Heterogeneous nucleation of short glass fibre–polypropylene composites

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(Received 8 October 1992; revised 8 February 1993)

The heterogeneous nucleation of polypropylene homopolymer and discontinuous glass fibre (critical fibre length, $L_c \geqslant 3$ mm) reinforced polypropylene was performed by using sodium benzoate as the nucleating agent. Isothermal crystallization of the compression-moulded nucleated polypropylene, non-nucleated polypropylene, nucleated composite and non-nucleated composite was carried out over a temperature range of 370–398 K. Comparison of the shift in the bulk crystallization peak temperatures, as well as the rate of isothermal crystallization of the samples, showed that the incorporation of the nucleating agent resulted in a significant improvement in the crystallization of the polypropylene homopolymer. The short glass fibres nucleated the polypropylene matrix to the extent that the crystallization and morphology of the matrix differ appreciably from those of the homopolymer. Detailed Avrami kinetic analysis was carried out at 390 K for the samples and values of the Avrami constants K and n, ranging from 2.3×10^{-5} to 2.4×10^{-3} and 2.01 to 1.66 for the polypropylene homopolymer to the nucleated composite, respectively, were obtained. Optical microscopic analysis showed spherulitic crystallization for the homopolymer, crystallitic crystallization for the nucleated polypropylene, and mixed crystallitic and axialitic crystallization for the discontinuous composite.

(Keywords: heterogeneous nucleation; glass fibre; polypropylene)

INTRODUCTION

The incorporation of fibrous reinforcement into polymeric materials usually results in significant improvement in their mechanical properties. The improvement in the mechanical performance of polymer-based composites, especially glass fibre reinforced semicrystalline polymers, has been attributed to the excellent mechanical properties of the reinforcing fillers[1–5]. The capability of the reinforcing fillers to nucleate the matrix and consequently enhance further the stiffness and the strength of the composite is very exciting to investigators. The enhancement in the physical and mechanical properties of semicrystalline polymers such as polypropylene, may be attributed partly to the significant changes in the morphology of the matrix due to the presence of the heterogeneous nucleating agent. Beck has reported the heterogeneous crystallization of polypropylene using sodium benzoate as the nucleating agent. The nucleated polypropylene showed an improved rate of nucleation crystallization over the non-nucleated samples[6,7]. The nucleating agent is usually incorporated into the homopolymer and the composite to produce a consistent property of the matrix. It is expected that the nucleating agent will affect polypropylene and the short glass fibre reinforced polypropylene in the same way. This would therefore enable us to differentiate between the contribution to the mechanical properties of the composites arising from the rigidity and the strength of the reinforcement from that due to the filler-induced crystallization of the matrix. The present study focuses on the heterogeneous nucleation of compression-moulded commercial polypropylene and its short glass fibre composites.

EXPERIMENTAL

Materials

Isotactic polypropylene Pro-Fax 6524 in the form of granules and the short glass fibre reinforced polypropylene Pro-Fax Pc-073 containing 30 wt% glass fibres supplied by Hercules Inc., were used. Sodium benzoate (99.9% pure) was obtained from Aldrich Chemical Company and used without further purification.

Sample preparation

About 0.5 wt% of the nucleating agent was dry mixed with the homopolymer Pro-Fax 6524 and the composite Pro-Fax Pc-073, respectively. Four grades of the nucleated polypropylene, non-nucleated polypropylene, nucleated composite and non-nucleated composite (NPP, PP, NGRPP and GRPP, respectively) were compounded to ensure effective blending of the nucleating agent with

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0032-3861/93/224747-05

the homopolymer and the composite, respectively. A twin screw extruder model DSK 42/5, manufactured by Brabender Ohg Duisburg, was operated at 220°C and screw speed of $\sim 10\,\mathrm{rev\,min^{-1}}$. The extruder has an output of $\sim 20\,\mathrm{g\,min^{-1}}$ at $10\,\mathrm{rev\,min^{-1}}$ and is characterized by the length of the screw zone, screw zone channel depth, pitch and length of mixing of 105, 6, 30 and 105 mm, respectively[8,9]. The samples PP and GRPP in the form of granules, were dry mixed with the powdery nucleating agent and fed into the extruder through the hopper. The melt was expelled through a 3 mm diameter die in the form of a continuous cylindrical rod. The extrudate was chopped into 2–3 cm pieces as it exited through the die to facilitate granulation. The granulated samples were compression-moulded into $145 \times 145\,\mathrm{mm^2}$ sheets using the Hydropak hand press (Tangyeys Ltd). The moulds were filled with samples (~ 50 g) and held between the platens previously heated to 220°C at the contact pressure for 10 min. A pressure of 10×10^3 kg on a ~ 10 cm diameter ram was applied for 5 min and then released for 1 min. The pressure was then increased to 15×10^3 kg and held for 3 min. It was then released for 1 min. Finally, the pressure was raised to 25×10^3 kg and held for 2 min. The mouldings were cooled under pressure by circulating tap water at $25^\circ\mathrm{C\,min^{-1}}$.

Differential scanning calorimetry

A Perkin–Elmer DSC-2 was used to perform the crystallization of the samples over the temperature range of 370–398 K. A standard indium sample was used for calibration. The samples were initially heated to 500 K at $20\mathrm{K\,min^{-1}}$ and maintained at this temperature for 5 min, to ensure total relaxation. Isothermal crystallization was performed at 370, 375, 380, 385, 390 and 398 K, respectively. The zero time of crystallization was taken as the time indicating thermal equilibrium[10,14,15].

A time-base recorder was made until crystallization was completed. The area under the curve was integrated in 15-s intervals using Simpson's rule. The heights of the chart after each 15-s interval, h, were added in sequence and the sum at each time interval, $\sum h$, recorded. Each of the $\sum h$ values was divided by the total value $\sum^{\infty} h$ to give the fraction of crystallization θ, which was then plotted against time t. Typical fraction crystallization *versus* time curves were plotted for the samples. This procedure has the advantage that a standard set of $\ln[-\ln(1-\theta)]$ and $\ln t$ values are used and the progress of crystallization is more equally sampled. The microscopic analysis of the samples was performed under cross polars. The samples for optical microscopy were microtomed into 25 μm thick films and mounted on the stage of a Nikon polarizing microscope by means of glass slides.

THEORY

The isothermal crystallization kinetics of polymers can be expressed using the Avrami equation for a phase change represented by[10–12]:

$$\theta = 1 \pm e^{-Kt^n} \qquad (1)$$

where θ is the fractional extent of crystallization at time t, and n and K are the Avrami constants. The rate of enthalpy change is measured as a function of the time at the crystallization temperature, T_c.

If T_c is the recorder response at time t, then:

$$\theta = \frac{\sum^{t} h}{\sum^{\infty} h} \qquad (2)$$

$$\frac{d\theta}{dt} = \frac{h}{\sum^{\infty} h} \qquad (3)$$

where $\sum^{\infty} h$ corresponds to the area under the d.s.c. curve[13]. Integration of equation (1) gives the relation:

$$\ln[-\ln(1-\theta)] = \ln K + n \ln t \qquad (4)$$

Linear regression analysis using equation (4) gives $\ln K$ and n as the intercept and slope, respectively.

RESULTS AND DISCUSSION

Figure 1 shows the inverse of the half-time of crystallization for the samples as a function of the temperature of crystallization. PP showed the slowest rate of nucleation crystallization. A significant increase in the rate of crystallization occurred for NPP. The polypropylene composites NGRPP and GRPP gave about the same rate of crystallization, which is about one order of magnitude higher than that for NPP and about two orders of magnitude higher than that for PP. The short glass fibre reinforcements therefore improved the nucleation crystallization of the composites. The d.s.c. result showed that the sodium benzoate nucleating agent had only a slight impact on the isothermal crystallization of the composites.

Figures 2–5 show the isothermal fraction of crystallinity of the samples as a function of time at different temperatures (375, 380, 385, 390, 395 and 398 K, respectively). The fraction of crystallinity, at any given time, decreased with increased temperature of crystallization. For PP, the fraction of crystallinity

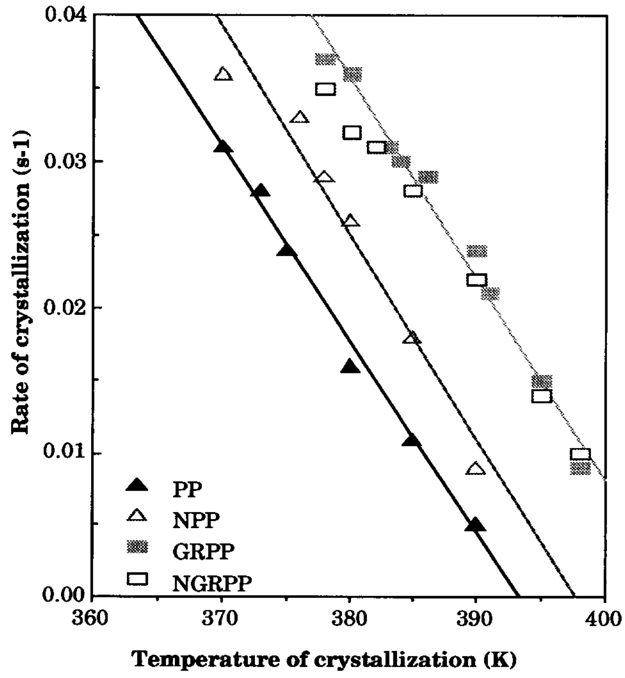

Figure 1 Rate of crystallization of the samples as a function of the crystallization temperature

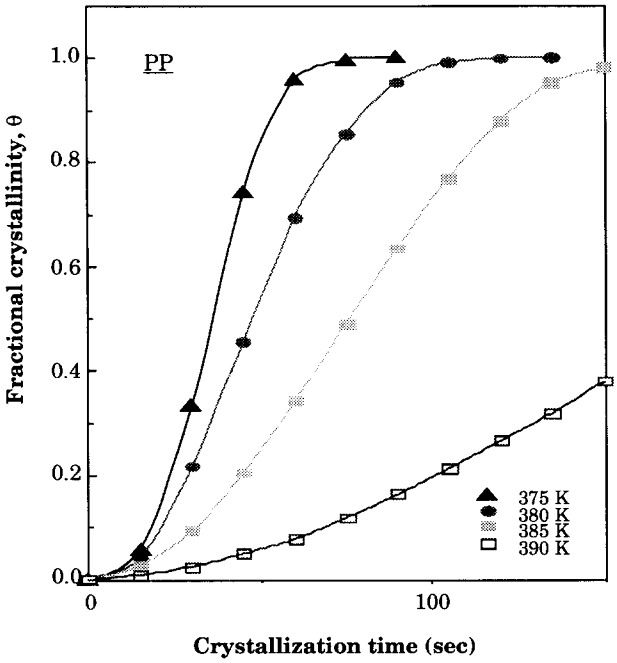

Figure 2 Isothermal crystallization of polypropylene

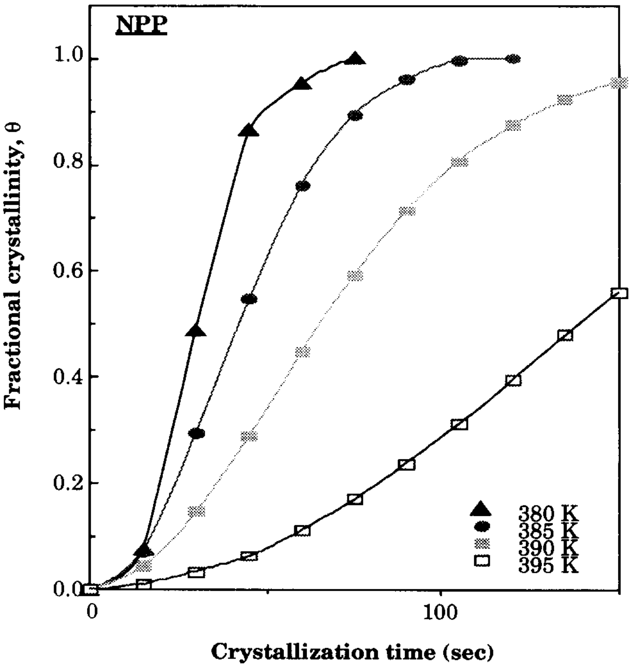

Figure 3 Isothermal crystallization of nucleated polypropylene

increased from ~18% at 390 K to ~90% crystallinity at 100 s when the crystallization temperature was decreased from 390 to 375 K (*Figure 2*). The same trend was observed for the other samples (*Figures 3–5*). *Figure 6* shows the combined fractional crystallinity plots *versus* time for PP and NPP. NPP showed a higher rate of crystallization (estimated from the slopes of the isothermal crystallization curve) than PP at any given temperature of crystallization. The composites NGRPP and GRPP showed a decreased rate (slope) of isothermal crystallization with increased crystallization temperature (*Figures 4* and *5*) as was expected. Comparison of the rate of isothermal crystallization for all the samples is shown in *Figure 7*. The composites NGRPP and GRPP, respectively, showed a significant increase in the rate of isothermal crystallization over the polypropylene samples NPP and PP. There was, however, a slight difference between the isothermal crystallization behaviour of the nucleated and non-nucleated composites.

Though the incorporation of the nucleating agent resulted in an increase in the rate of crystallization and a reduction in the induction time for crystallization, a more quantitative measure of the nucleation ability is the effect of the nucleating agent on the degree of supercooling and the complimentary shift in the peak crystallization temperature T_p. The nucleated samples NPP and NGRPP possessed higher T_ps than PP (*Table 1*). About a 7 K increase in the T_p of polypropylene

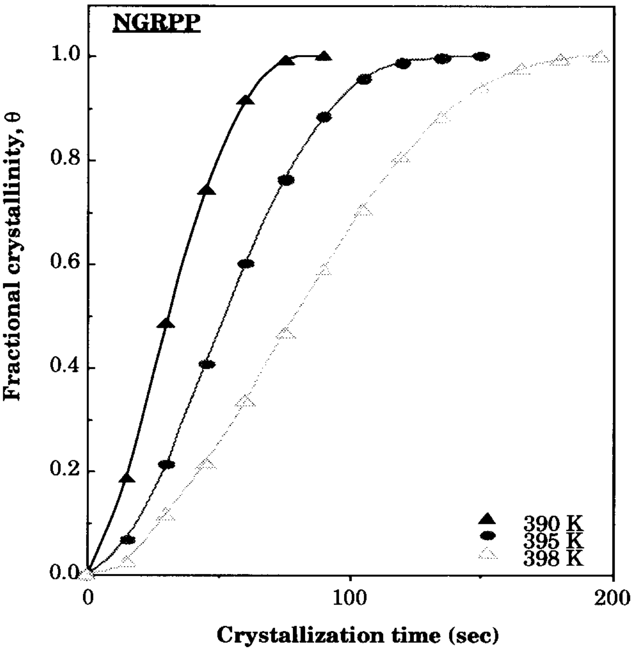

Figure 4 Isothermal crystallization of nucleated short glass fibre reinforced polypropylene

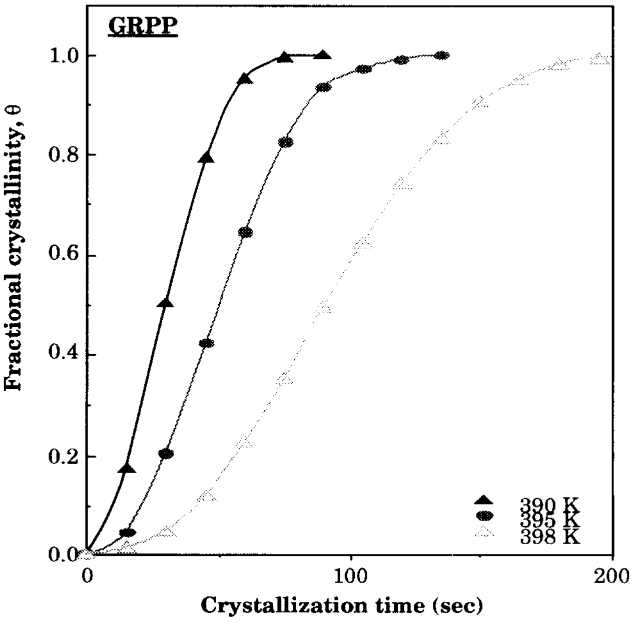

Figure 5 Isothermal crystallization of short glass fibre reinforced polypropylene

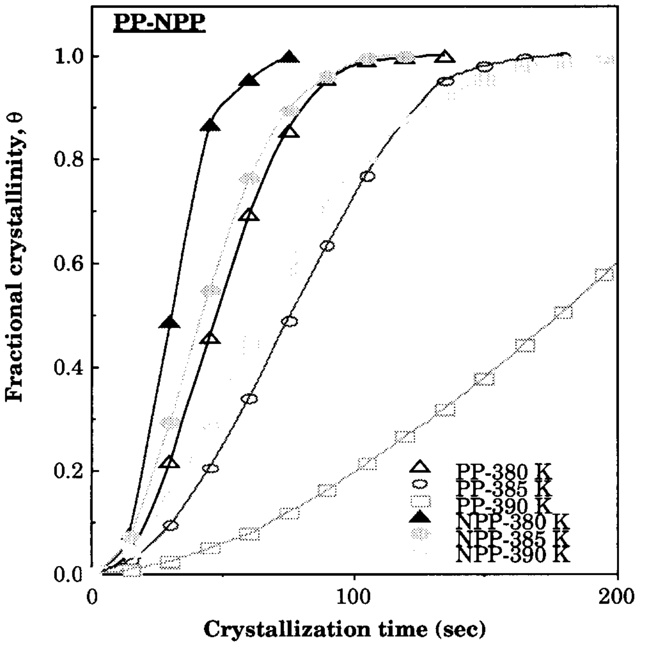

Figure 6 Isothermal crystallization of PP and NPP at 380–390 K

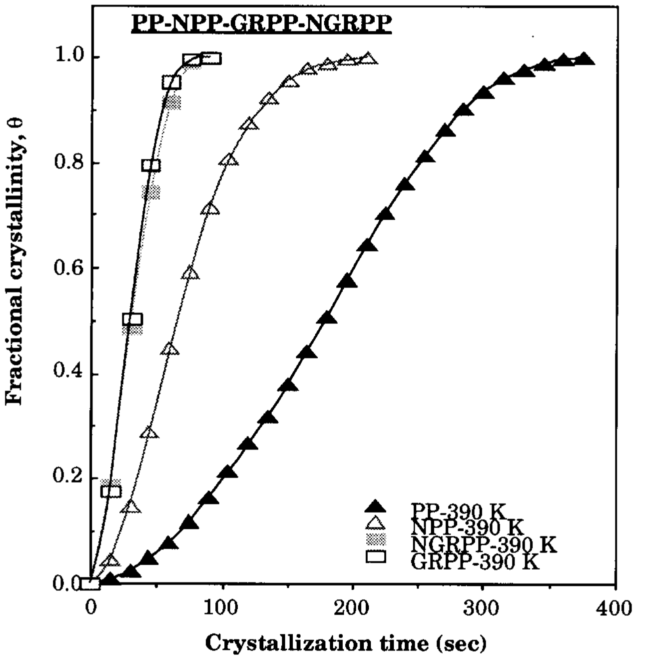

Figure 7 Isothermal crystallization of PP, NPP, GRPP and NGRPP at 390 K

Table 1 Avrami constants K and n and the characteristic temperatures for PP, NPP, GRPP and NGRPP at 390 K

Sample	T_p (K)	T_i (K)	T_b (K)	T_m (K)	$T_i - T_p$ (K)	K ($\times 10^4 s^{-2}$)	n
PP	371.0	381.0	365.0	440.0	9.0	0.24	2.01
NPP	378.0	386.5	367.0	440.0	8.5	2.91	1.85
GRPP	382.5	391.0	376.0	440.0	8.5	24.20	1.66
NGRPP	383.0	391.0	374.0	441.0	8.0	24.20	1.66

[a] T_p, peak crystallization temperature; T_i, onset of crystallization temperature; T_b, temperature for the end of bulk crystallization; T_m, melting temperature

occurred as a result of the incorporation of sodium benzoate. The effectiveness of the short glass fibres as a heterogeneous nucleating agent for polypropylene is confirmed by the 12 K increase in the T_p for the composite GRPP (*Table 1*). There was also an ~0.5 K increase in the T_p for the nucleated over the non-nucleated composites.

Table 1 also shows the Avrami constants K and n determined at 390 K for the samples PP, NPP, GRPP and NGRPP. The ln K values for the samples were -10.7, -8, -6 and -6 for PP, NPP, GRPP and NGRPP, respectively. These K values suggest that the rate of crystallization for PP increased remarkably with heterogeneous nucleation. The composite samples GRPP and NGRPP have the same K value of 2.4×10^{-3}, which is about one and two orders of magnitude higher than for NPP and PP, respectively. The n values of 2.01 and 1.85 for PP and NPP are less than the value of 3 predicted for spherulitic crystallization. The n values for the composites of 1.66 were also lower than that predicted for three-dimensional growth. The combination of the effect of temperature and contact with the extraneous nuclei imposes a mixed mode of nucleation crystallization for the composites. The composites were nucleated by the glass fibres which force some sort of rod-like axial crystallization. It was earlier reported by Sharples that

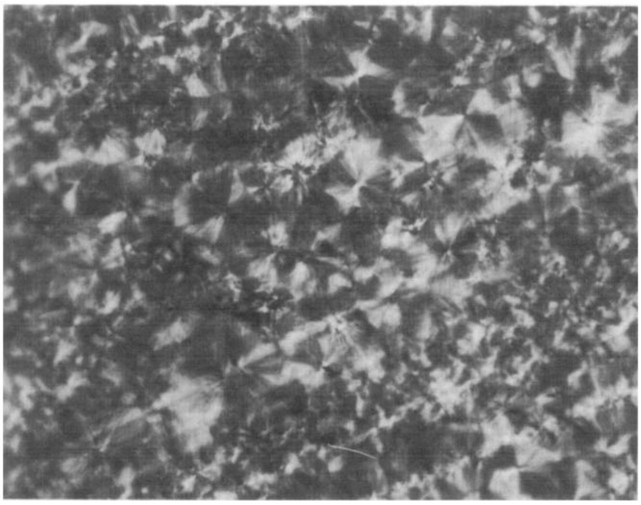

Figure 8 Optical micrograph of polypropylene (×10)

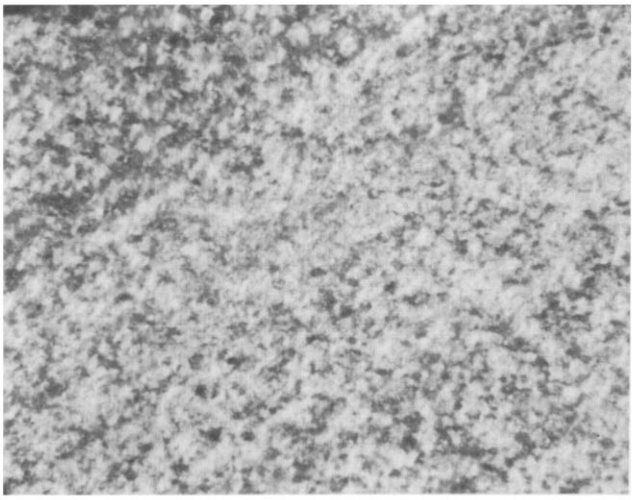

Figure 9 Optical micrograph of nucleated polypropylene (×10)

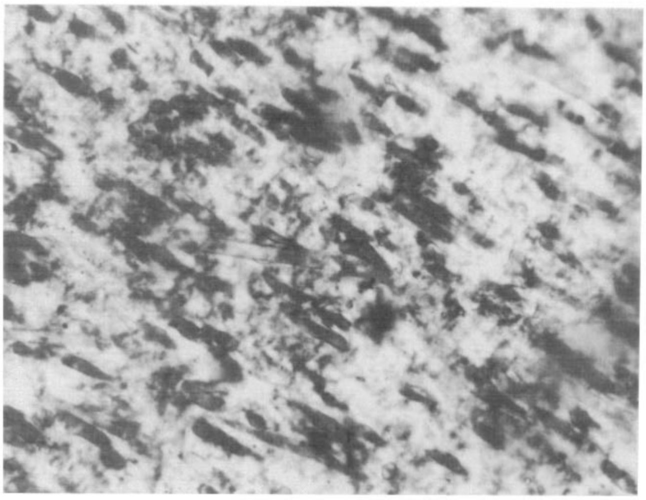

Figure 10 Optical micrograph of discontinuous glass fibre–polypropylene composite (× 10)

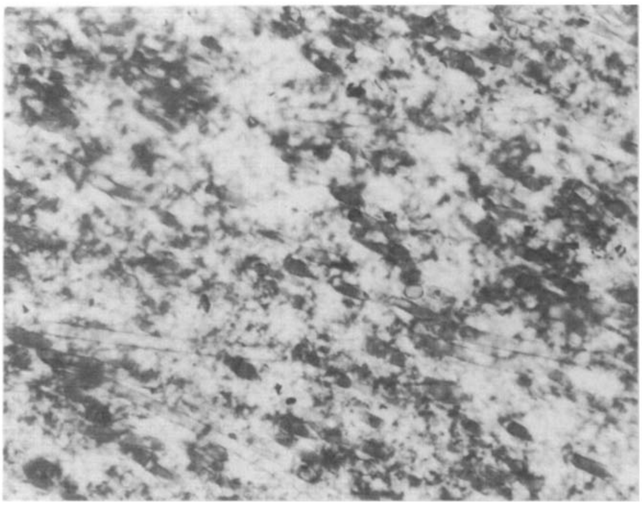

Figure 11 Optical micrograph of nucleated composite (× 10)

the *n* and *K* values obtained depend to a great extent on the degree of supercooling and therefore vary with the temperature of crystallization[10]. *Figures 8–11* show the optical micrographs for the samples. PP showed spherulitic morphology (*Figure 8*). NPP produced smaller sized spherulites (*Figure 9*). Note that these samples were subjected to the same thermomechanical history; the only factor that accounts for the difference in their morphology is the extraneous nucleating agent. The composites showed a complex morphological feature of fibrous rods embedded in a dense crystallitic matrix (*Figures 10* and *11*).

CONCLUSIONS

The rate of crystallization of polypropylene has been greatly improved by the introduction of a heterogeneous nucleating agent. The incorporation of ~0.5 wt% sodium benzoate into the polypropylene homopolymer resulted in an ~50% increase in the rate of crystallization. Sodium benzoate is undoubtedly an excellent nucleating agent for isotactic polypropylene. The short glass fibre reinforced polypropylene, however, showed an exceptionally high rate of nucleation crystallization of about one and two orders of magnitude greater than that for NPP and PP, respectively. The enhanced nucleation crystallization of the composite is attributed to the ability of the short glass fibres to nucleate and accelerate the crystallization of the polypropylene matrix. The crystallization of the composites was virtually unaffected by the addition of the extraneous chemical nucleating agent. The short glass fibres modified the polypropylene matrix by *in situ* heterogeneous nucleation to the extent that the chemical nucleating agent had no significant effect on the modified matrix. Optical microscopy under cross polars indicated a spherulitic and crystallitic crystallization for the PP homopolymer and the NPP, respectively, and mixed crystallitic and axialitic crystallization for the discontinuous glass fibre reinforced polypropylene.

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