

Effect of Thermal Conductivity and Heat Transfer on Crystallization, Structure, and Morphology of Polypropylene Containing Different Fillers

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ABSTRACT: The crystallization behavior, structure, and morphology developed was investigated for polypropylene containing different fillers such as silica, calcium carbonate, talc, mica, graphite, etc. by using compression-molded samples prepared at several cooling rates. It was observed that the crystallinity obtained for any given composition depended on the thermal conductivity of the filler and the PP composite containing it as well as the cooling rate to which it was subjected. These composites exhibited skin-core type of morphology and the skin layer thickness was found to

depend not only on the cooling rate but also on the type of filler, its thermal conductivity, etc. These various experimental findings were discussed in light of the phenomenological model described in our earlier work, which correlates thermal conductivity and degree of crystallinity for various compositions of PP containing additives. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 615–623, 2004

Key words: polypropylene; fillers; thermal properties; crystallization; morphology

INTRODUCTION

The crystallization behavior and structure development in polypropylene (PP) has received considerable attention in recent years because it has a wide range of applications in many areas and in some cases as replacement of low-end-use engineering polymers.^{1–4} In the polymer processing industry, many types of fillers are incorporated for improving the properties such as tensile strength, impact resistance, etc. Among other additives, mineral fillers, such as calcium carbonate, talc, silica, wollastonite, and mica, have been found to be effective in PP. However, the utility of the final molded product depends on the processing-induced changes such as dimensional changes/shrinkage, warpage, weld lines, etc. All of these parameters are related to the crystallization behavior of polymer and its dependence on the incorporation of different additives in the polymer together with the processing conditions used for molding. Many studies have been reported in the past, including by the present authors, on the crystallization behavior of PP containing wide ranges of additives.^{5–12} These studies showed that large changes occur on the induction time, crystallization half-time, spherulite size, etc., due to the presence of additive. However, the exact role of the heat-trans-

fer process and thermal conductivity of such fillers on the crystallization kinetics has been brought out only recently and a model is suggested for the same.¹³ The aim of the present work was the quantitative examination of the crystallization of PP containing different types of additives to establish the corelationships between degree of crystallinity, cooling rate, thermal conductivity of the filler, and/or composite and to compare the same with the phenomenological model described earlier.

EXPERIMENTAL

The PP particulate composites with different fillers were prepared by taking a desired quantity of PP powder (Indothane, SM85N, MFI 8–12, IPCL, India) and mixing the same with the desired amount of filler powder in an agate pestle and mortar and then compression molding the same. Fillers used were lab-grade powders obtained from standard suppliers. The composition of filler was varied from 0 to 40 wt % with respect to PP. Typically, samples were prepared by first compacting the powder mixture in single end compaction die at 2-ton pressure for 1 min to form pellets. These were then compression molded (Techno Search, tabletop programmed press) at a melt temperature of 180°C for 10 min to form 1.3-mm-thick sheets and cooled at the desired cooling rates. Four methods of cooling (designated A to D) were employed, where A, B, and C correspond to program cooling, self-cool-

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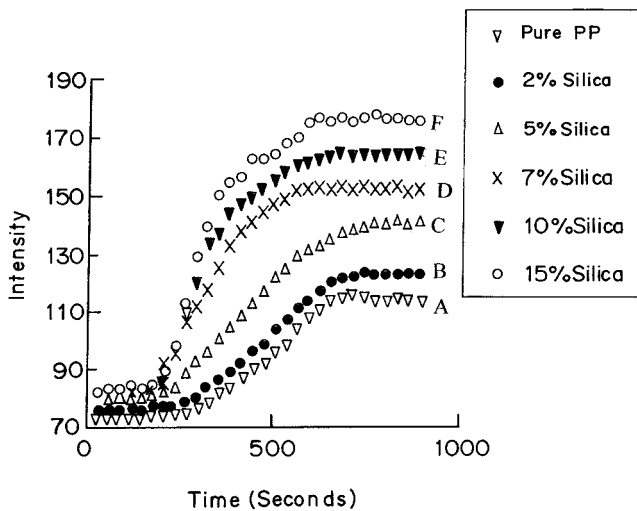


Figure 1 Isothermal crystallization curves for PP containing silica at various concentrations. Curve A is for pure PP, whereas curve B to F correspond to PP containing 2, 5, 7, 10, and 15% silica, respectively.

ing, and water cooling, respectively, while D corresponds to quenching. In the case of program cooling (A), the sample after molding at 180°C was allowed to cool in steps of 20°C, during which period the heater power was slowly reduced. In the case of self-cooling (B), the sample was allowed to cool without providing any type of coolant, while in method (C), the cooling water was forced through channels in the mold. Last, for method (D), the samples were quenched directly in the coolant. The coolant used was chilled ice water. In all cases, the sample temperature was recorded continuously with time to determine the actual cooling rate (°C/min). The samples and their sections were then studied by wide-angle X-ray diffraction (XRD) and optical polarizing microscopy techniques, respectively, in the same manner as reported elsewhere.¹³⁻¹⁵

RESULTS AND DISCUSSION

Crystallization behavior

The isothermal crystallization behavior of PP containing different fillers was investigated by using optical polarizing microscopy. Figure 1 shows the typical crystallization curves (in terms of transmitted intensity under cross-polar conditions^{9,10,13-15}) for PP containing silica. Curves A to F correspond to silica concentrations of 0, 2, 5, 7, 10, and 15%, respectively. It is clear that the induction period for the onset of crystallization and the growth rate are dependent on the silica content in the sample. Similar crystallization curves were recorded for different types of fillers added to PP and the data were analyzed for induction

TABLE I
Variation of Induction Period for Crystallization with Thermal Conductivity of PP with Different Fillers at 10 wt %

Composition (10 wt %)	Thermal conductivity ^a (W/mK)	Induction period ^b (s)
Pure PP	0.23	263
PP + wollastonite	0.263	191
PP + glass fiber	0.271	183
PP + silica	0.277	138
PP + talc	0.285	135
PP + mica	0.286	140
PP + calcium carbonate	0.286	130
PP + carbon fiber	0.292	108

^a Estimated from equations in Ref. 13 and using K values for fillers from Ref. 21.

^b Samples isothermally crystallized at 115°C from starting melt at 200°C.

time, crystallization half-time, growth rate, etc. The variation of induction period for different fillers is shown in Table I, which also gives the value of thermal conductivity for the fillers. Thermal conductivity values were calculated from the Nielsen model, the details of which have been described in our earlier article.¹³ The phenomenological model described in the earlier article can be used to correlate the time required to cool the sample from melt to the temperature for onset of crystallization with the induction time observed experimentally. This model briefly con-

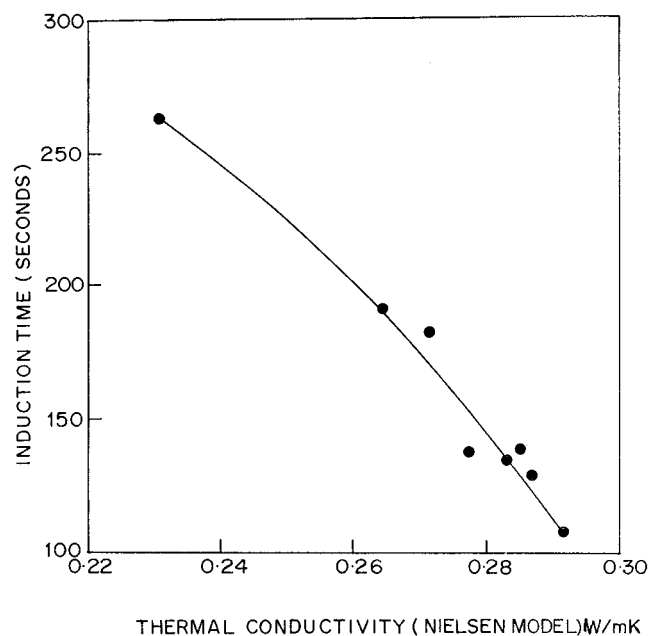


Figure 2 The variation of induction time derived from the cooling curves with respect to the thermal conductivity of PP filled with different fillers at 10 wt %.

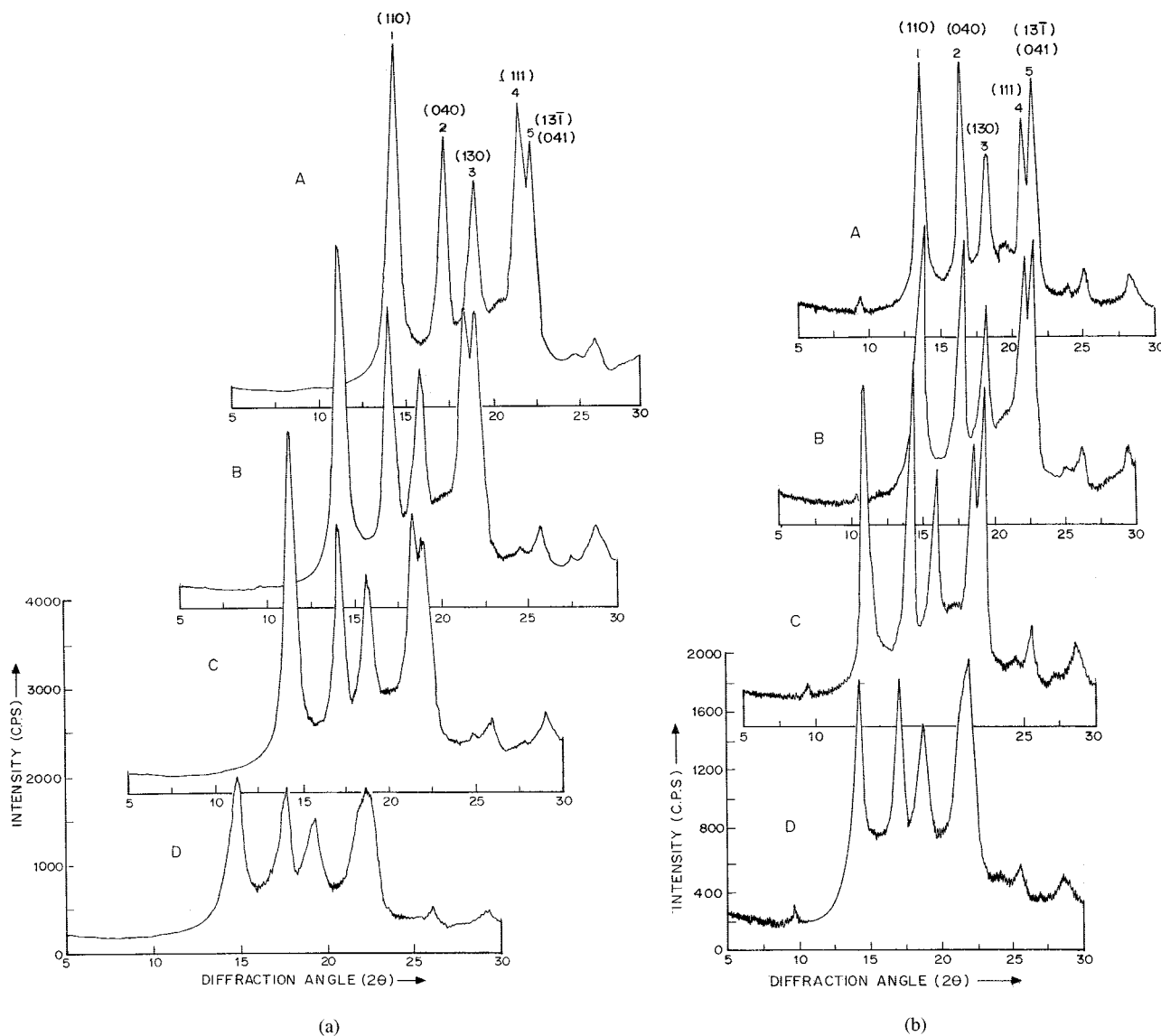


Figure 3 XRD scans of PP containing silica at various concentrations (0–40 wt %). A, B, and C correspond to programmed cooling, self-cooling, and water cooling, respectively, while D corresponds to quenching. (a) Pure PP, (b) 5%, (c) 10%, (d) 20%, (e) 30%, and (f) 40% of silica, respectively.

tains the estimation of thermal conductivity of polymer composite at different compositions of the filler, using the same values of thermal conductivity for evaluating the cooling curves (from melt temperature) and the time required to reach the onset temperature of crystallization. On comparison of data in Table I, it is evident that higher thermal conductivity of the filler leads to shorter induction time and faster crystallization. Figure 2 gives the variation of induction time estimated from crystallization curves of PP containing 10% of different types of fillers with respect to the thermal conductivity of the composite. It is quite obvious from this figure that the thermal conductivity of the filler/composite plays an important role in the overall crystallization behavior of PP with additives,

higher thermal conductivity leading to faster cooling, and lower induction periods.

Structure development and crystallinity

XRD scans for PP filled with different filler contents (ranging from 0 to 40 wt %) for four methods of cooling used are indicated in Figure 3(a–f), Figure 4 (A, B), and Figure 5 (A, B). The main diffraction angle (2θ) region of interest (5 to 30°) only has been shown in which PP exhibits five intense peaks. It can be recognized that, in all these cases, the crystalline structure of PP is α -type (monoclinic $a = 6.66 \text{ \AA}$, $b = 20.8 \text{ \AA}$, $c = 6.49 \text{ \AA}$, and $\beta = 99.6^\circ$).^{4,5,11–13} However, it can be noted that the relative intensities of these peaks de-

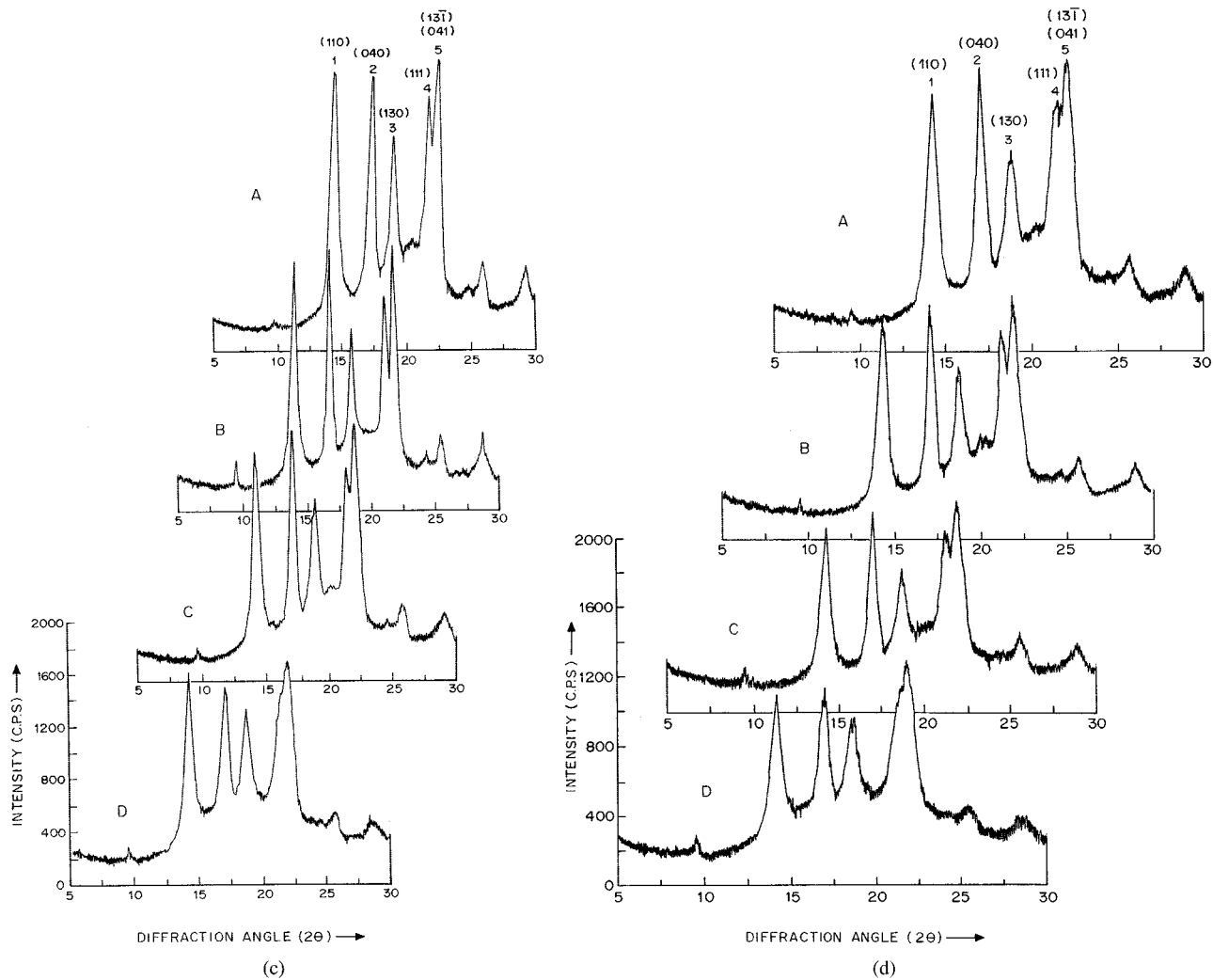


Figure 3 (Continued from the previous page)

pend on both the composition and the cooling rate used. These aspects are discussed later in this article. The overall crystallinity ($C_i\%$), determined from these XRD scans, was also found to depend on the composition as well as the cooling rate. Further, for any fixed cooling method such as quenching or self-cooling, the high filler containing samples exhibited lower C_i values. Table II indicates the results of changes in degree of crystallinity for the pure PP and PP filled with silica (ranging from 0 to 40 wt %), which were crystallized from melt at different cooling rates. The decrease in crystallinity value changed from 69 to 43% when the silica content in PP is varied from 0 to 40 wt %, which is quite significant. The effect of thermal conductivity of the composite is mainly on the heat transfer process from the melt to the mold wall and hence the net cooling rate, which in turn decides the degree of crystallinity.

These various observations could be explained on the basis of the role of thermal conductivity of the

composite and the heat transfer from the same to the surrounding during the crystallization process. The higher the silica content, the faster the cooling, and this leads to a lower value of crystallinity. To confirm this hypothesis, the values of thermal conductivity of PP-silica composites were estimated from Nielsen's equation as mentioned earlier.¹³ All these observations were compiled in the form of a 3D plot indicated in Figure 6, which shows the crystallinity as a function of cooling rate as well as thermal conductivity value for that composition. It is evident that high thermal conductivity and high cooling rate lead to low C_i values. Interestingly, there appears a plateau region where there is another competitive process that shifts the crystallinity to higher values than expected. This effect is seen for comparatively slow cooling rate at which there is sufficient time for the growth of the crystallites/spherulites. On the other hand, for quenching or water cooling, the heat transfer process dominates and hence the C_i value gets affected in

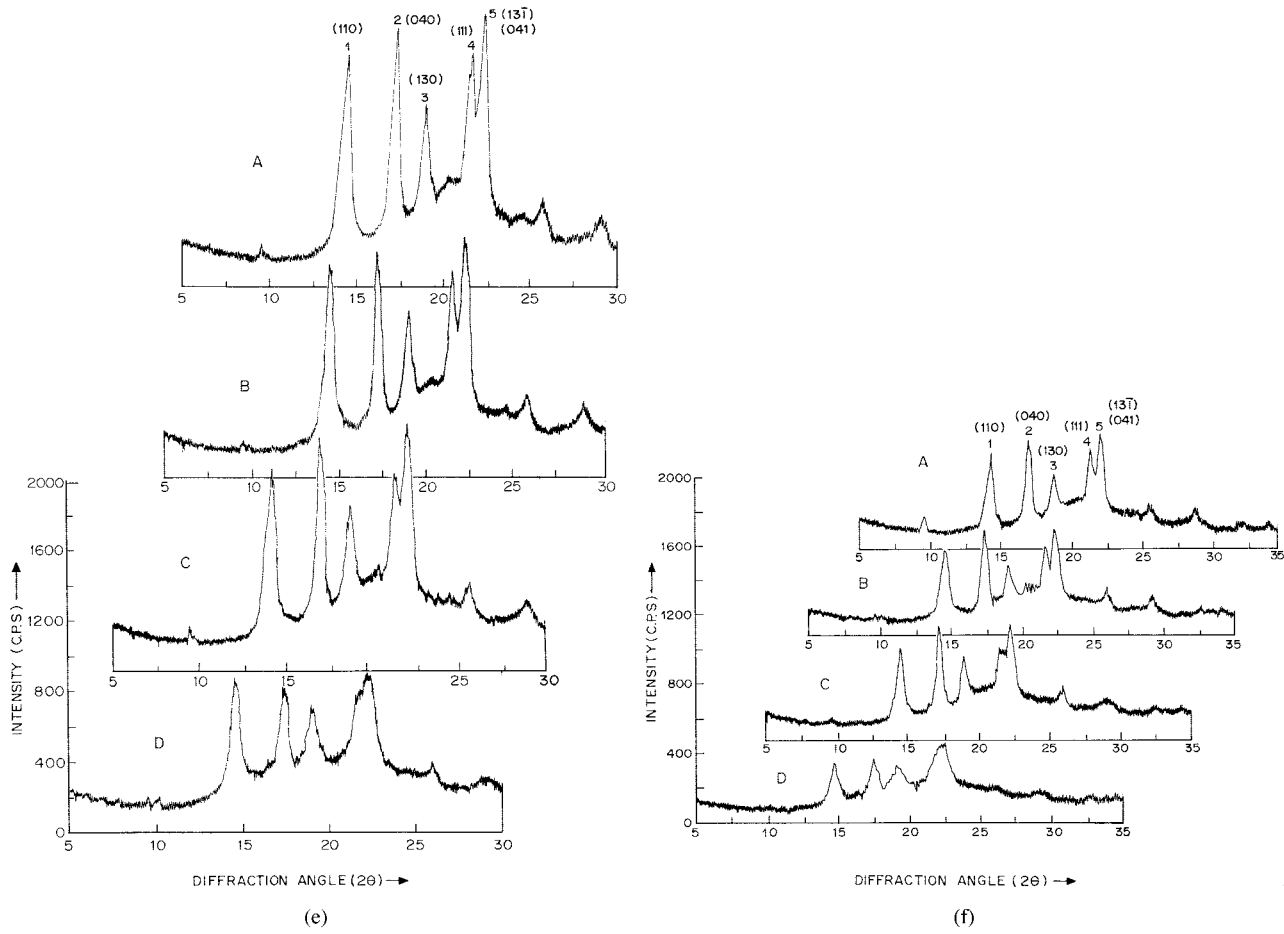


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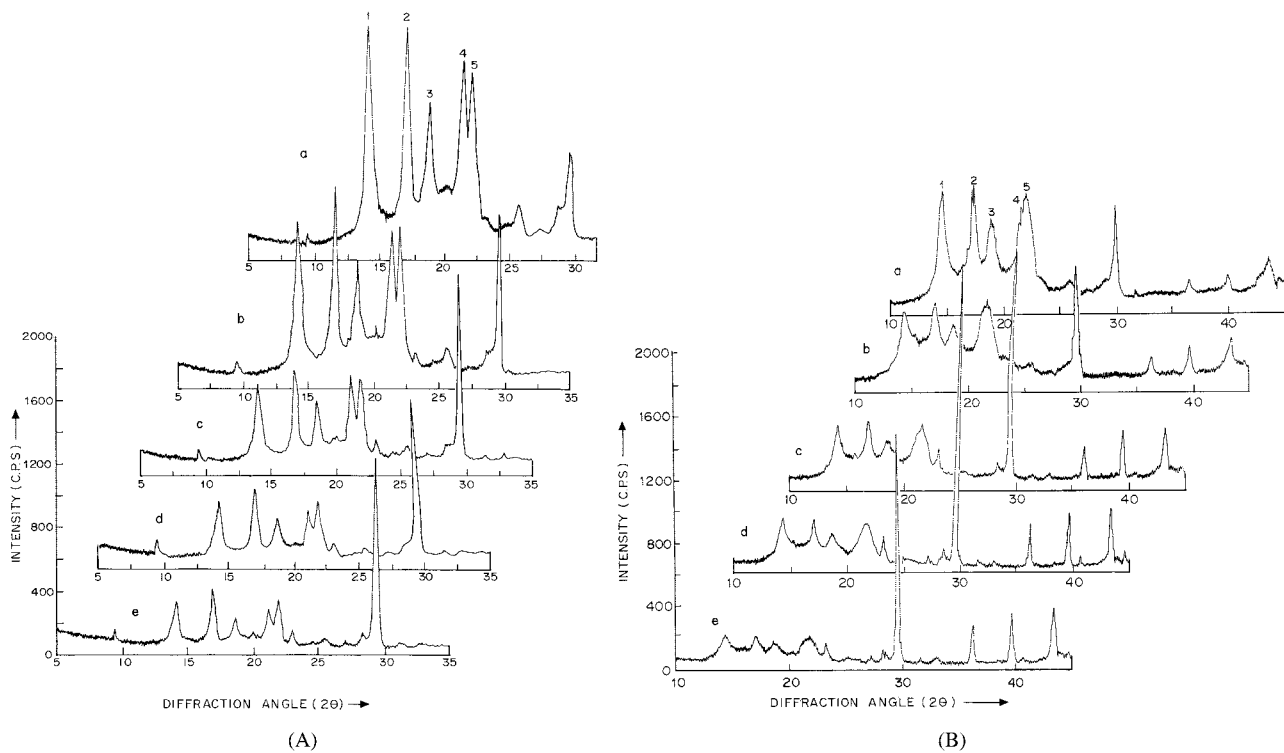


Figure 4 XRD scans of PP containing calcium carbonate at various concentrations (0–40 wt %). (A) corresponds to program cooling while (B) corresponds to quenching. Curves (a) 5%, (b) 10%, (c) 20%, (d) 30%, and (e) 40% of calcium carbonate (CC), respectively.

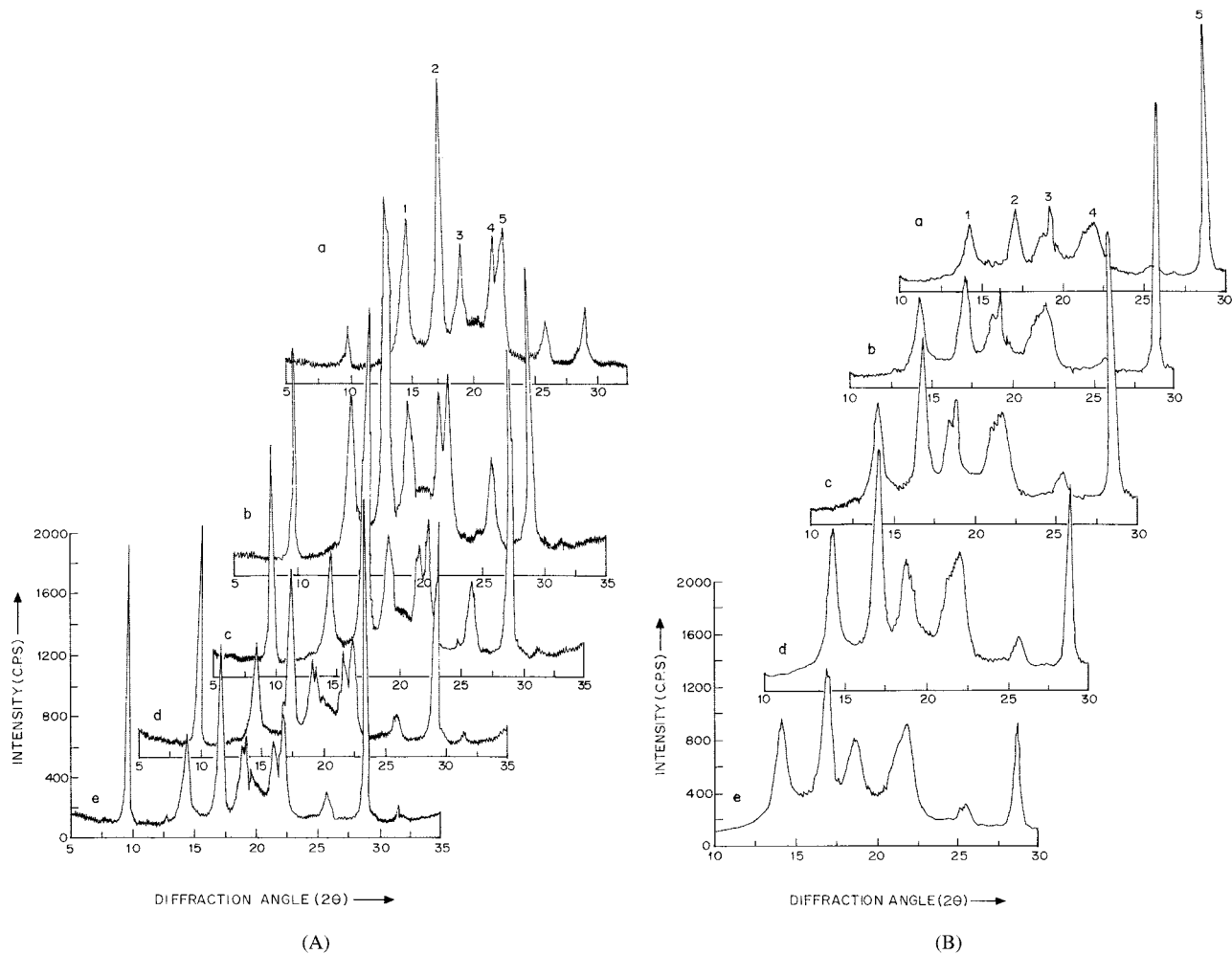


Figure 5 XRD scans of PP containing talc at various concentrations (0–40 wt %). (A) corresponds to program cooling while (B) corresponds to quenching. Curves (a) 5%, (b) 10%, (c) 20%, (d) 30%, and (e) 40% of talc (TC), respectively.

more by the thermal conductivity. It may be mentioned here that although the cooling method used in the latter cases may be the same, the actual temperature drop with time depended on the composi-

TABLE II
Degree of Crystallinity of PP and PP Containing Various Silica Contents

Method of cooling	Crystallinity values for PP with silica					
	Silica content (wt %) in PP					
	0	5	10	20	30	40
A	69	69	71	63	57	62
B	68	66	69	62	55	54
C	67	65	63	61	54	52
D	64	55	52	48	46	43

A, Programmed cooling; B, self-cooling (air); C, water circulation in molds; D, quenching.

tion of the sample, which was measured and used for the cooling rate graph. Also, the data in Table II indicate that the degree of crystallinity decreased with increasing silica content and high cooling rate, which is clearly in keeping with the above hypothesis.

From the XRD scans (Figs. 3–5), it appears that distinct peaks in the 2θ range of $5\text{--}30^\circ$ occur in all cases, which suggests that the crystalline phase is mainly α -phase. However, the difference occurs in the relative intensities of the peaks, especially the intensity of peak 2 (040 plane reflection), which increases considerably as the silica content increases for the same cooling rate. The ratio of the intensity of the peak 2 [$2\theta = 17.2^\circ$, (040) plane reflection] to that of peak 1 [$2\theta = 14.5^\circ$, (110) plane reflection] was determined from the XRD scans and presented in Table III as a function of composition/thermal conductivity. It is interesting to note that for the same

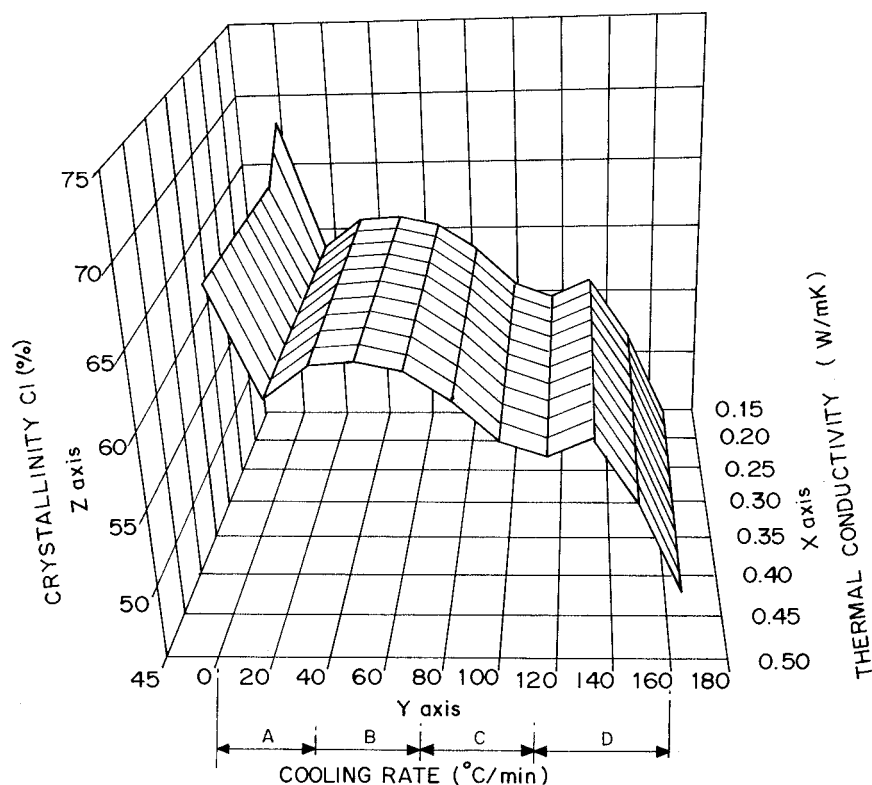


Figure 6 Degree of crystallinity as a function of cooling rate as well as thermal conductivity value for PP containing silica at various concentrations (0–40 wt %).

cooling rate, the intensity ratio of the peak 2 with respect to peak 1 decreases with an increase in thermal conductivity (silica content) and for the same silica concentration, it changes in the complex manner with cooling rate. This change in the intensity of peak 2 for the same silica concentration and different cooling rates in the latter case can be due to faster crystallization rate and higher cooling rate. These variations are more clearly seen in a 3D map of peak intensity ratio (P_2/P_1) with respect to cooling

rate as well as thermal conductivity (silica content), as shown in Figure 7. The effect of cooling rate as well as thermal conductivity on C_i clearly indicates in some cases the nucleation effects of the additive. These also affect the intensity ratios of the peaks, indicating that certain crystallographic planes (040) get developed preferentially in the presence of the additive. The preferential orientation of the b -axis (or the 040 reflection intensity) has been reported for talc-filled PP by other authors also.^{16–18}

TABLE III
Effect of Thermal Conductivity on Intensity Ratio for XRD Peaks (P_2/P_1) of PP Containing Various Silica Concentrations

Silica (wt %)	Thermal conductivity (W/mK)	Intensity ratio (P_2/P_1)			
		Method of cooling used			
		A	B	C	D
0	0.23	1.21	1.33	1.35	1.09
5	0.208	1.05	0.98	1.01	1.04
10	0.228	1.03	0.94	0.90	1.08
20	0.28	0.93	0.93	0.94	0.96
30	0.35	0.90	0.97	0.87	1.04
40	0.45	0.87	0.86	0.82	0.95

A, Programmed cooling; B, self-cooling (air); C, Water circulation in moulds; D, quenching.

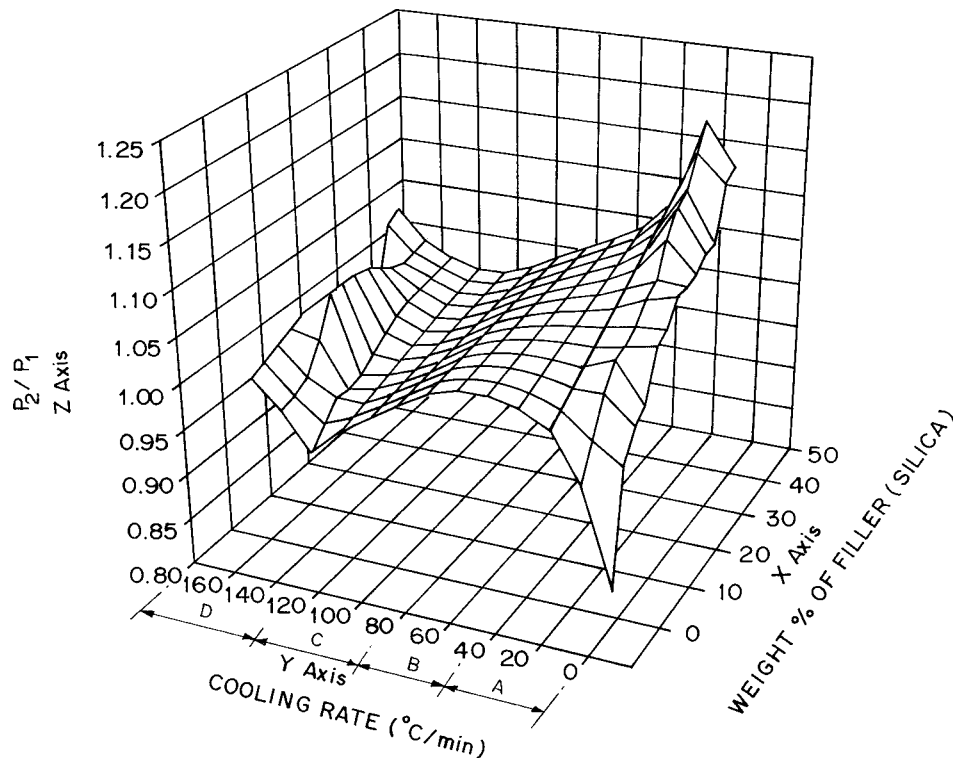


Figure 7 Variation of intensity ratio for XRD peaks on cooling rate at various concentrations of silica in PP.

Morphological features

The fast cooling rate at the polymer–mold wall interface leads to different crystallization rate, crystallinity, and hence, formation of a skin layer which is distinct from the bulk of the sample. This type of skin-core morphology is evident in these sheets molded from PP containing different fillers. The skin layer thickness was measured for all the samples by taking a cross section and observing under reflection mode with a cross-polarized microscope. The variation of skin layer thickness with increasing filler concentration is shown in Figure 8 for three fillers. In all cases, it is evident that the skin layer thickness increases up to a certain filler concentration and then attains a constant value of about $70\ \mu\text{m}$ for a sample of about $1.0\ \text{mm}$ thickness. Thus, higher thermal conductivity of the composite leads to large heat transfer and faster cooling rate near the melt surface in contact with the mold wall giving higher skin layers than the original polymer. It may be mentioned that similar observations have been reported in other studies for PP injection-molded samples^{19–21} but no clear explanation has been given by the authors. Their results can now be explained by taking into account the thermal conductivity and the factors affecting heat transfer/cooling rate for the different fillers presented here.

CONCLUSION

The crystallization, structure, and morphology of PP filled with different fillers were investigated to study the effect of thermal conductivity of the filler and/or the composite on the same. The results suggested that the degree of crystallinity was significantly affected by thermal conductivity of the filler, concentration, and cooling rate. It was also observed that the higher the thermal conductivity of filler, the faster the cooling rate will be and the lower will be the crystallinity value. Thus, the degree of crystallinity of the polymer decreased with an increase in thermal conductivity and cooling rate. This also affects the skin-core type of morphology obtained in the molded product: the skin layer thickness depends on the concentration and type of filler present in PP. It may be mentioned here that this can in turn affect the surface-related properties such as hardness, gloss, wettability, etc. The present investigation thus clearly brings out the important role of heat transfer and thermal conductivity in polymer melt processing. The present data clearly suggest that it would be essential to control the cooling rate accurately in each case of additive so as to obtain a good product having better properties.

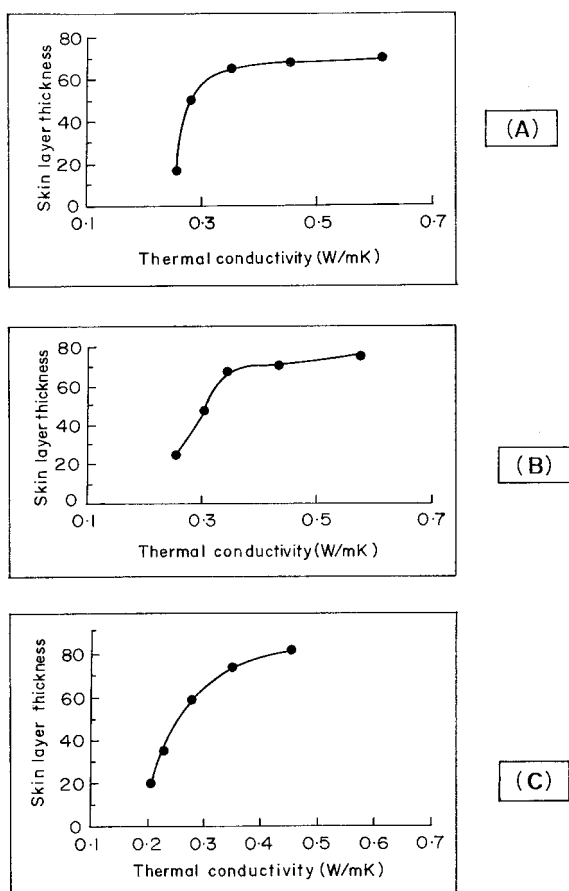


Figure 8 The variation of skin layer thickness of compression-molded PP containing different amounts of fillers. The graphs correspond to (A) silica, (B) calcium carbonate, and (C) talc, respectively.

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