Structure Development in Processing of Polypropylene Films with Additives

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SYNOPSIS

The crystallization behavior, modification of crystalline form, and orientation in polypropylene processed by blow film extrusion was studied as a function of processing parameters as well as different types of additives. The isothermal crystallization rate was greatly enhanced in the presence of certain additives, especially $CaCO_3$. The crystalline form was predominantly α type in both compression molded or blow extruded films. However, there was an unusually large intensity of the α_{040} peak in the X-ray diffraction of the latter case films. The variation of the peak intensities and the increase of birefringence with increase of take-up speed has been explained on the basis of orientation induced by uniaxial stress in the machine direction. This orientation contained two components, namely the orientation of the b axis of the crystallites and the orientation of loosely bound polymer chains in the amorphous regions. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Structure development in polymers has recently received considerable attention because of potential use in enhancing the properties of commodity plastics to such an extent that these could be made equivalent to other engineering polymers.[1-4] In this respect polypropylene (PP) has been studied extensively and its crystallization behavior with a number of nucleating agents has been well documented.[5-9] Most of these studies report isothermal crystallization of PP under laboratory conditions using differential scanning calorimetry or optical microscopy. There are some reports available on the structure development of PP during melt processing such as injection molding and melt spinning that give the effect of processing parameters on the orientation factors. Although pigments and coloring agents are routinely added to PP films used in articles such as food packaging, carryall bags, etc., their effect on the crystallization behavior and in turn the mechanical strength, elongation, etc., has not been reported in detail earlier. Some pigments are known to preferentially nucleate the β form in PP.[10,11] In view of this, the structure development in PP processed by blow film extrusion and the effect of additives on the same were studied and are described in the present article.

EXPERIMENTAL

To study the effect of additives on crystallization behavior, PP (Grade SM85N) was first precipitated in the form of fine powder by dropping its xylene solution into acetone and subsequently drying the same in a vacuum (10^{-2} torr) for 24 h at 40°C. This powder was then mixed with the required quantity of additive in a mortar and pestle with a small quantity of methanol in order to facilitate better dispersion. The mixed powder was further dried for 5 h. The crystallization behavior was studied by first melting the powder with additives at 190°C on microscopic glass slides on a thermostatted hot plate and quickly transferring the same to the hot stage of a microscope preset to the crystallization temperature. The spherulitic growth was recorded with

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Table I Characteristics of Materials Used

Material	Grade	Manufacturer/Supplier	Remarks
Polypropylene	SM85N	Indian Petrochemicals Ltd., Baroda, India	MFI 19.5
$CaCO_3$	Commercial	Sarabhai Chemicals Ltd., India	Fine powder, particle size, 2.5 μm
Lab-$CaCO_3$	Lab synthesized	Laboratory	Pure, particle size, 5 μm
Silica	Minusil	Pennsylvania Glass & Sand Corp. USA	Particle size, 5 μm
Phthalocyanine Blue	Pigment	Amar Dye Chem Pvt. Ltd. Bombay, India	Particle size, 1 μm

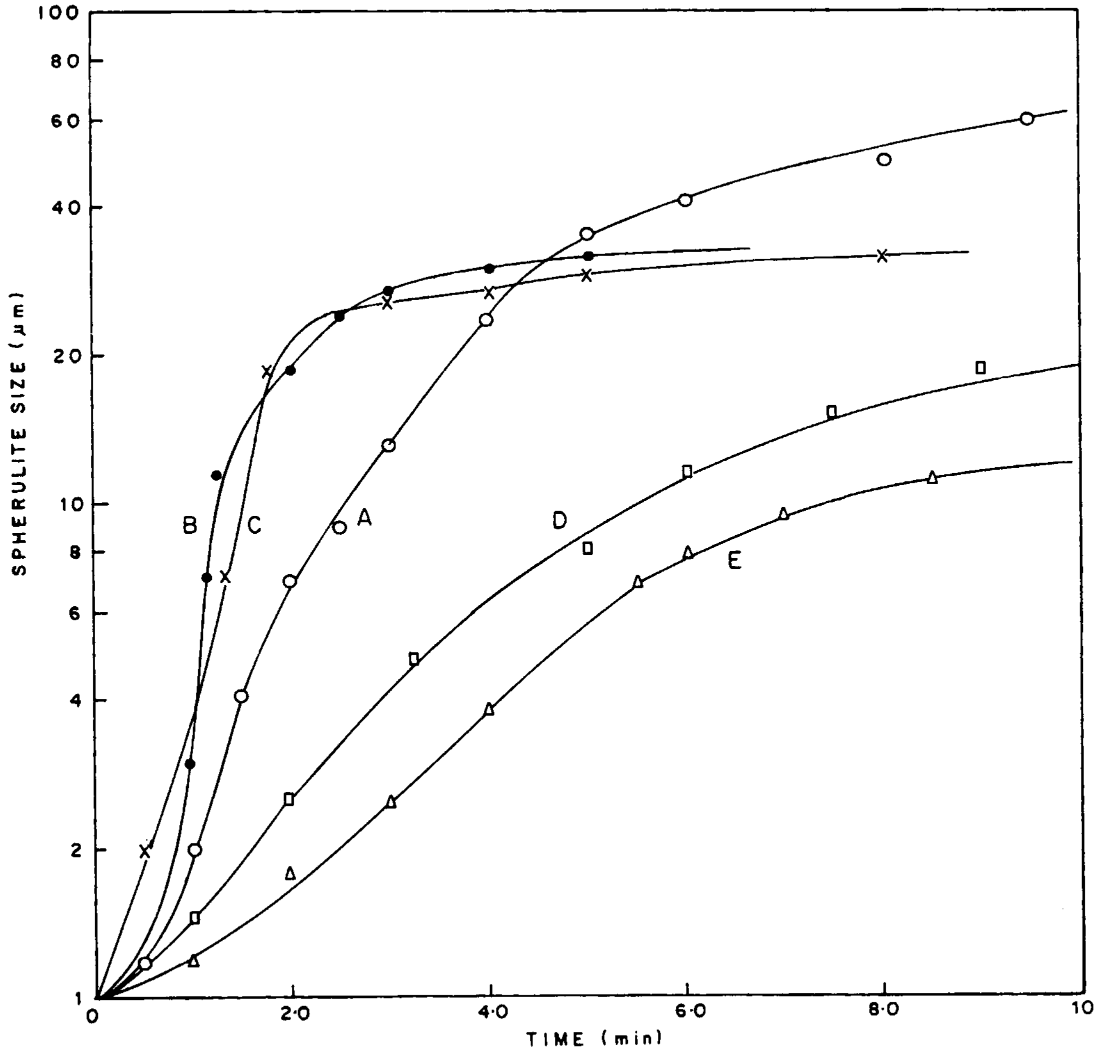

Figure 1 Isothermal crystallization of PP with additives at 110°C. Curves correspond to (A) original PP, (B) with commercial $CaCO_3$, (C) with lab-$CaCO_3$, (D) silica, and (E) phthalocyanine pigment.

Table II Film Extrusion Conditions

Take-up Speed[a] (cm/s)	Elongation Ratio[b]	Blow Ratio[c]
9.5	3.1	3.85
12.5	4.1	3.85
15.0	5.1	3.85
16.0	5.6	3.85
18.0	6.2	3.85
20.0	6.5	3.85

[a] Feed zone temp., 180°C; screw speed, 40 rpm.
[b] Melt zone temp., 200°C; *L/D*, 20.
[c] Die temp., 210°C, Die dia., 50 mm.

respect to time, temperature, and different types of additive. The material characteristics are given in Table I.

The large quantity of polymer required for blow film extrusion was compounded with 2% filler in a single screw extruder; the extrudate was quenched in water, cut, dried, and fed to the blow film extruder. The film extruder (Kolsite Machine Fabr.) was set to following conditions: feed zone temperature 180°C, melt zone 200°C, die temperature 210°C, screw speed 40 rpm, *L/D* 20, die diameter 50 mm, cooling ring diameter 23 cm, air pressure 1.2 kg/cm^2. The take speed was varied by changing the rpm of the take-up rollers and was varied from 8 to 21 cm/s. The blow ratio was kept constant at 3.85. The elongation obtained, the increase of take-up speed, and other details are given Table II.

The structure and morphology of the films were studied by wide angle X-ray diffraction (WAXD) and optical microscopy in the same manner as reported earlier.[12-14]

RESULTS AND DISCUSSION

The crystallization behavior was studied from the growth rate of spherulites as shown in Figure 1 for PP with and without additives. It is seen that there is a large change in the rate of crystallization in the presence of additives (0.5–2.0% w/w). The crystallization half-time ($t_{1/2}$) as well as the induction time for onset of rapid growth, decreased from 150 and 250 s in pure PP to 60 and 90 s, respectively, in the presence of additives, especially $CaCO_3$ (see curves B and C). It is interesting to note that spherulitic dimensions are reduced considerably in the presence of silica and phthalocyanine pigment (see curves D and E), which may be due to two factors: high nucleation efficiency of these materials giving rise to a large number of spherulites being simul-

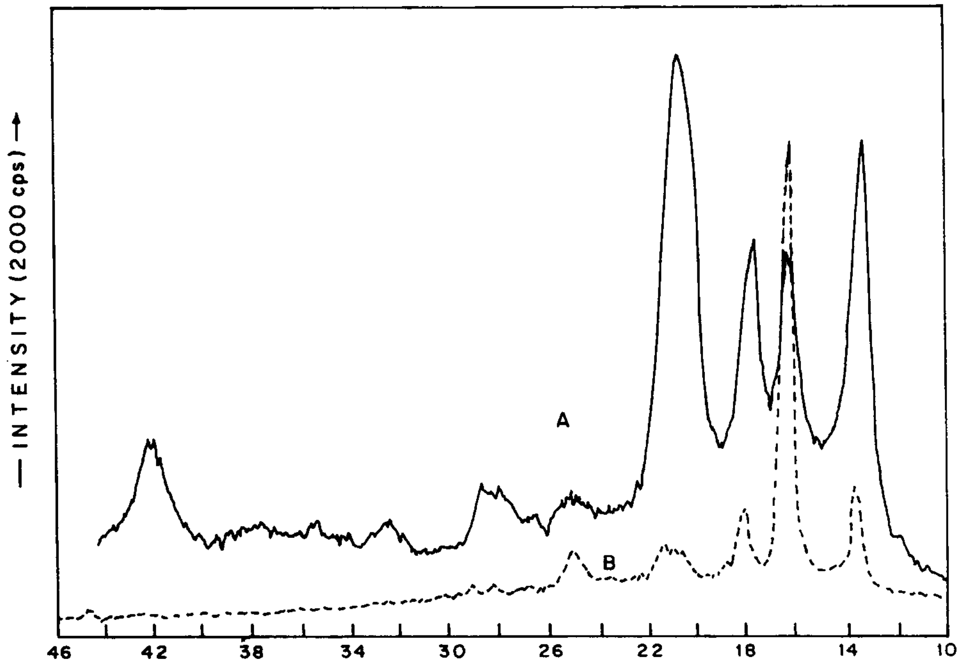

Figure 2 X-Ray diffraction scans for PP samples after (A) compression molding and (B) blow film extrusion.

Table III Wide Angle X-Ray Diffraction in Polypropylene Processed by Different Techniques

Blow Extruded Film		Compression Molded Disk		α-PP[18]		β-PP[19]	
d (Å)	I/I_o	d (Å)	(I/I_o)	d (Å)	I/I_o	d (Å)	(I/I_o)
6.46	25	6.41	82	6.34	100	6.25	5
5.35	100	5.27	66	5.32	70	5.56	100
4.90	25	4.87	63	4.84	56	5.24	7
4.23	14	4.27	100	4.25	40	4.60	5
						4.25	28
4.15	18	4.15	13	4.10	58	3.79	7
3.53	14	3.49	7	3.50	20	3.56	4
3.16	5	3.3	17				
2.94	3	3.07	17	3.10	8	3.13	5
2.26	3		10				
2.04	4	2.13	25	2.11	10		

taneously formed that subsequently collide, and nucleation of another crystalline phase that has different spherulitic morphology as compared to normal PP.[15,16] The WAXD studies were carried out in order to differentiate these various factors.

The blow extruded films exhibited most interesting results when examined by WAXD. Figure 2 shows the comparison of WAXD patterns obtained for PP without additives after (A) compression molding (B) and blow extrusion. The marked differences in the two cases are quite evident. However, there are some noteworthy features to be observed: the peak positions in both the cases remain more or less same; the intensity of the peak occurring at the

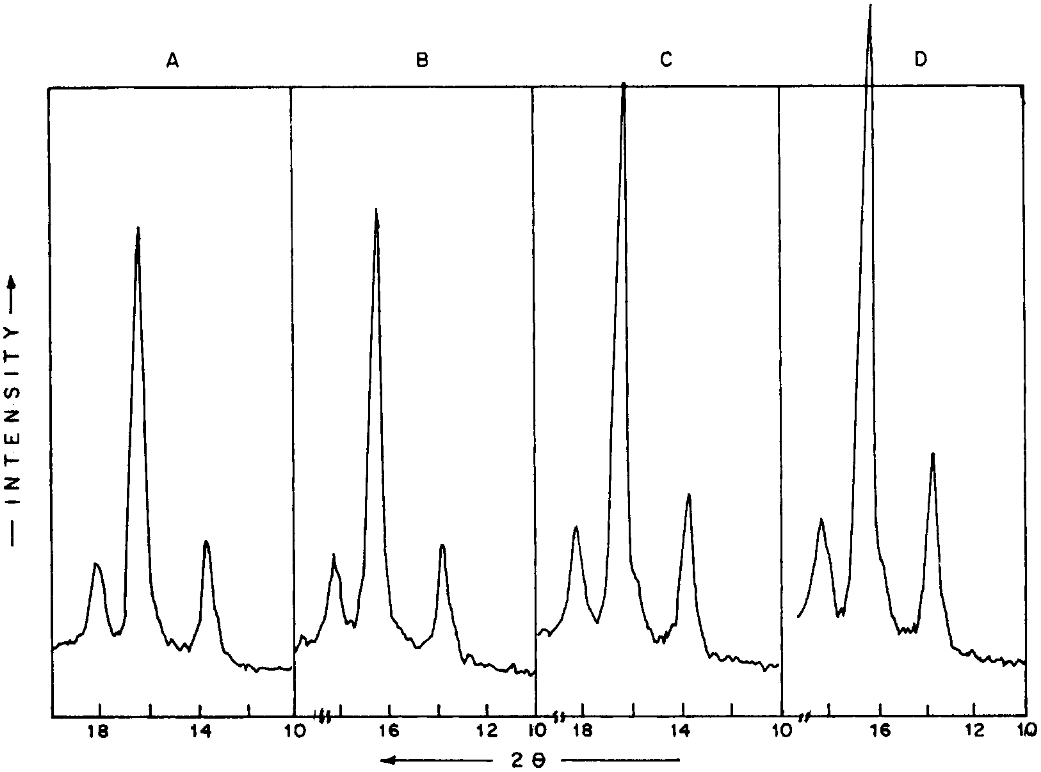

Figure 3 Effect of take-up speed on the WAXD pattern of PP films. Curves A–D correspond to take-up speed of 9.5, 12.5, 14.6, and 18 cm/s that give elongations of 3.1, 4.1, 4.7, and 6.2 cm/cm, respectively.

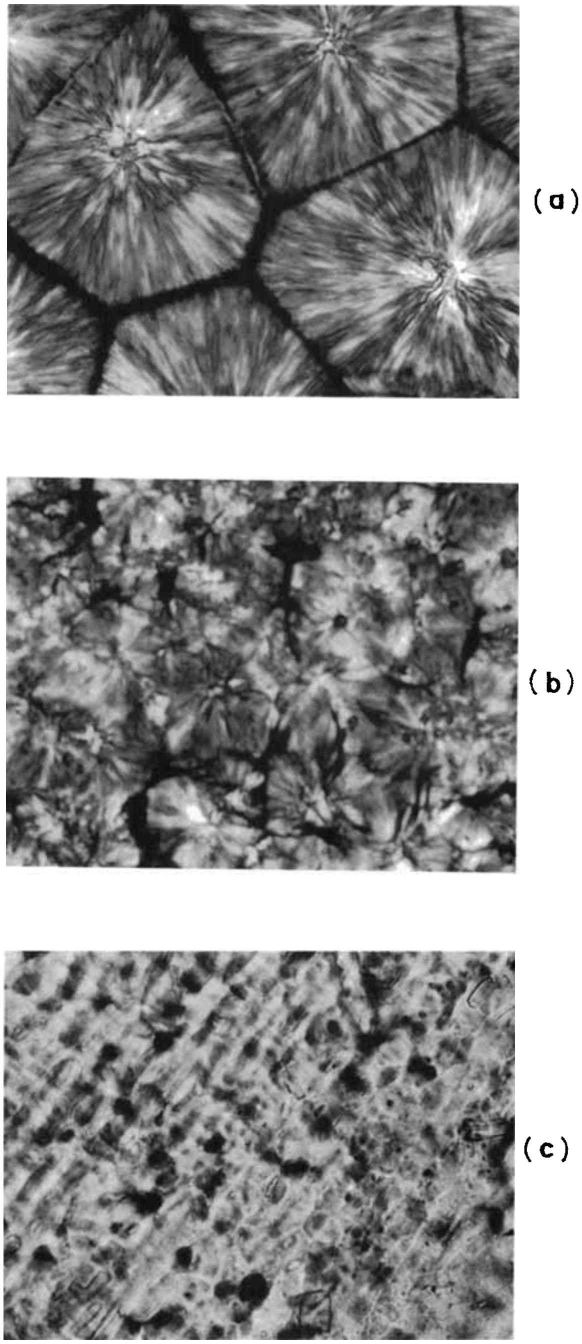

Figure 4 Optical polarizing micrographs of PP films prepared with different methods: (a) isothermally crystallized at 110°C, (b) same as (a) but with additives, and (c) blow film extruded film with take-up speed of 18 cm/s.

diffraction angle of 16.8 is very high for blow extruded films; and the intensities of two major peaks occurring at 14° and 21° are high in the compression molded samples while considerably low in blow extruded films. In the first instance it may seem that the blow film extruded PP contains a different crystalline phase (probably β) than the compression molded one. However, it may be noted that the hexagonal β phase of PP has two major reflections with d spacings of 5.52 and 4.25 Å corresponding to 2θ values of 16.0° and 21.1°, respectively.[17] These are not observed in the present case. Further, there are many reflections distinctly occurring in the WAXD of blow film extruded PP that closely match the reflections from the α phase. Table III gives the detailed analysis and comparison of present data with that reported for α and β phases of PP. From these data it is clear that the crystalline phase in both compression molded and blow film extruded films is the same as the α type, but there is a large variation of intensities of WAXD peaks suggesting development of orientation.[20]

The effect of take-up speed in blow film extrusion on the structure is shown in Figure 3. All other parameters such as blow ratio, rpm of the screw, temperatures at various zones, etc., were held constant. It is seen from the figure that there is an appreciable increase of intensity of α_{040} reflection with the increase of take-up speed. On the other hand, the intensities of other reflections (110, 111 etc.) remain more or less the same. It thus becomes clear that the change in the intensity of α_{040} is associated with the particular processing parameter, the take-up speed, that causes uniaxial stress in the machine direction. These findings suggest that there is a large degree of orientation induced in blow extruded films in the machine direction as well as depending on the take-up speed used. Because the intensity of the α_{040} peak increases, the (OkO) planes or the b axis become oriented. The development of uniaxial orientation was confirmed by optical polarizing microscopy, which is discussed later in this article.

The morphological changes in the isothermal crystallization as well as orientation in blow extruded PP film were examined by optical polarizing microscopy. Figure 4 shows the optical polarizing micrographs of PP samples prepared by different methods: isothermally crystallized from melt at 110°C, isothermally crystallized from melt with additive at 110°C, and blow film extruded PP film with take-up speed of 18 cm/s. The sharp change in spherulitic dimensions and the development of orientation is quite evident. To quantify the orientation produced, the total birefringence in these films was estimated by noting the color (or extinction wavelength) under cross-polar conditions with a full wave plate at two orthogonal directions (45° and 135° to

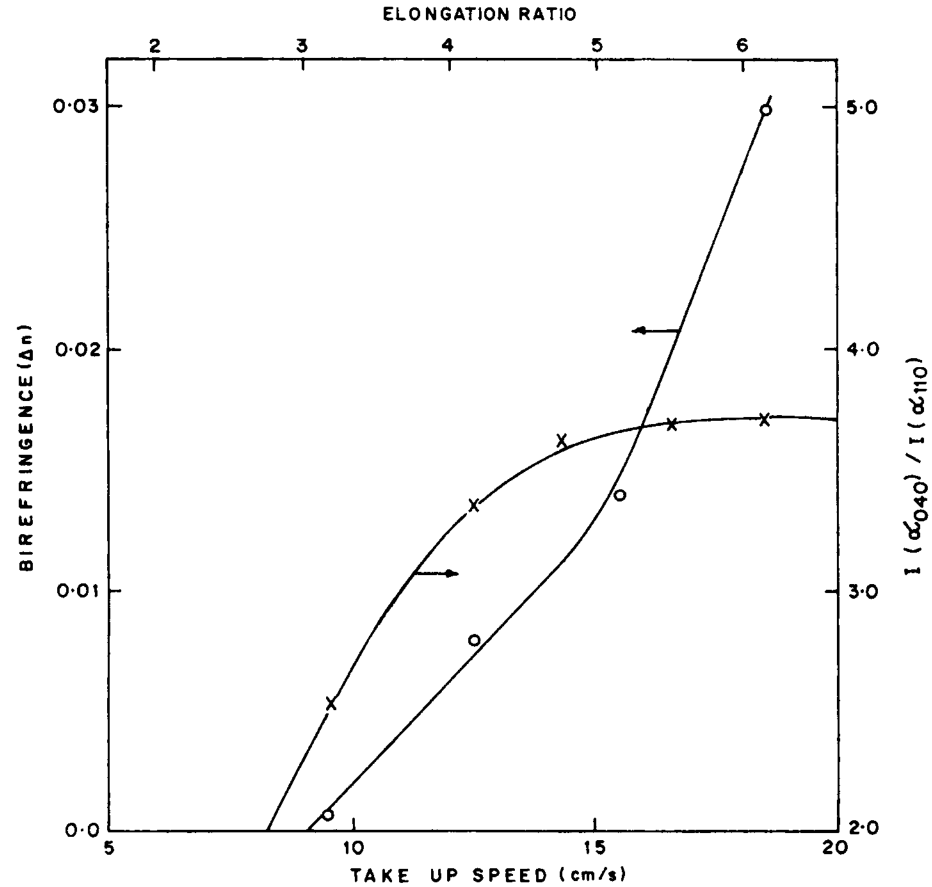

Figure 5 Development of orientation in PP films with take-up speed: (o) birefringence from optical microscopy and (x) relative intensity of α_{040} peak. The upper scale indicates the elongation ratio obtained for these processing conditions.

the main axis) by rotating the stage. The birefringence could then be estimated by using a Michel–Levi chart and the known value of thickness.[21] Figure 5 shows the variation of birefringence as well as the ratio of intensities of the α_{040} peak to α_{110} in the WAXD as a function of take-up speed. It is interesting to note that, although the intensity of the diffraction peak increases first and then tends to a limiting value of 3.85 for take-up speeds above 15 cm/s, the birefringence value shows continuous increase with the increase of the take-up speed. This can be explained as follows. Application of uniaxial stress to semimolten film, as one would expect under high take-up speed, causes orientation of crystallites and orientation of polymer in the amorphous region. The total birefringence consists of these two components of orientation. Because the extent to which the crystallites can be oriented depends upon their number, size, and degree of packing as well as the interaction between the tie molecules, there is an upper limit to the extent of orientation of such crystallites. On the other hand, the amorphous region has a large amount of free volume with loosely bound chains that can be easily oriented. Hence, the increase of birefringence in the films prepared at high take-up speeds, > 15 cm/s, is due to orientation of the chains in the amorphous regions. It is interesting to note that there are spherulitic domains that are distorted but also aligned along the axis of orientation in these films.

SUMMARY AND DISCUSSION

The structure development in PP processed by blow film extrusion has been studied by X-ray diffraction and optical microscopy and compared with that in compression molded samples. The crystalline phase is mainly the α type but there is an unusually large intensity of the α_{040} peak in blow extruded films.

The effect of small concentrations of additives on the crystallization behavior of PP indicates a faster crystallization process with lower induction time in the case of $CaCO_3$ than in other cases. This suggests higher nucleation efficiency for this filler than the others. The unusually high intensity of a particular reflection in the X-ray diffraction scan of blow extruded PP film has been explained on the basis of orientation of the *b* axis of the crystallites with increase of take-up speed confirmed by optical polarizing microscopy.

These various results suggest that although one normally expects biaxial orientation in blow film extruded films, it is possible to induce uniaxial orientation in the machine direction by increasing the take-up speed. The extent of orientation developed by this technique would no doubt depend on the relative uniaxial stress generated in the machine direction as compared to that in the perpendicular direction caused by blowing action. These two factors would have to be optimized to obtain large biaxial orientation in PP films. Our experiments with PP containing various additives gives a clear indication that pigments added, even in small quantities, can affect the crystallization behavior. Therefore an appropriate choice must be made if good properties are desired for the PP films used in packaging. Further work is in progress for characterizing various properties of these films in order to correlate with different parameters used during the blow film extrusion process.

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REFERENCES

1. I. M. Ward, *Developments in Oriented Polymers,* Vols. 1, 2, Applied Science Publishers, London, 1982.
2. A. E. Zachradias and R. S. Porter, *High Modulus Polymers,* Marcel Dekker, New York, 1988.
3. G. Gruenwald, *Plastics—How Structure Determines Properties,* Hanser Verlag Publishers, Munich, 1993.
4. J. C. Seferis and P. S. Theocaris, Eds., *Interrelations Between Processing, Structure and Properties of Polymeric Materials,* Elsevier, Amsterdam, 1984.
5. S. J. Pan, H. R. Brown, A. Hiltner, and E. Baer, *Polym. Eng. Sci.,* **26,** 997 (1986).
6. M. Ahmed, *Polypropylene Fibre—Science & Technology,* Elsevier, Amsterdam, 1982.
7. R. R. Saraf and R. S. Porter, *J. Polym. Sci., Polym. Phys. Ed.,* **26,** 1049 (1988).
8. S. Bruckner, S. V. Meille, V. Petracconi, and B. Pirozzi, *Progr. Polym. Sci.,* **16,** 361 (1991).
9. P. Corradini and G. Guerra, *Adv. Polym. Sci.,* **100,** 185 (1992).
10. R. A. Campbell, P. J. Phillips, and J. S. Lin, *Polymer,* **34,** 4809 (1993).
11. G. Zhou, Z. He, J. Yu, and Z. Han, *Makromol. Chem.,* **187,** 633 (1986).
12. S. Radhakrishnan and S. G. Joshi, *Euro. Polym. J.,* **23,** 819 (1987).
13. S. Radhakrishnan and R. Joseph, *Ferroelectrics,* **142,** 189 (1993) (Spec. Issue on Cryst. & Cryst. Growth).
14. S. Radhakrishnan and J. M. Schultz, *J. Cryst. Growth,* **116,** 378 (1992).
15. R. J. Samuel and R. Y. Lee, *J. Polym. Sci. A2, Polym. Phys.,* **10,** 385 (1972).
16. A. J. Lovinger, J. O. Chua, and C. C. Gryte, *J. Polym. Sci., Polym. Phys. Ed.,* **15,** 641 (1977).
17. E. J. Addink and J. Beintema, *Polymer,* **2,** 185 (1961).
18. G. Natta and P. Corradini, *Nuovo Cimento Suppl.,* **15,** 40 (1960).
19. A. Turner-Jones, J. M. Aizelwood, and D. R. Beckett, *Makromol. Chem.,* **75,** 134 (1966).
20. L. E. Alexander, *X-ray Diffraction Methods in Polymer Science,* Wiley, New York, 1969.
21. J. M. Haudin, in *Optical Properties of Polymers,* G. H. Meeten, Ed., Elsevier, London, 1986, p. 167.

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