Increasing the clay content in PP-MA330k/clay, a well-dispersed two-component system, caused the impact strength to decrease while the crystallization kinetics and the spherulite size remained almost the same. On the other hand, PP/PP-MA330k/clay, an intercalated three-component system containing some dispersed clay as well as the clay tactoids, showed a much smaller size of spherulites and a slight increase in impact strength with increasing the clay content. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 85: 1562–1570, 2002

Key words: polypropylene/clay nanocomposites; crystallization

INTRODUCTION

In recent years, organic–inorganic nanoscale composites have attracted a great deal of interest from researchers, both in industry and in academia, because they often exhibit superior hybrid properties that are synergistically derived from the two components. One of the most promising composites is the hybrid based on organic polymers and inorganic clay minerals consisting of layered silicates.

Remarkable breakthroughs in catalyst and process development as well as an attractive combination of low cost, low density, a heat distortion temperature above 100°C, and extraordinary versatility in terms of properties, applications, and recycling, have stimulated fast growth of polypropylene (PP) production in comparison to other thermoplastics. To improve the competitiveness of PP for engineering plastics applications, it is an important objective in PP compounding to simultaneously increase its dimensional stability, heat distortion temperature, stiffness, strength, and impact resistance without sacrificing easy processability.

Researchers at Toyota and other laboratories[1–6] have reported that it is possible to prepare PP–clay hybrids by simple melt mixing of three

components, i.e., PP, maleic anhydride-modified polypropylene oligomers (PP-MA), and clay intercalated with octadecylammonium ion.

In this article, a series of PP/clay nanocomposites were prepared by melt mixing in a twin-screw extruder with focus on the effect of molecular weight of PP-MA on mechanical properties of PP/clay hybrids. Three commercially available PP-MAs were used, M_w = 9k, 52k, and 330k. For simplicity, the ratio of clay/PP-MA was kept constant at 1 : 1 (i.e., the typical examples of composition of three-component system PP/PP-MA/clay would be 90/5/5 or 80/10/10 in wt %). The clay dispersion in composites was investigated by X-ray diffraction (XRD) and transmission electron microscopy (TEM). The effect of clay on the crystallization kinetics and spherulite size was studied by DSC and optical microscopy.

EXPERIMENTAL

All polymers used in this study are commercially available. The PP with trade name P4G4Z-011 (melt flow index 12 g/10 min, ASTM D1238) was obtained from Huntsman. The PP-MAs are listed in Table I, and named according to their molecular weights listed in the third column (e.g., PP-MA330k). The nanoclay, Cloisite® 20A (Southern Clay), is a natural montmorillonite modified with a quaternary ammonium salt, dimethyl, dihydrogenatedtallow ammonium chloride, where HT is a hydrogenated tallow (~65% C_{18}; ~30% C_{16}; ~5% C_{14}).

Table I   Maleic Anhydride-Modified Polypropylenes (PP-MA)

Name	Company	Molecular Weight (M_w)	MA content (wt.%)
PP-MA (Epolene E43)	Eastman Chemical	9100[a]	4.1[b]
PP-MA (Epolene G3003)	Eastman Chemical	52,000[a]	0.8[b]
PP-MA (PB3150)	Uniroyal Chemical	330,000[a]	0.5[c]

[a]Average molecular weight was provided by the vendor.
[b]MA content was calculated base on PP-MA acid number, which was provided by the vendor.
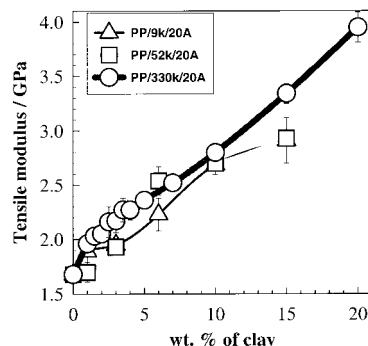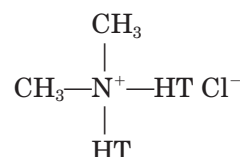[c]MA content was provided by the vendor.

Figure 1   Tensile modulus as a function of clay content.

$$CH_3-N^+-HT \; Cl^-$$

with CH_3 above and HT below the nitrogen.

For melt compounding of nanocomposites, a Leistritz ZSE-27 fully intermeshing twin-screw extruder with L/D = 40 and D = 27 mm was used in the corotating mode. The barrel temperatures were set at 165–185°C, and the screw speed was fixed at 300 rpm. To achieve good mixing, the feeding rate was kept low at 2 kg/h. A Sumitomo 200-ton injection-molding machine was used for the preparation of tensile bars and impact specimens. Mechanical tests were performed according to tensile (ASTM D638) and Izod impact (ASTM D256) standards, respectively. An Instron tensile tester was used to measure the tensile properties, while an Izod impact tester from Tester Machines was used for the measurement of notched impact strength. For tensile strength tests, the value of 5 bars were averaged. For impact strength tests, 10 specimens were used to obtain an average. An
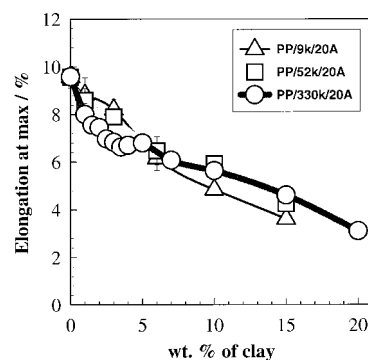

Figure 2   Elongation at the maximum stress as a function of clay content.
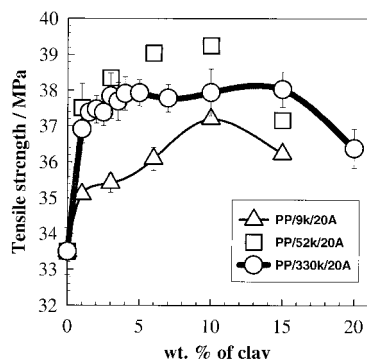
Figure 3 Tensile strength as a function of clay content.

X-ray diffractometer, Scintag XDS2000, was used to analyze the average clay dispersion. For the transmission electron microscopy (TEM) analysis, the specimen was microtomed to an ultrathin section of 70 nm thickness using an ultracryomicrotome with a diamond knife. The structure was observed under a Phillips CM 12. For the crystallization kinetics, a TA Instruments Differential Scanning Calorimeter, DSC 2920, was used. The crystallinity, X_C, was calculated by $X_C = \Delta H^*/\Delta H^{\circ}_{pp}$, where ΔH^* is the enthalpy of fusion per gram of PP in the composite, and ΔH°_{pp} is the heat of fusion per gram of 100% crystalline PP ($=209$ J g^{-1}).[7] For the observation of spherulite structure, an Olympus BH2 optical microscope equipped with a CCD camera connected to a computer was used.

RESULTS AND DISCUSSION

Mechanical Properties

In the first part of discussion, a comparison among three three-component composites is
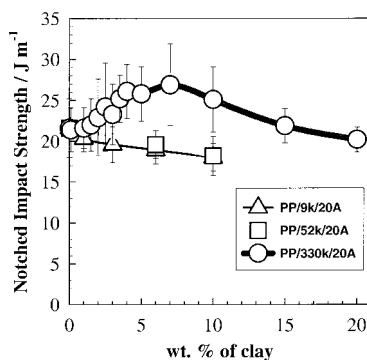

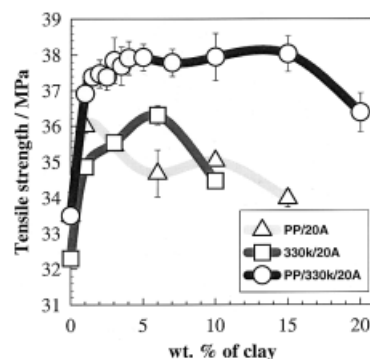**Figure 4** Notched impact strength as a function of clay content.

Figure 5 Tensile strength as a function of clay content.

made, for the purpose of comparing the effect of the molecular weight of PP-MA on composite properties. As shown in Figures 1 and 2, the presence of clay increases the tensile modulus and decreases the elongation. The pure PP and the composites with a low clay content show yielding behavior in the stress–strain curve, with an ultimate elongation larger than 200%. Strain whitening was observable during testing. However, composites with a clay content greater than 7% did not show any yielding behavior, and the samples broke soon after reaching the maximum stress. There was no strain whitening. In this study, the elongation at the maximum stress instead of the ultimate elongation was compared, as shown in Figure 2. The molecular weight does not influence the modulus and the elongation significantly. However, the tensile strength and the impact strength are affected by the molecular weight of PP-MA, as shown in Figures 3 and 4, respectively. Better tensile strength is obtained for composites containing the PP-MA52k and 330k. There is a sharp increase of tensile strength
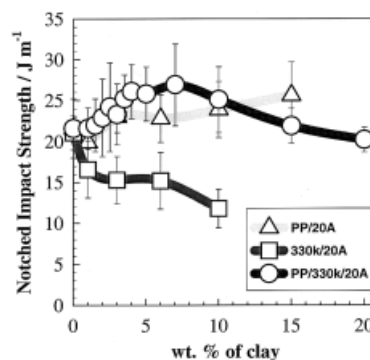

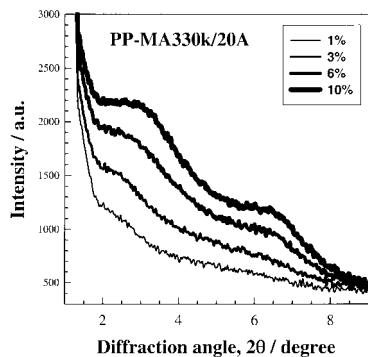**Figure 6** Notched impact strength as a function of clay content.

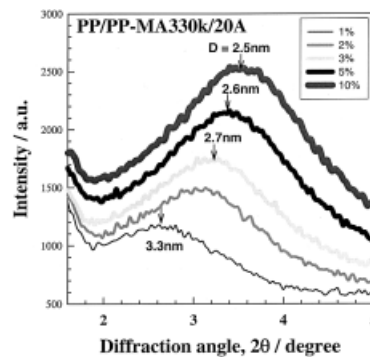**Figure 7** XRD results for PP-MA330k/20A.

Figure 9 XRD results for PP/PP-MA330k/20A.

from 0 to 1% of clay. Further addition of clay improves the tensile strength only moderately. After reaching the maximum value, the further addition of clay decreases the tensile strength. For each system there seems to be a slightly different optimal clay concentration of around 10%. As shown in Figure 4, when the clay content increases, the impact strength decreases for composites containing PP-MA9k and 52k, but increases for composites containing PP-MA330k. Overall, the composite PP/330k/20A seems to have the best mechanical properties. This composite was further investigated in the two-component PP-MA330k/20A system. For comparison, the PP/20A composite was also prepared. A comparison of tensile strength and impact strength of these two-component systems is shown in Figures 5 and 6, respectively. Both PP/20A and PP/330k/20A systems show slightly improved impact strength, but PP-MA330k/20A shows a decrease in impact strength. The three-component PP/330k/20A system has the best tensile strength and impact strength that does not originate from the simple addition of properties of the two-component systems. To understand this difference, an

investigation on clay dispersion and crystal morphology was performed by XRD, TEM, and optical microscopy.

Clay Spacing by XRD

Figures 7 to 9 show the XRD results for different systems. The best dispersion of clay was found in the PP-MA330k/20A system as shown in Figure 7. For 1 and 3% of clay, nearly exfoliated structure was obtained as verified by the absence of any distinct diffraction peak, as well as by TEM observation (shown later). For composites with a clay content of 6 and 10%, the presence of a shoulder is visible, but still no peak is present. In contrast, the PP/20A and PP/330k/20A systems show the presence of a peak, moving to a smaller angle with decreasing clay content (see Figs. 8 and 9). The clay spacing D is plotted as a function of clay content in Figure 10. The behavior of the PP/20A and PP/330k/20A systems is almost identical. The clay spacing increases greatly as the clay content decreases. This is because the PP-MA vs. clay ratio is 1:1 in the three-component system. The high molecular weight PP-MA330k is unable to disperse the clay when the concentra-
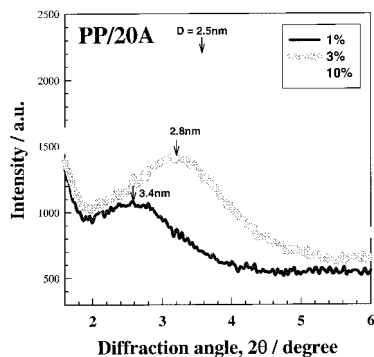

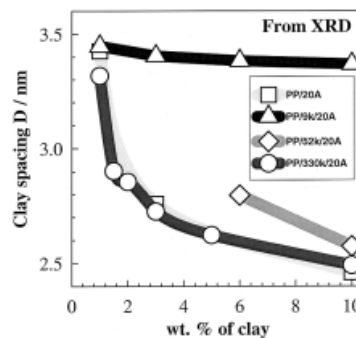**Figure 8** XRD results for PP/20A.
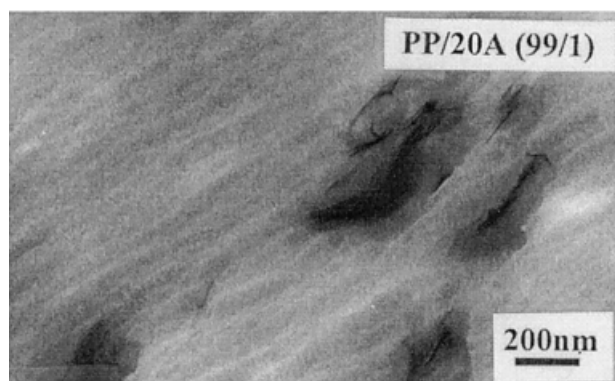

Figure 10 Clay spacing vs. clay content from XRD.
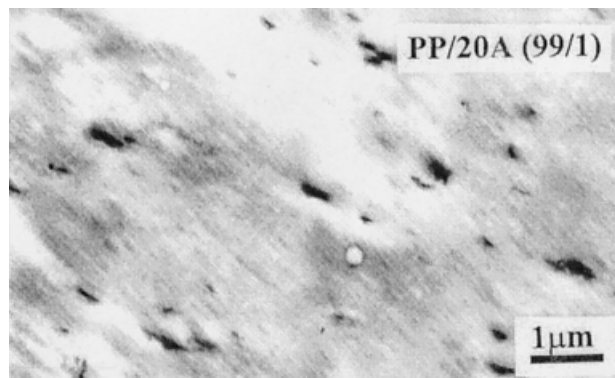
Figure 11   TEM of PP/20A composite.

Figure 12   TEM of PP-MA330k/20A composite.

tion is high. This is not the case for low-molecular weight PP-MA9k based composites, where the clay spacing remains large even for a high loading of clay. The molecular weight of PP-MA9k is very low, and thus its diffusion into the clay gallery is better than for the higher molecular weight PP-MAs.

Clay Dispersion by TEM

The two-component PP/20A composite has a majority of clay present as tactoids, as shown in Figure 11. This is probably the reason why the tensile strength decreases steeply when more than 1% of clay is added. The tactoids contributes to flaws during mechanical stretching, leading to the sample breakage. The TEM photos of the two-component PP-MA330k/20A composite are shown in Figure 12. The clay is dispersed very well, and no clay tactoids are present. This result is consistent with the XRD curve in Figures 7 and 8.

The TEM photo of the PP/330k/20A system is shown in Figure 13. The morphology seems to be a combination of those shown in Figures 11 and 12. Some clay is present in the matrix as exfoliated layers, while most of the clay is present in

tactoids. The well-dispersed clay in the matrix may be responsible for improving the tensile strength, while the clay tactoids act as a nucleation agent for crystallization, thereby significantly decreasing the spherulite size and improving the impact strength, as will be discussed below.

Crystallization Kinetics by DSC

Polypropylene is a semicrystalline polymer, and it is well known that its mechanical properties are greatly affected by the overall crystallinity, size of spherulites in microscale, and lamellar crystal in
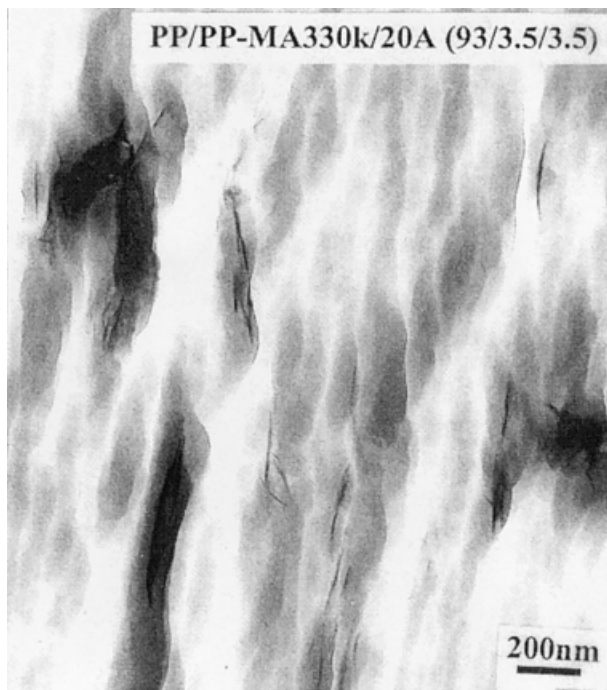

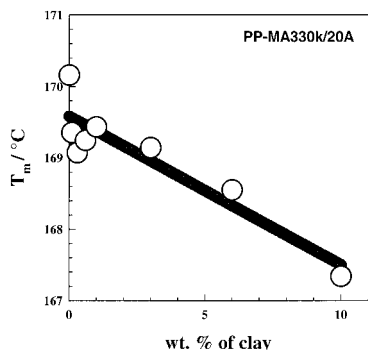**Figure 13**   TEM of PP/PP-MA330k/20A composite.

Figure 14 Melting point depression for PP-MA330k/20A from DSC.

Figure 16 Crystallization exothermal peak from DSC, at 135°C.

nanoscale.[8,9] Because of this, DSC and optical microscopy studies were conducted to investigate the influence of clay on the crystalline structure.

Figure 14 shows a slight decrease in the melting point by adding clay to the two-component PP-MA330k/20A system. This suggests a reduction in the overall size of lamellae, probably because the clay forms an obstacle, thereby retarding the growth of individual lamellae.

Figure 15 shows the crystallinity measured by DSC with respect to the weight fraction of the polymer phase. The crystallinity of samples that were quickly quenched in the mold of the injection-molding machine is compared with the crystallinity of samples that were first melted, then underwent isothermal crystallization at 137.5°C for 2 h. As expected, after isothermal annealing at a higher temperature, the crystallinity increased about 7%; however, the presence of clay did not seem to influence the crystallinity much. This may be a result of well-dispersed clay in the polymer matrix.
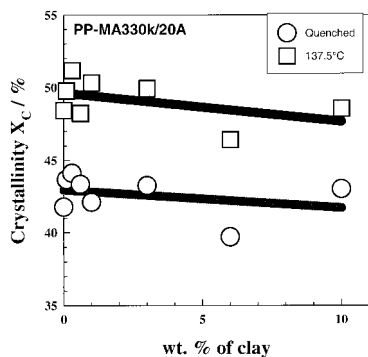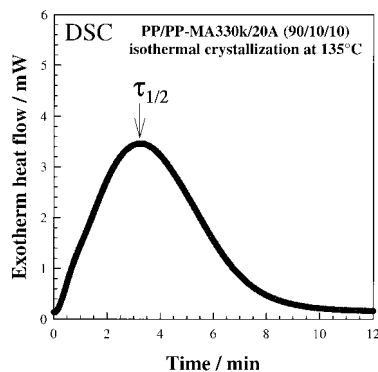
Isothermal crystallization was performed using DSC. Samples were first melted and then quenched to 135°C and maintained at this temperature during the experiment. The exothermal heat flow was measured by DSC leading to a half-time of crystallization $\tau_{1/2}$, as shown in Figure 16. The half-time of crystallization is then plotted as a function of clay content in Figure 17. For the well-dispersed PP-MA330k/20A system, almost no change is observed in the bulk crystallization kinetics. However, this is not the case for the PP/PP-MA330k/20A system. Even though the data are widely scattered, there is a clear trend in the curve. The crystallization rate was increased up to eight times by adding only 3% of clay, compared to the pure PP. The data scattering of the crystallization kinetics for the three-component composites may arise from the very high sensitivity of bulk crystallization to the dispersion of clay in the matrix, i.e., the number and size of the clay tactoids. Optical microscopy was performed to better understand this phenomenon.
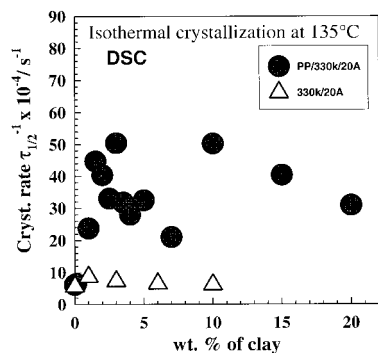

Figure 15 Crystallinity obtained from DSC.

Figure 17 Crystallization rate at constant temperature from DSC.
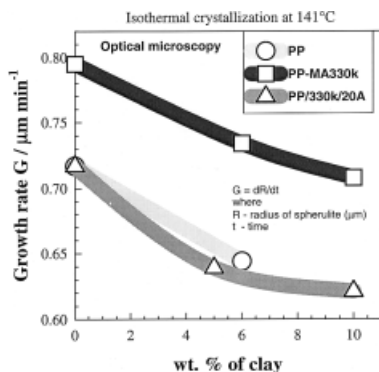
Figure 18 Spherulite growth rate at 141°C by optical microscopy.

Optical Microscopy

By observing a single spherulite growing in time during isothermal annealing, one can evaluate the growth rate G, as shown in Figure 18. Both the pure polymers and the composites showed a similar trend of a decreasing spherulite growth rate with an increasing clay content. One can speculate that the clay layers somehow decrease the radial lamellar growth rate; however, they cannot stop it completely. The growth probably continues through bridges between the clay particles and then by branching. The situation may be comparable to that of polymer blends, in which the spherulites also grow through the bridges between domains, as shown by TEM.[10]

The size of spherulites after isothermal crystallization was also investigated. There is a major difference in the crystalline structure of different composites as shown in Figures 19 and 20. Because it is difficult to see the spherulite structure of samples quenched to room temperature, all samples were crystallized isothermally at 141°C in the DSC chamber. After a fixed time, they were taken out of DSC and quenched to room temperature by placing the cover glass on a cold metal slab. The spherulite structure was observed by optical microscopy. Figures 19(a) and (b) show the photos of pure PP-MA330k and PP-MA330k/20A (90/10) systems, respectively. The size of spherulites was not affected by the presence of 10% clay. The clay is dispersed in PP-MA so well that it does not serve as a nucleation agent. In terms of the impact strength, we may conclude that the presence of well-dispersed clay decreases the impact strength when the size of the spherulites is not changed.

In contrast, when the clay is not dispersed very well and the tactoids of clay are present, they may play a role as the nucleation agent. Thus, the clay greatly increases the number of spherulites in a given volume. The size of the spherulites is much smaller compared to that of pure PP, as shown in Figures 20(a)–(c). The much smaller size of the spherulites may be responsible for the increase in impact strength, as shown for the pure PP.[8] The effect of clay on the average size of spherulites for different systems is summarized in Figure 21. Although there is almost no change in the well-dispersed PP-MA330k/20A system, there is a decrease of spherulite size for the PP/20A system
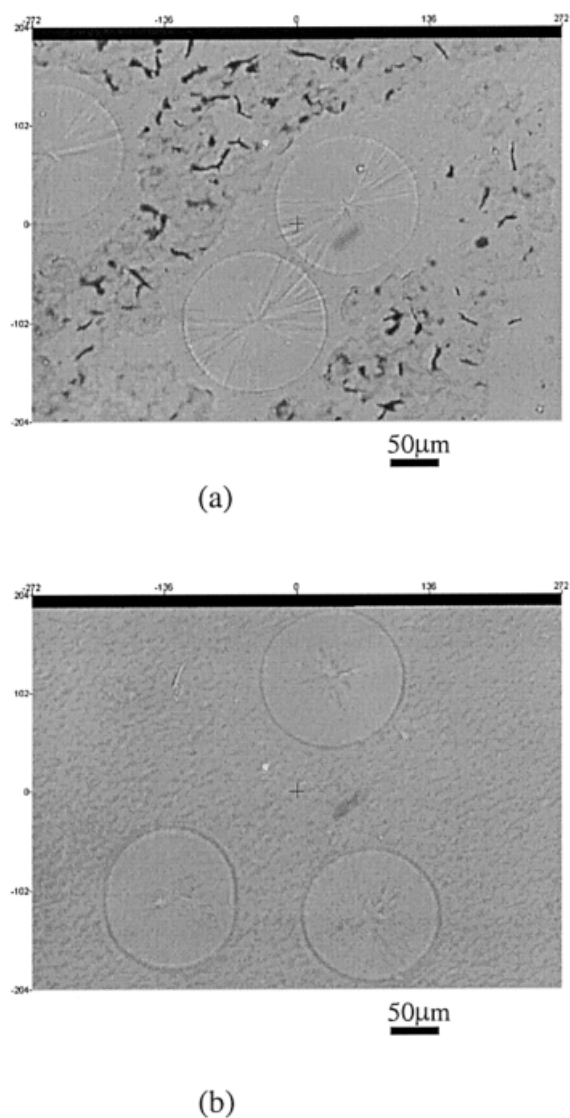

(a)

(b)

Figure 19 Optical microscopy after isothermal crystallization at 141°C. (a) PP-MA330k after 92 min. (b) PP-MA330k/20A (90/10) after 101 min.
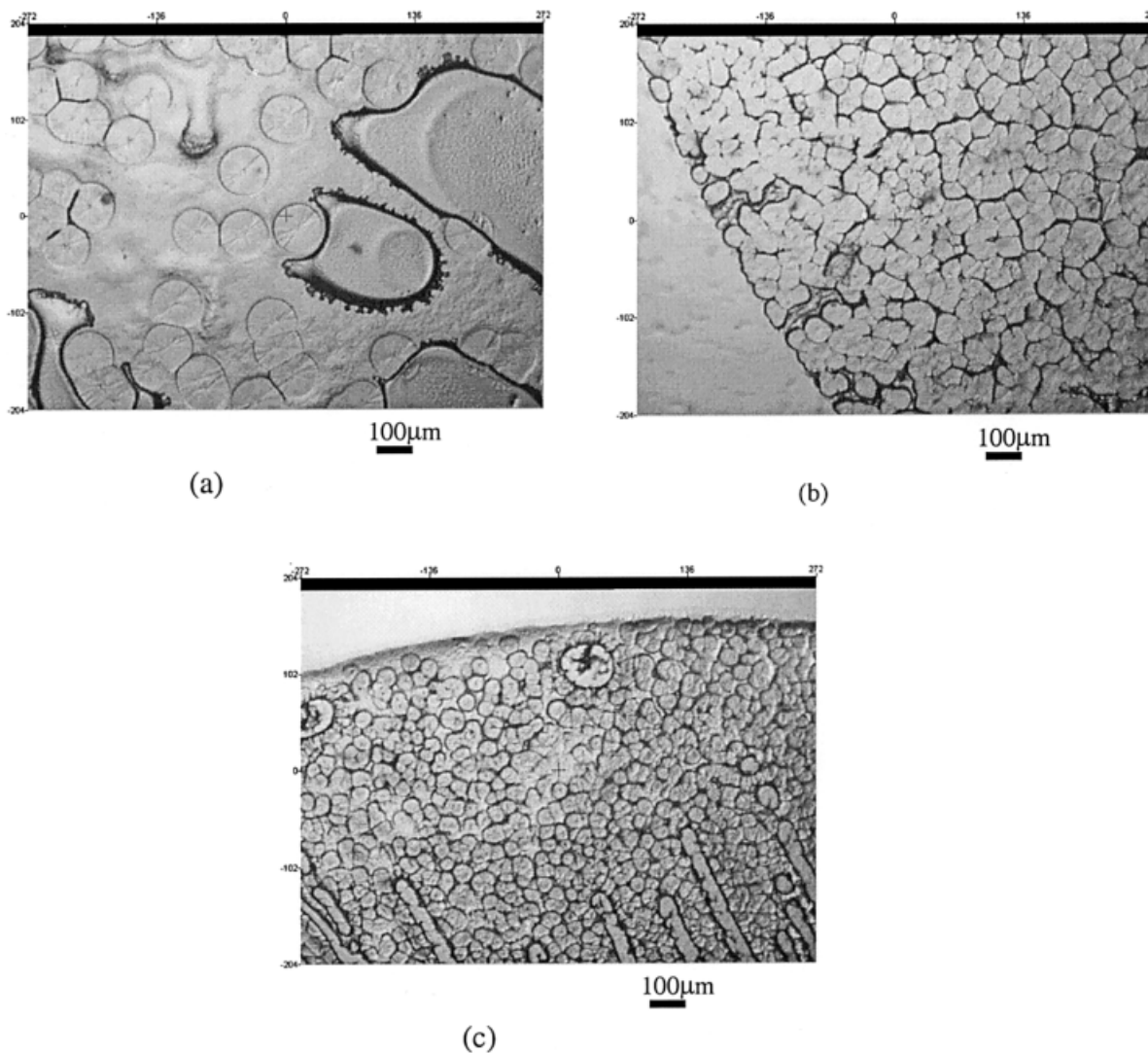
Figure 20 Optical microscopy after isothermal crystallization at 141°C. (a) PP after 92 min. (b) PP/20A (90/10) after 93 min. (c) PP/330k/20A (90/10/10) after 35 min.

and an even more pronounced decrease for the PP/PP-MA330k/20A system.

CONCLUSION

The addition of clay to PP always improves the tensile strength and tensile modulus, but reduces its ultimate elongation, regardless of the molecular weight of PP-MA. The most significant increase in tensile strength occurs with the addition of 1 to 2% of clay. Further addition of clay mainly improves the tensile modulus. Tensile strength and impact strength are affected by the molecular
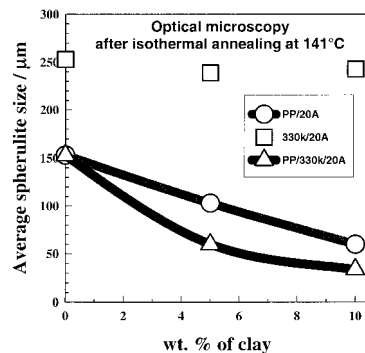

Figure 21 Average spherulite size from optical microscopy.

weight of PP-MA. The composite containing PP-MA with the highest molecular weight, 330k, has the best overall properties.

In the two-component PP-MA330k/20A system, the clay is dispersed very well with no XRD peak and the spherulite size remains constant. The impact strength is decreased significantly. For the three-component PP/PP-MA330k/20A system, both well-dispersed clay and large clay tactoids exist in the composite. Although well-dispersed clay in the matrix is supposed to decrease the impact strength, the tactoids serve as the nucleation agent to decrease the size of the spherulites. The smaller spherulite size tends to increase the impact strength.

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