

Effect of Nylon 6 Inclusions on the Crystalline Morphology of Polypropylene–Nylon 6 Blends

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ABSTRACT: Crystallization behavior and crystalline morphology of plain polypropylene (PP) and its blend with 0 to 30 wt % nylon 6 were studied by the hot-stage polarized light microscopy method. Radial growth rate and the size and number of PP spherulites were measured as a function of both the isothermal crystallization temperature and the nylon 6 content of the blend. The study revealed that a reduction in the isothermal crystallization temperature from 135 to 120°C, for both the plain PP and its blend with nylon 6, leads to the formation of a large number of fast-growing, small spherulites. Moreover, the size and growth rate of PP spherulites decreased on increasing the nylon 6 content of the blend; whereas the number of PP spherulites decreased sharply on initial addition of 10% nylon 6 and, thereafter, increased slightly by further addition of nylon 6. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 75: 1769–1775, 2000

Key words: polypropylene blend; polypropylene–nylon 6 blend; crystalline morphology; growth rate; nucleation density; spherulite size.

INTRODUCTION

The morphology of the crystalline phase in a blend containing two crystallizable polymers, such as polypropylene (PP) and nylon 6, can be controlled by changing the crystallization characteristics.^{1–3} The key factors for controlling the crystalline structure and morphology are the nucleation, growth, average size, and size distribution of spherulites.^{4–8} These crystallization characteristics are, in turn, strongly temperature-dependent.^{9–10} The farther the crystallization temperature (T_c) from the equilibrium condition ($T_c \ll T_m$), the less perfect the structure produced (a lower degree of crystallinity, a wider distribution of crystallite size, and a lower melting point), implying a lower structural stability and, hence, poor mechanical properties.¹¹

Crystallization behavior of PP in its blends with other polymers has gained tremendous at-

tention in recent years.^{12–21} It is known that crystallization of the PP component in its blend gets influenced by the presence of the second component. Depending on the nature of this foreign inclusion, it may assist the crystallization process by enhancing the nucleation rate or it may cause some obstacle for PP crystallization path front, in the form of changes in the nucleation, growth, average size, and size distribution of PP crystallites.

In our previous work²² on the crystallization behavior of PP in its blend with a crystallizable polymer, namely, nylon 6, we observed, from the analysis of variations in differential scanning calorimetry (DSC) crystallization exotherms, changes in the crystallization nucleation rate, the crystallite size distribution, the crystallization growth rate, and crystallinity, depending on the blending ratio. Polarized light microscopy, which was used as supporting evidence, revealed an interesting effect, namely, the growth of PP spherulites on the surface of nylon 6 spherulites.

In this work, we report the further study of this effect by varying the crystallization conditions for

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isothermal crystallization at various blending ratios. The polarized light microscopic data are presented and analyzed in terms of the average size, radial growth rate, and number density of the spherulites as a function of time at various temperatures of isothermal crystallization and blending ratios.

EXPERIMENTAL

Materials and Blend Preparation

The PP used in this work was Koylene S3030 of Indian Petrochemical Corp. Ltd., Baroda, India, and nylon 6 (Gujlon M28RC) was a product of Gujarat State Fertiliser Corp. Ltd., Baroda, India. The melt flow index, obtained under similar testing conditions, that is, at 230°C and a 2.16-kg load, were 18.2 and 25.0 g/10 min for PP and nylon 6, respectively. PP–nylon 6 blends were prepared using a twin-screw extruder (Brabender Plasticorder PLE 651). PP and nylon 6 were dried in a vacuum oven at 70°C for over 24 h. The granules were dry-mixed in appropriate ratios and were extruded at 230°C and at a screw speed of 10 rpm. Plain PP and nylon 6 samples were also processed under similar conditions to serve as reference materials. The extruded strands were cooled by quenching in a water bath at 30°C and were granulated and injection-molded into test specimens.

Measurements

Hot-stage polarized light microscopy measurements were made on a Mettler FP82 hot-stage and Leitz polarizing microscope. Samples in the form of flat chips of about 5 mm² area, cut from injection-molded specimens, were isothermally crystallized on the microscope hot stage in the temperature range of 120–135°C. The formation of spherulites and their growth were observed and photographed under both polarized and unpolarized light. Before crystallization, samples were melted and annealed for 2 min at 230°C in order to destroy all self-seeding nuclei, then they were rapidly cooled to the desired isothermal crystallization temperature. The number of spherulites were counted after completion of crystallization and then used to calculate the number of nuclei per unit volume of PP in the blend (the thickness of the sample and the area occupied by counted spherulites were measured). The radial growth rates of PP spherulites were obtained

Table I Crystallization Parameters of Melt-Crystallized Polypropylene

Crystallization Temperature (°C)	Nucleation Density (10 ⁴ /cm ³)	Growth Rate (μm min)
120	338.21	20.0
125	113.66	11.9
127	71.94	8.6
130	27.7	4.6
135	16.65	1.8

from measurement of the radius of the spherulites as a function of time during the isothermal crystallization.

RESULTS AND DISCUSSION

Effect of Temperature

The data for the PP sample melt annealed at 230°C prior to crystallization and then crystallized isothermally in the temperature range of 120 to 135°C are presented in Table I. From these data, it is apparent that a reduction in the isothermal crystallization temperature (T_c) leads to the formation of a larger number of smaller spherulites, which grow faster at lower T_c . Similar studies were also carried out for the PP–nylon 6 (90/10) blend. Figure 1(a)–(d) represents some of the micrographs of this blend at different T_c s. PP spherulites showed birefringence patterns as Maltese cross-truncated by impingement. Similar patterns were observed when a sample of plain PP crystallized from the melt isothermally,²² however, a plain nylon 6 sample upon cooling from a molten stage did not show such well-developed spherulites like PP. In fact, the crystallization of the nylon 6 at about 195°C was so fast that it led to instantaneous formation of a very large number of small spherulites, which covered the entire area of the sample. For the blend sample, the more perfect spherulites were observed at higher T_c , i.e., at 135°C, while with decreasing T_c , the PP spherulites became relatively coarse with irregular Maltese cross-extinction. This is due to the fact that at lower T_c s, the crystal growth is relatively faster, and the molecular chains do not have enough time to arrange themselves to form a perfect crystalline structure.

Effect of Time

Figure 2(a)–(d) represents a typical series of PLM photographs at T_c equal to 135°C for different

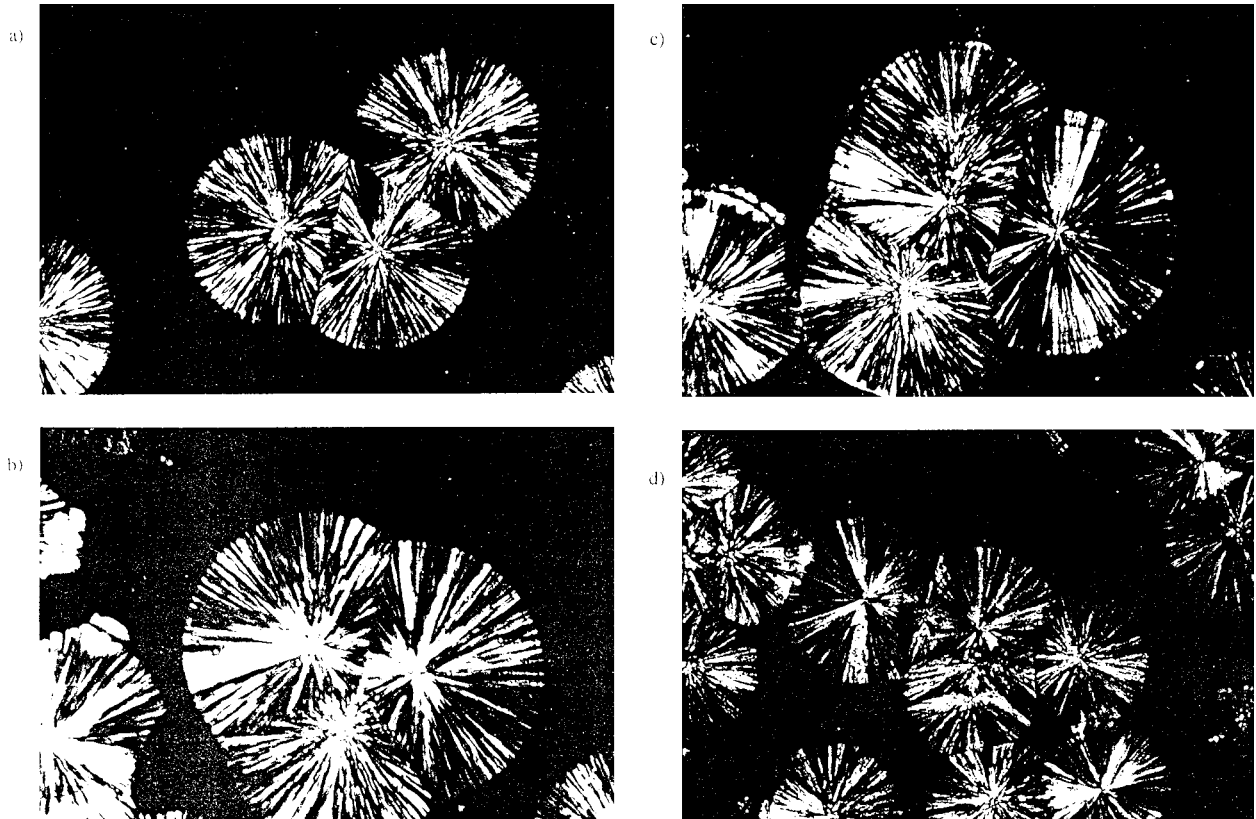


Figure 1 Polarized light micrographs of a PP-nylon 6 blend at T_c equal to (a) 130, (b) 127, (c) 125, and (d) 120 °C.

time intervals. From these photographs, the changes in average spherulite diameter were measured as a function of time. Figure 3 shows that the PP spherulites' size changes linearly with time at different T_c , for the PP-nylon 6 (90/10) blend. The slopes of these lines are the radial crystal growth rates of the PP fraction of the blend at the different T_c s. If one plots the relationship between the radial growth rate versus T_c , a general trend of exponentially decreasing growth rate with increasing T_c is evident, as shown in Figure 4.

The effect of the crystallization temperature (T_c) on the average number of PP spherulites for the PP-nylon 6 (90/10) blend is presented in Figure 5. It is evident that the number of effective nuclei is also strongly temperature-dependent, and it increases sharply with decreasing T_c .

Effect of Blending Ratio

The isothermal crystallization temperatures, that is, 125 and 127°C, were chosen for further study of the effect of the blending ratio on the size, radial growth rate, and average number of PP

spherulites. Measurement of the radius of PP spherulites as a function of time during isothermal crystallization in plain PP and its blends with nylon 6 showed that the growth of PP spherulites is linear with time, as shown in Figure 6 (a) and (b), at all the blend compositions studied. However, on increasing the nylon 6 content of the blend from 0 to 30%, the reduction in the PP spherulites size was more than 50%. This reduction in size of PP spherulites indicates its nucleation on the surface of the already formed nylon 6 spherulites.

Dependence of PP spherulite growth rates on the blend composition, as shown in Figure 7 at two isothermal crystallization temperatures, shows that the radial growth rate of PP spherulites decreases with the increasing nylon 6 content of the blend, and the decrease is more pronounced at lower temperature. This decrease in the radial growth rate of PP shows that presence of the foreign inclusion (i.e., already crystallized nylon 6 particles) in the crystallization path front disturbs the crystallization, thereby causing dissipation of some amount of energy of the moving

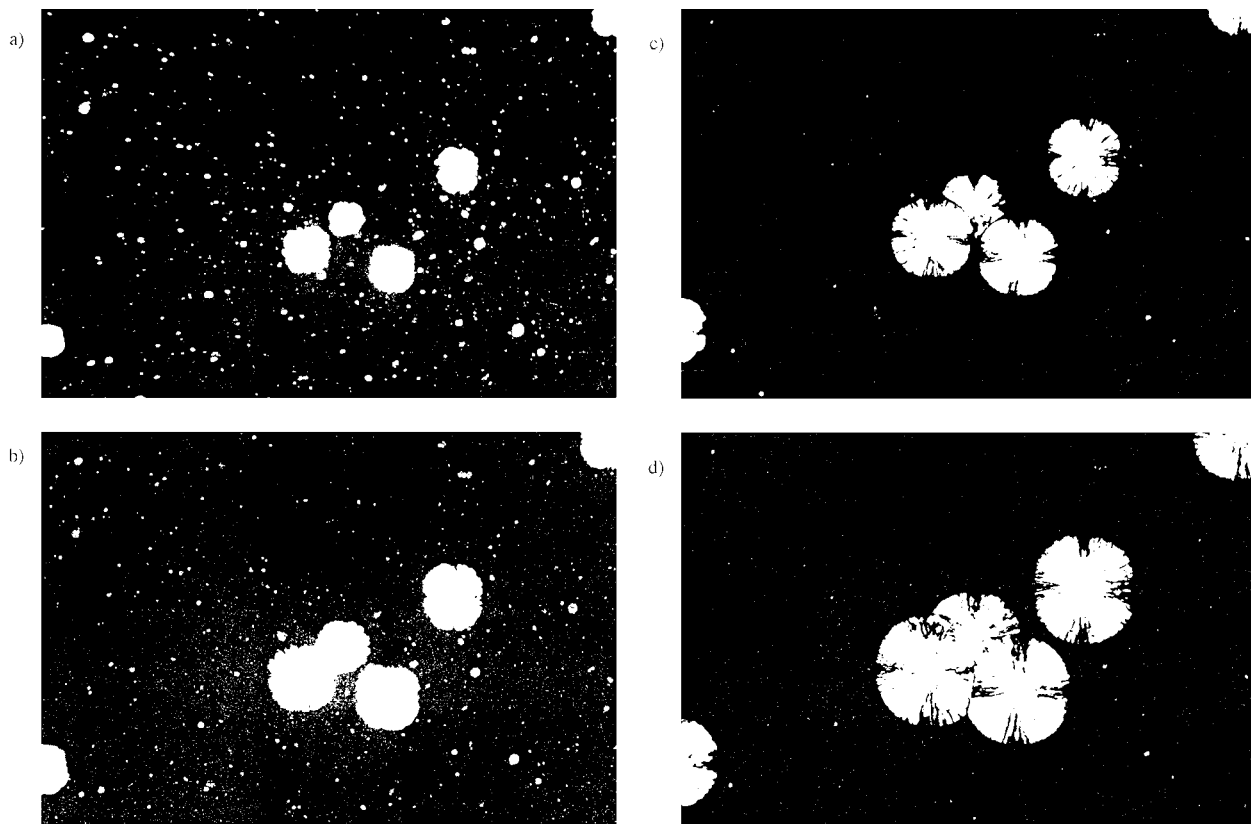


Figure 2 Polarized light micrographs of a PP-nylon 6 blend crystallized at T_c equal to 130°C at the following time intervals: (a) 30, (b) 45, (c) 60, and (d) 75 min.

crystallization path front. This dissipated energy will produce effects like rejection or engulfment of the foreign particle or simply a deformation of the

foreign particles.¹¹ The foreign particles, in this case, being nylon 6 spherulites, are not deformable by this energy. Hence, rejection or engulf-

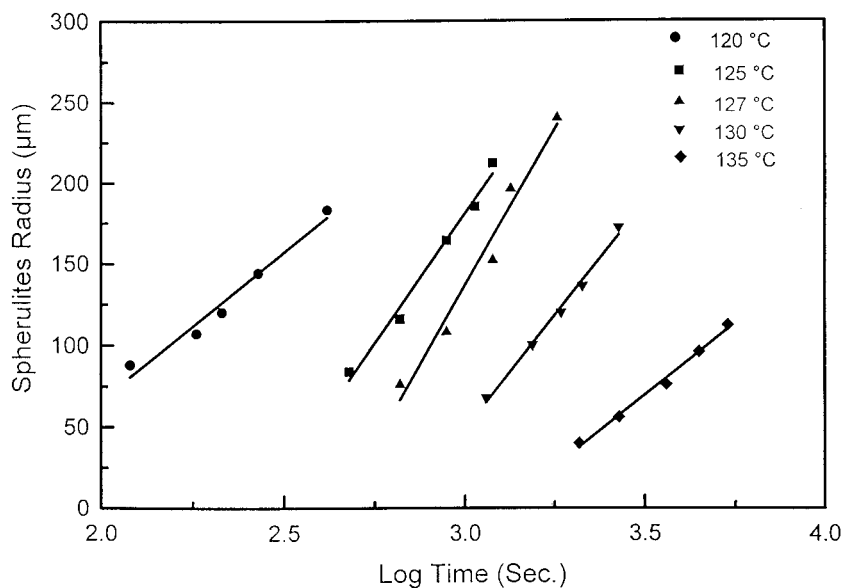


Figure 3 Effect of the crystallization temperature on the average size of PP spherulites in a PP-nylon 6 blend.

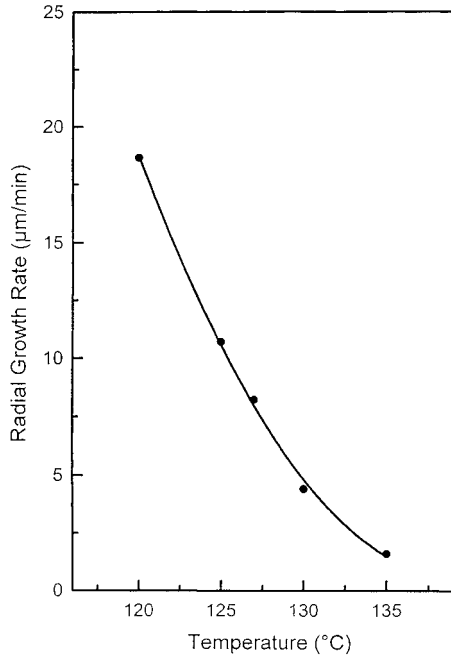


Figure 4 Effect of the crystallization temperature on the growth rate of PP spherulites in a PP-nylon 6 blend.

ment are more likely to occur. From the observed growth of PP spherulites surrounding the surface of nylon 6 spherulites,²² it may be concluded that the dissipated energy of the crystallization path

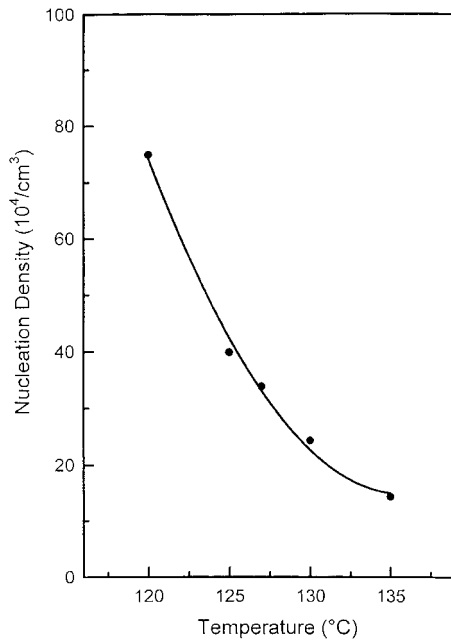


Figure 5 Effect of the crystallization temperature on the number density of PP spherulites in a PP-nylon 6 blend.

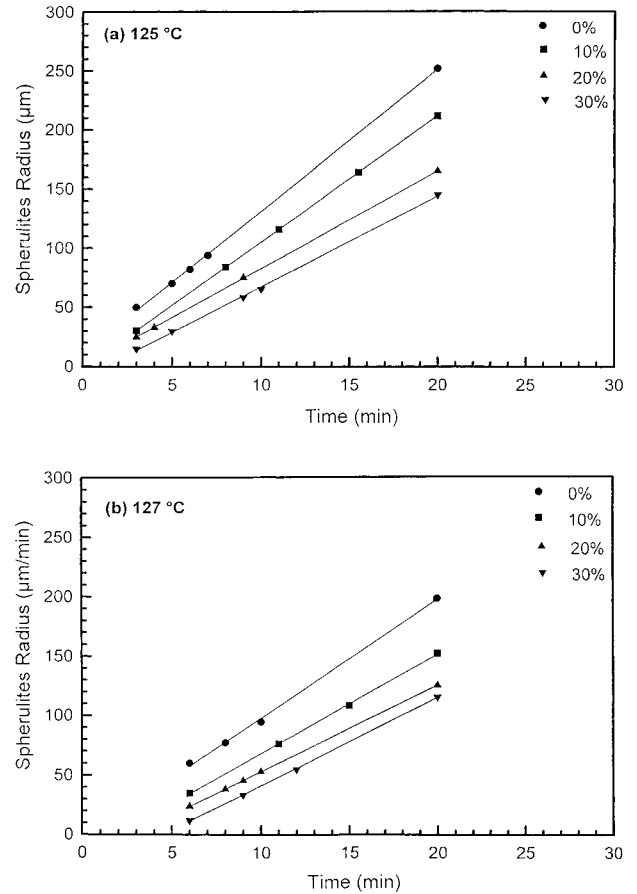


Figure 6 Variations of the PP spherulite size with time at the following different isothermal crystallization temperatures for a PP-nylon 6 blend: (a) 125 and (b) 127 °C.

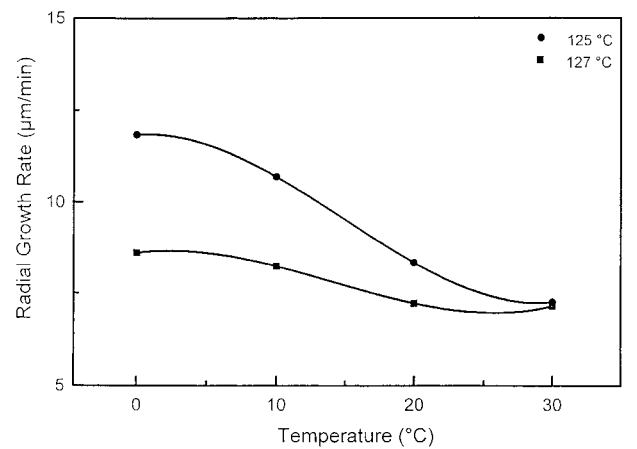


Figure 7 Variations of the PP spherulite growth rate in a PP-nylon 6 blend with blend compositions (wt % nylon 6 content) at two isothermal crystallization temperatures.

front causes engulfment of already crystallized nylon 6 particles present in the PP melt [see Fig. 8(a) and (b)].

As shown in Figure 9, the average number of PP spherulites per unit volume decreases sharply on the initial addition of 10% nylon 6 and thereafter slightly increases by further addition of nylon 6 at both isothermal crystallization temperatures (125 and 127°C). The observed increase in the number of PP spherulites at a higher concentration of nylon 6 could be explained by the fact that some of the PP spherulites had grown centrally around the already crystallized nylon 6 particles.²² This observation indicates the possibility of some nucleation of PP, assisted by nylon 6 particles in the blend. Crystallization of PP in the blend, irrespective of its composition, compared to pure PP, clearly shows a decrease in the rate of nucleation (i.e., the number of spherulites per unit volume) of PP in the presence of nylon 6. The possible reason for the drastic drop in the nucleation density could be the migration of heterogeneous nuclei from PP to nylon 6 during mixing of the blend in the molten stage. Such migration has

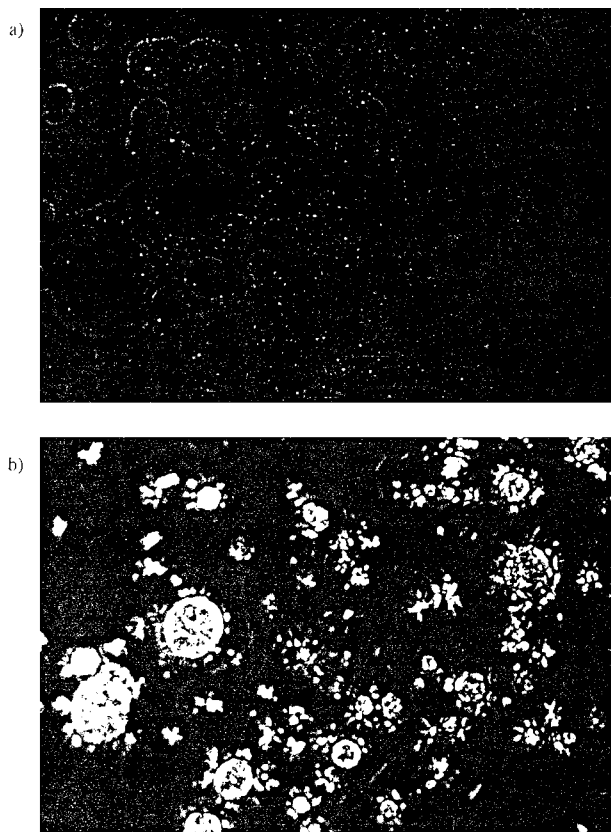


Figure 8 Micrographs of a PP-nylon 6 (70/30) blend at T_c equal to 125 °C: (a) unpolarized and (b) polarized light.

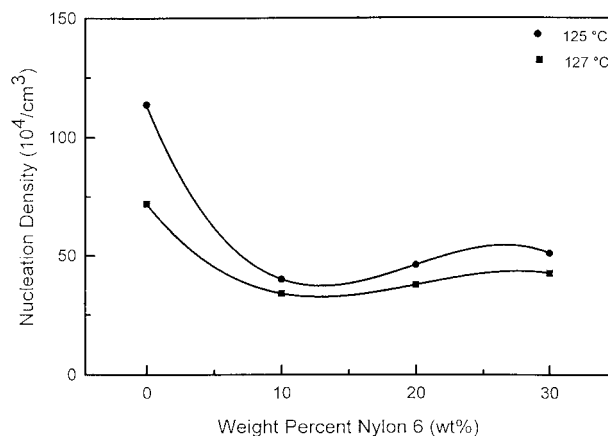


Figure 9 Variations of the PP spherulite number density in a PP-nylon 6 blend with blend compositions (wt % nylon 6 content) at two isothermal crystallization temperatures.

already been reported by Bartczak and coworkers^{23,24} in PP-based blends.

CONCLUSION

Crystallization characteristics and crystalline morphology of plain PP and the PP-nylon 6 blend are strongly temperature-dependent. When these samples crystallize isothermally at higher T_c s, both the nucleation density and the growth rate are small, implying a lower overall rate of crystallization. On the other hand, a decrease in T_c [i.e., the farther the crystallization temperature from the equilibrium condition ($T_c \ll T_m$)] leads to the formation of a larger number of faster growing, smaller spherulites. The effect of the blending ratio on crystallization characteristics and crystalline morphology is such that, at a higher nylon 6 content of the blend, some of the already crystallized nylon 6 droplets act as nucleating sites for the formation and growth of PP spherulites. At a lower concentration, this phenomenon was not observed. Moreover, the size and growth rate of PP spherulites were decreased by increasing the nylon 6 content of the blend. Whereas the number of PP spherulites is lower for the blend containing 10% nylon 6, it increases with the increasing nylon 6 content of the blend.

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