

Effect of β -Phase Nucleating Additives on Structure and Properties of Blow Extruded Polypropylene

S. RADHAKRISHNAN,¹ M. TAPALE,² N. SHAH,² E. RAIRKAR,² V. SHIRODKAR,² H. P. NATU²

¹Polymer Science and Engineering, National Chemical Laboratory, Pune 411008

²Department of Polymer Engineering, Maharashtra Institute of Technology, Pune 411004, India

Received June 27, 1996; accepted June 28, 1996

ABSTRACT: The structure development and mechanical properties of blow extruded polypropylene containing β -phase nucleating additives was studied. Quinacridone red and cadmium red were both found to nucleate the β phase in polypropylene, the former being a much more efficient nucleator than the latter. The β -phase spherulites formed in the presence of these nucleating agents were small and extensively volume filled, yielding high crystallinity. The modulus increased 2–3 times, elongation at break decreased, and there was a sharp break point without much yield when the β -phase nucleating agents were added as compared to the pure α -phase polypropylene. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 1247–1253, 1997

INTRODUCTION

The enhancement of properties of commodity plastics by modification of structure, orientation, and morphology has received considerable attention in recent years.^{1–4} In this context polypropylene (PP) has been studied extensively and a couple of new high crystallinity grades were introduced recently.^{5,6} Many of the earlier studies reported isothermal crystallization of PP under laboratory conditions, but very few are available on the structure development during extrusion blow molding. Although, pigments and coloring agents are routinely added to the PP films, their effect on the crystalline structure has not been studied in detail. Some authors reported that pigments such as quinacridone red (QR) can preferentially nucleate the β phase in PP.^{7,8} However, the effect of such additives on the properties of blow extruded PP films has not been reported before. In view of the large changes expected in the

properties when changing the crystalline structure, it was interesting to study the effect of β -phase nucleating additives on the structure development and properties of PP films. The results of these studies are described in the present article.

EXPERIMENTAL

To study the crystallization behavior of PP in the presence of nucleating agents for the β phase, the PP (grade SM85N, IPCL, Baroda) was first precipitated in powder form by dropping its xylene solution into acetone and subsequently filtering and drying the same in a vacuum (10^{-2} torr) for 24 h. This pure powder was then mixed with the desired amount of nucleating additives. Two pigments, QR (CI 46500, Lona Industries, India) and cadmium red (CR, Hoechts, Colour Chem, India) were used as the nucleating agents of the β phase in PP. The additive and the polymer powder were thoroughly mixed in an agate pestle mortar until uniform coloration was obtained. The isothermal crystallization of these compositions was studied

Correspondence to: S. Radhakrishnan.

© 1997 John Wiley & Sons, Inc. CCC 0021-8995/97/071247-07

by observing the spherulitic growth in the melt that was kept under the hot stage of a polarizing microscope. The blow extruded films were made in the same manner as described elsewhere⁹ using the film extruder (Kolsite Machine Fabrik) set at the following conditions: feed zone 180°C, melt zone 200°C, L/D 20, die diameter 50 mm, cooling ring diameter 23 cm, and take-up speed of 12.5 cm/s. The exact concentration of the pigment in the extruded films was determined by comparison of their optical absorption spectra with that of a standard solution of the same pigment (10^{-3} mol in cyclohexanone/toluene). The tensile properties of the films were measured in the machine as well as in transverse direction of extrusion by a standard technique (ASTM D638-89) with the help of an Instron Series IX automated material testing system 1.04. The structure and morphology were characterized in the same manner as reported earlier.^{9,10}

RESULTS AND DISCUSSION

The effect of the CR and QR additives on the crystalline phase was first investigated by wide angle X-ray diffraction (WAXD). Figure 1 shows the WAXD scans for (A) pure PP and that containing (B) 10% CR and (C) 2% QR, respectively. All these samples were subjected to the same isothermal crystallization conditions; melt temperature 180°C, crystallization temperature 110°C, and crystallization time 20 min. It is clearly seen from these WAXD scans that for pure PP there are a number of sharp peaks while that for PP with QR and CR additives consists mainly of two strong peaks. A detailed analysis of these is given in Table I, which indicates the interplanar spacings (d values) for the observed scans together with those reported for the α and β phases. The comparison of the various values indicates that pure PP crystallizes in the α form, that containing CR has $\alpha + \beta$ mixed phases, and PP with QR is almost wholly the β phase. The fraction of the β phase present in the PP sample was determined by taking the ratio of the intensities¹¹ of the main β_{300} peak ($d = 5.51 \text{ \AA}$) to that of α_{110} peak ($d = 6.54 \text{ \AA}$) as $I(\beta)/[I(\beta) + I(\alpha)]$. Figure 2 shows the variation of the β -phase content with the concentration of the additives. It is seen from this figure that in the case of CR, the β -phase content increases gradually with the increase of CR concentration up to about 10% and then decreases slightly with the further increased concentration

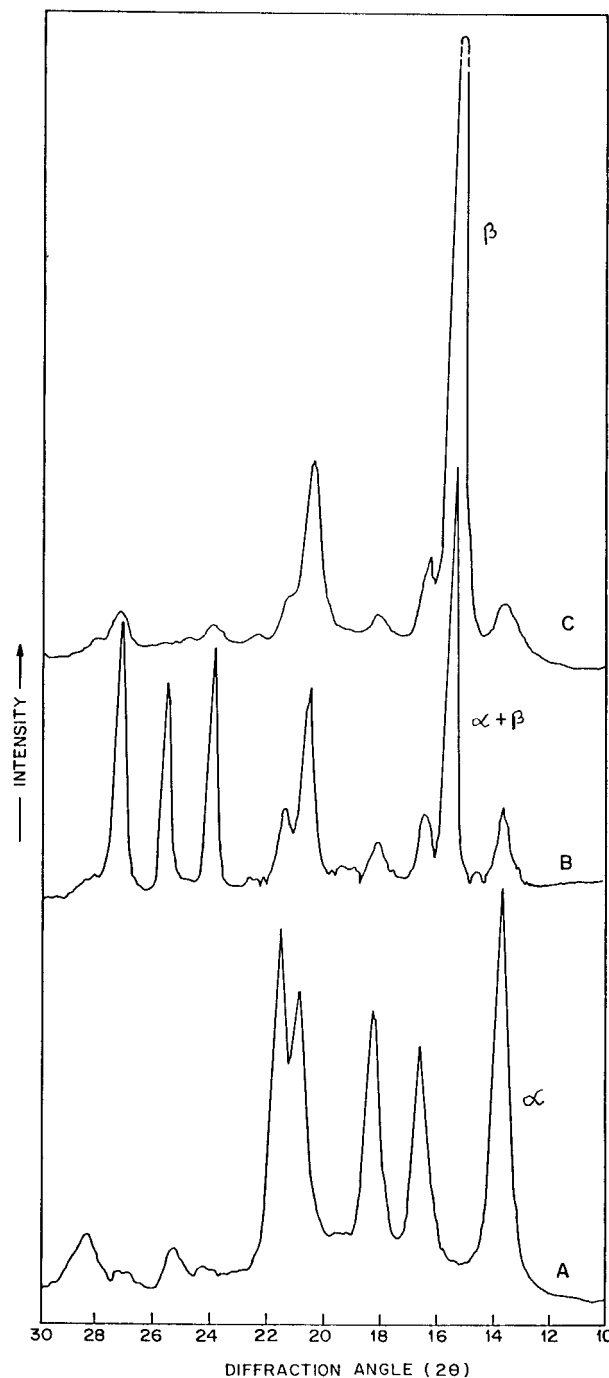


Figure 1 The wide angle diffraction scans for polypropylene isothermally crystallized at 110°C: (A) pure PP, (B) with 10% cadmium red, and (C) with 2% quinacridone red nucleating agent.

of the additive. On the other hand, in the case of QR, the β -phase content increases very sharply, even for a low concentration of QR, and remains at the high value (90% of total) for higher concentrations of QR. These findings clearly suggest that

Table I X-ray Diffraction Analysis of β -Phase Nucleated PP

PP + QR (2%)		PP + CR (10%)		β -Phase PP			α -Phase PP		
d	I/I_0	d	I/I_0	d	I/I_0	hkl	d	I/I_0	hkl
		6.32	16				6.34	100	110
6.2	7	6.2	5	6.25	5	210			
5.48	100	5.48	100	5.56	100	300			
							5.32	70	040
5.20	10	5.28	25	5.24	7	220			
							4.84	56	130
4.6	6	4.78	19	4.6	5	310			
4.17	25	4.18	51	4.25	28	301	4.25	40	131
		4.08	25				4.10	58	041
3.57	7			3.56	4	410	3.5	20	060
3.08	4			3.13	5	330	3.1	8	220

CR and QR are both good nucleating agents for the β phase and QR is a much more efficient nucleator than the CR pigment. The slight decrease in the β -phase content at higher loading of the additive could be due to the aggregation of the pigment particles leading to lower surface area and/or effective number of available sites for nucleation of the particular phase. It is thus seen that CR and QR pigment nucleate the β phase giving at least 70% of this type of crystals in the PP.

The morphology of the β -phase nucleated PP was also found to be distinctly different from that of the α phase as revealed by optical polarizing microscopy. Figure 3 indicates the typical optical micrographs obtained for pure PP and PP containing the β -phase nucleating agents, the crystallization conditions being the same in both cases. It is seen that pure PP exhibits mainly

large spherulites (50–100 μm in diameter), but in the PP containing CR the morphology consisted of a few small spherulites interspersed with large spherulites. The small spherulites had distinctly different internal morphology and more brightness (higher birefringence) than the normal large ones. On the other hand the PP containing QR showed extensive volume filling, small sized spherulites that developed within a very short time of crystallization [see Fig. 3(c)]. The isothermal crystallization of PP containing these additives was studied by observing the spherulitic growth at constant temperature (110°C). The crystallization half-time was derived from these data (figures not given) and it was less than 5 s for PP with QR as compared to 100 s for PP with CR and 250 s for pure PP. The comparison of the large change in morphology between pure PP and the β -phase nucleated PP is made in Fig. 3(c) which shows the optical polarizing micrograph of the sample containing pure PP on one side and PP with QR (1%) on the other. The slide was subjected to identical crystallization procedures. The marked difference in the morphology in the two cases is quite evident.

The blow extruded films of PP with the CR and QR nucleating agents were also analyzed for the structure and morphology as above. Their WAXD scans were similar to those in Fig. 1(b), and hence one can conclude that they contained predominantly the β phase. Optical polarizing microscopy revealed (see Fig. 4) that these films had an extensive number of densely placed small spherulites (3–4 μm) as compared to much bigger ones noted for pure PP films (15–20 μm).

The mechanical properties of the blow extruded

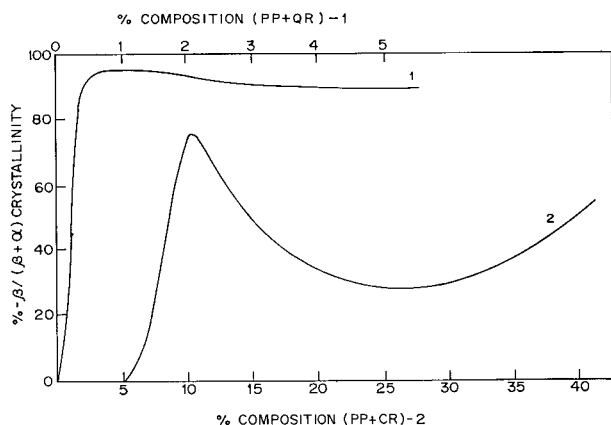


Figure 2 The β -phase content in polypropylene nucleated with (curve 1) quinacridone red and (curve 2) cadmium red with respect to composition.

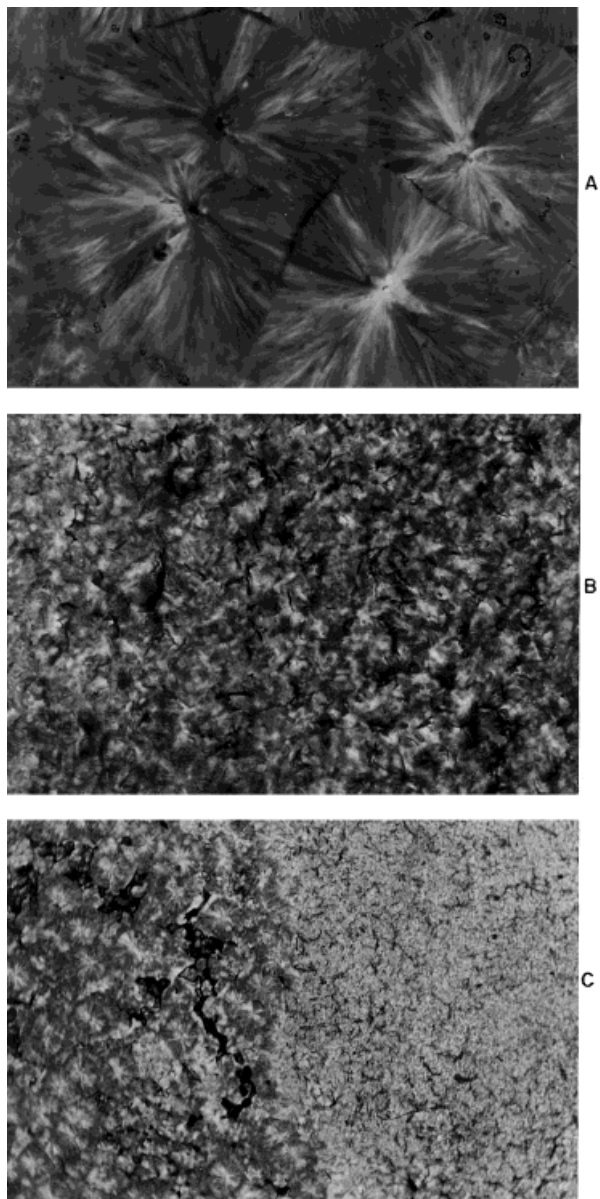
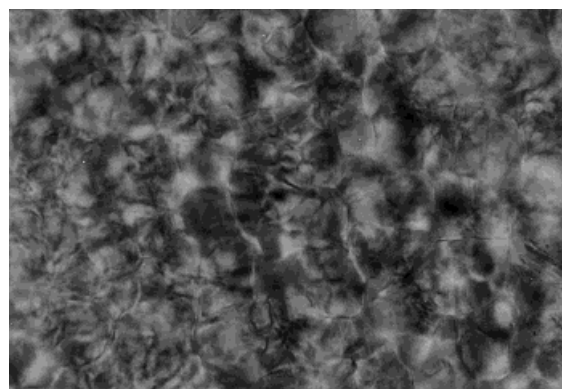


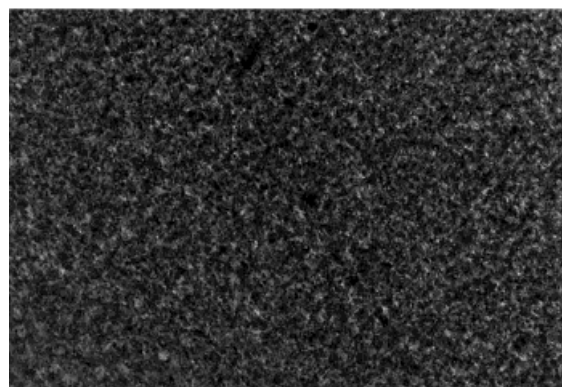
Figure 3 The optical polarizing micrographs for isothermally crystallized polypropylene: (A) pure PP with α phase, (B) with β phase, and (C) same slide containing half portion nucleated with β phase (right side) indicating extensive nucleation. Original magnification for (A, B) $\times 600$ and (C) 150.

films were measured in two major directions by using samples cut out with the long direction parallel and perpendicular to the machine axis. The typical load–displacement curves obtained for these films with different concentrations of the nucleating agent are indicated in Fig. 5(a–d). The various values such as tensile modulus, stress at break, elongation at break etc., derived from these curves are indicated in Table II. It is seen

from the comparison of the curves and the different values in Table II that whereas pure PP films exhibit well-defined yield points with large elongation at break, that for the PP films containing β -phase nucleating agents exhibit a sharp break point, low elongation at break, and high modulus values. In the latter case, the films are much stiffer to handle than the former. These various changes can be attributed to the development of the β phase in the films. It may be noted that α phase has a monoclinic structure with lattice parameters of $a = 6.66 \text{ \AA}$, $b = 20.78 \text{ \AA}$, $c = 6.49 \text{ \AA}$, and angle $\beta = 99.6^\circ$; the β phase of PP has a pseudohexagonal structure with lattice parameters of $a = 12.47 \text{ \AA}$ and $c = 6.35 \text{ \AA}$.^{12–14} In the latter case the chains are packed in much closer configuration than the former and hence more dif-



A



B

Figure 4 The optical polarizing micrographs for blow extruded polypropylene: (A) without the nucleating agent and (B) with β -phase nucleating agent. Original magnification $\times 600$.

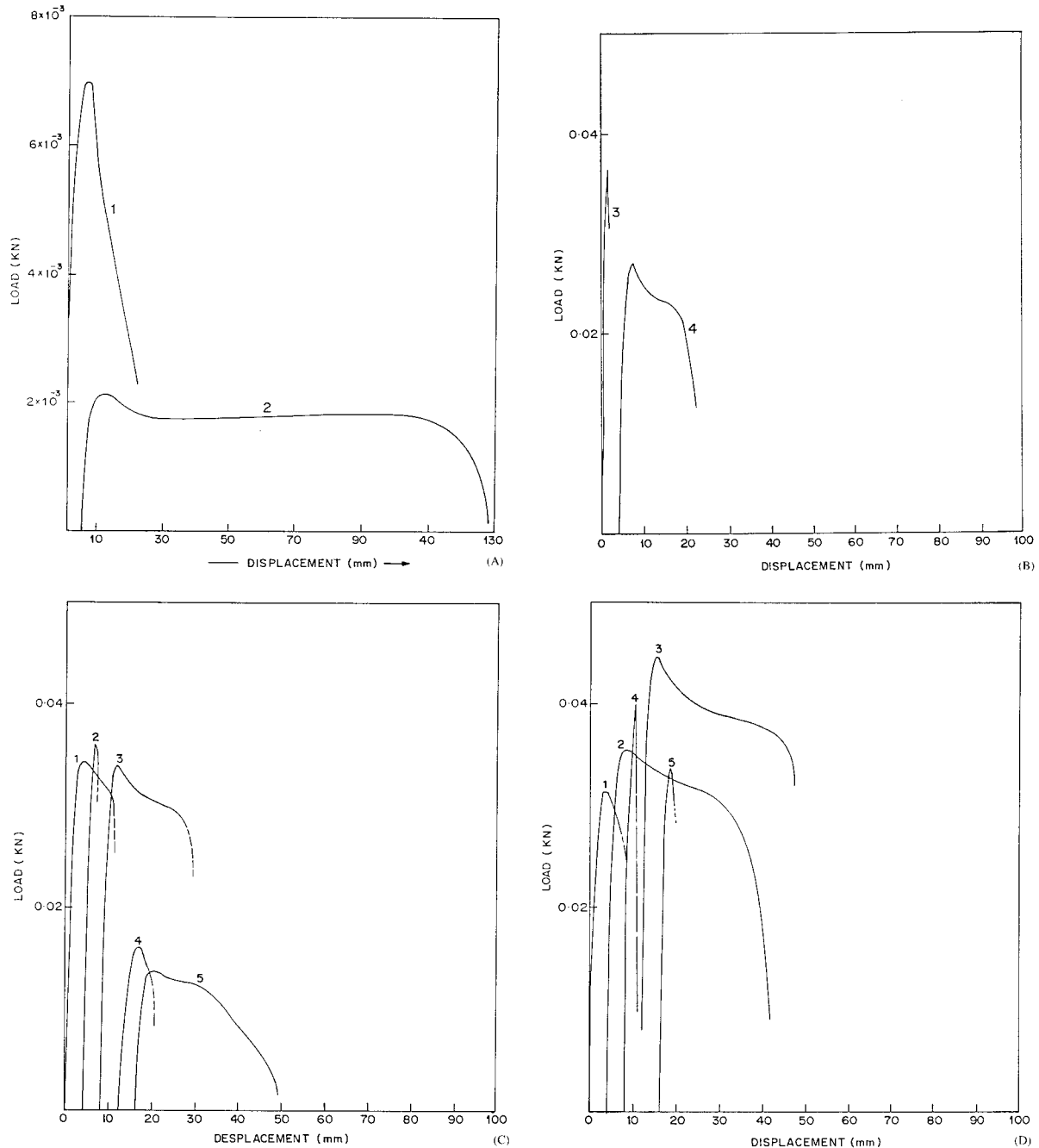


Figure 5 The stress-strain curves for blow extruded polypropylene containing different amounts of quinacridone: curves (A) 1 and 2 correspond to 0% and (B) 3 and 4 to 0.6% in the machine, and transverse direction. Curves in (C) correspond to 0.2, 1.0, 1.5, 2.0, and 4.1%, respectively, in the transverse and (D) the same in machine direction.

difficult to displace the same. The spherulites in the β phase are also smaller and extensively packed with higher crystallinity, which makes the films stiffer, giving much higher modulus as observed by us. It is also interesting to note that the elongation at break for the β -phase nucleated films is

much smaller (less than 20%) as compared to the PP containing predominantly the α phase (more than 200%). Further, this value is much lower in the transverse direction than the machine direction, suggesting that the chain/crystallite axis is oriented more in the machine direction than nor-

Table II Mechanical Properties of β -Phase Nucleated PP

Sample No.	QR%	Displ.	Strain	Load at	Stress	Displ.	Strain	Stress	Modulus (MPa)
		at Peak (mm)	at Peak (%)	Peak (kN)	at Peak (MPa)	at Break (mm)	at Break (%)	at Break (MPa)	
1	0.0 T	5.14	8.56	0.0075	12.5	24	41	8.0	400
	M	5.6	9.33	0.0072	12.1	20	33	4.5	607
2	0.2 T	4.89	8.15	0.041	25.1	26	43	12.7	1210
	M	3.49	5.81	0.042	26.01	4.02	6.7	24.3	951
3	0.6 T	3.93	6.55	0.034	18.94	20	34	15.4	899
	M	2.74	4.57	0.036	20.16	2.34	4.7	19.7	1008
4	1.5 T	3.51	5.85	0.027	14.9	18	29	8.1	805
	M	1.89	3.15	0.037	20.3	1.8	3.1	20.1	1208
5	4.1 T	4.1	6.7	0.045	27.8	35	58	21.3	1211
	M	2.4	4.1	0.041	25.01	2.0	4.1	25.1	1361

T, transverse direction; M, machine direction.

mal to it.^{15,16} It may be mentioned that the β -phase nucleated PP films show a sharp rupture edge while those with the α phase tend to show fibrillation at the rupture surface. These differences in the properties of the films can be associated with the higher crystallinity, closer chain packing, and orientation of the crystallites in these films.

SUMMARY AND CONCLUSION

The crystallization behavior, morphology, and mechanical properties of PP blow extruded films containing CR and QR were investigated. The QR was found to be a very efficient nucleating agent for the β -type crystalline phase in PP, which was confirmed by the WAXD studies. The CR pigment gave a maximum β -phase content of about 70% at an additive concentration of about 10% while much higher β contents (90%) were obtained for QR, even at a low additive concentration of 2%. The morphology of the β -phase nucleated PP consisted of a large number of small sized spherulites in comparison to the large size of the spherulites observed for pure PP. The crystallization half-time for the β -phase nucleated PP was much smaller (5 s) than that for pure PP (200 s) when subjected to isothermal crystallization at 110°C. The blow extruded films containing the β -phase nucleators had much higher modulus values, little elongation, and sharper break point as compared to the pure PP films.

The above studies clearly highlight out the importance of the nucleating efficiency of different

pigments added to semicrystalline polymers, especially those having polymorphism. These in turn can bring about large changes in the properties due to modification of the crystalline phase and morphology. Hence, one would have to make a judicious choice of the pigments to be added to polymers. Although they may have the same tinting capacity, the properties obtained in the product after compounding them with polymers can differ considerably due to preferential nucleation of certain crystalline phases.

The authors wish to thank the director, National Chemical Laboratory and Prof. M. V. Joshi, Head, Polymer Engineering, Maharashtra Institute of Technology, Pune for encouraging this collaborative work. The financial support from the Department of Science & Technology, New Delhi is gratefully acknowledged.

REFERENCES

1. A. E. Zachradias and R. S. Porter, *High Modulus Polymers*, Marcel Dekker, New York, 1988.
2. G. Gruenewald, *Plastics—How Structure Determines Properties*, Hanser Verlag Publ., Munich, 1993.
3. J. Varga, *J. Polym. Eng.*, **1**, 231 (1991).
4. J. Krager-Kocsis, *Polypropylene—Structure Blend and Composites*, Vol. 1, Chapman & Hall, London, 1995.
5. J. H. Schut, *Plast. Technol.*, **27**, 31 (1991).
6. P. Mapleston, *Mod. Plast. Int.*, **March**, 48 (1995).

7. J. Varga and F. Toth, *Makromol. Chem. Makromol Symp.*, **5**, 213 (1986).
8. G. Shi, F. Chu, G. Zhou, and Z. Han, *Makromol. Chem.*, **190**, 907 (1989).
9. S. Radhakrishnan, K. Kane, A. Kadu, and H. P. Natu, *J. Appl. Polym. Sci.*, **58**, 571 (1995).
10. S. Radhakrishnan and J. M. Schultz, *J. Cryst. Growth*, **116**, 378 (1992).
11. P. Jacoby, B. H. Bersted, W. J. Kissel, and C. E. Smith, *J. Polym. Sci.*, **B24**, 461 (1986).
12. P. Corridini and G. Guerra, *Adv. Polym. Sci.*, **100**, 185 (1992).
13. S. Bruckner, S. V. Meille, V. Petraconi, and B. Pizzori, *Progr. Polym. Sci.*, **16**, 361 (1991).
14. S. Z. D. Cheng, J. J. Jaminak, and J. Rodriguez, in *Polypropylene Structure Blend and Composite*, Vol. 1, J. Krager-Kocsis, Ed., Chapman & Hall, London, 1995, p. 31.
15. P. M. Hay in *Science & Technology of Polymer Films*, Vol. 1, O. J. Sweeting, Ed., Interscience Publ., New York, 1968.
16. I. M. Ward, *Structure and Properties of Oriented Polymers*, Applied Science Publ., London, 1975, p. 27.