β-CRYSTALLINE POLYPROPYLENE (BEPOL™) AND ORIENTED FILM APPLICATIONS

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Abstract

Polypropylene with high β-crystalline content is obtained by employing a β-nucleator, such as γ-quinacridone, N,N'-dicyclohexyl-2,6-naphthalene dicaboxamide or a combination of a Group II metal salt or hydroxide and an organic di-acid compound. In this case, Bepol™, a β-crystalline polypropylene, contains a small amount of a Group II metal salt or hydroxide and an organic di-acid compound. In this study, various products of Beopl™ have been characterized and applied to oriented film.

Introduction

It is well known that three types of crystalline structures, i.e., α–, β– and γ–forms, exist in isotactic polypropylene (iPP) (1). Although the γ-form is known to be the most thermodynamically stable, the α-form is the preferred and predominant crystalline form (2). On the other hand, the β-form is the least stable, and tends to turn into the α-form when subjected to external parameters such as heat (3) or force (4).

The existence of β-form crystalline structure in iPP was first reported in the late fifties (5). In 1967, Leugering identified Permanent Red E3B (quinacridone) as a β-nucleator that provides relatively large quantity of β-crystal (6). Since then, more comprehensive investigations on β-crystalline iPP have been completed (7). Other types of β-nucleators identified to be effective are the alkali metal and di-acid compound (8) and N,N'-dicyclohexyl-2,6-naphthalene dicaboxamide (9). Using such nucleators, various properties of β-crystalline polypropylene have been examined in oriented film (10), molding (11), thermoforming (12) and fiber (13). For example, Toyobo disclosed that an iPP of β-crystalline form could produce opaque film that is microporous in nature (10).

In this study, various β-crystalline polypropylene products were produced using a di-acid and an alkali metal compound. The objective of this study was to examine the characteristics of β-crystalline versions of various isotactic polypropylene products and their applications in oriented film.

Experimental

A variety of 2 dg/min melt flow rate iPPs were employed in this study. They are homopolymers, random copolymers (RCP) having an ethylene content ranging from 0.5 to 2.7 % by weight, and impact copolymer (ICP) containing 2.5 and 8.5 % ethylene by weight. Each polymer was compounded with an anti-oxidant, acid neutralizer and β-nucleator package. The relative β–crystallinity (K) of iPP was determined by differential scanning calorimetry (DSC) and wide-angle X-ray scattering (WAXS).

For film preparation, polypropylene was extruded onto a cast roll to produce either 0.254 or 0.508 mm thick sheet. The temperature of cast roll was adjusted to maximize the relative β-crystallinity in the sheet. Samples (5.08 cm x 5.08 cm) were cut out of the sheet stock and stretched with a T. M. Long stretcher (T. M. Long Corporation, Somerville, NJ). This equipment allows simultaneous and/or consecutive biaxial orientation at an elevated temperature. Samples were stretched at a given stretching temperature and a fixed strain rate of 50.8 mm/sec. The tensile biaxial stress-strain curve is simultaneously generated during orientation. Morphological changes of polypropylene during orientation via a T. M. Long stretcher have been described elsewhere (14).

The tensile properties of the oriented film were determined by the method prescribed in ASTM 882. The morphology of the opaque film were observed via scanning electron microscopy (SEM).

Results and Discussion

Characteristics of various products of β-crystalline iPP

Table I gives the β-crystallinity and the thermal characteristics of various β-crystalline iPPs while Figures 1 and 2 show the corresponding DSC thermograms and WAXS scans, respectively. The low and high melting temperatures of the DSC endotherms are for β- and α-form crystals, respectively. From the DSC results, the ratio of the peak areas can be used to calculate the relative amounts of each form. From the WAXS data, the relative β-crystallinity, K, can be determined using the equation (1) proposed by Turner Jones et al. (1), when the γ-form crystals are absent,

$$\mathbf{K} = \frac{\mathbf{H}_{(300)}}{\mathbf{H}_{(300)} + \mathbf{H}_{(110)} + \mathbf{H}_{(040)} + \mathbf{H}_{(130)}} \qquad (1)$$

The above equation has been modified to the following equation (2) to determine K value when the γ-form crystals exist along with α- and β- form crystals,

$$\mathbf{K} = \frac{\mathbf{H}_{(300)}}{\mathbf{H}_{(300)} + \mathbf{H}_{(110)} + \mathbf{H}_{(040)} + \mathbf{H}_{(130)} + \mathbf{H}_{(111)} + \mathbf{H}_{(008)} + \mathbf{H}_{(117)}} \qquad (2)$$

where, $H_{(hkl)}$ represent the diffraction intensity of the (hkl) lattice plane of α- , β- and γ-form crystals. As shown in Figure 2, $H_{(300)}$ is from the β-form crystalline structure, $H_{(110)}$, $H_{(040)}$ and H $_{(130)}$ are from the α-form crystalline structure and $H_{(111)}$, $H_{(006)}$ and $H_{(117)}$ are from the γ-from crystalline structure.

Nucleating β-form crystals in a homopolymer results in two melting temperatures, 152°C for β-form crystal and 168°C for α-form crystal as given in Table I. It is apparent that the melting temperatures of both α- and β-form crystals decrease with increasing ethylene content of the random copolymer. Significantly less amounts of β-form crystals are formed when a random copolymer contains above 2 % ethylene by weight. This can be attributed to preferable formation of α- and γ-forms over β-form in random copolymers as reported elsewhere (15). As shown in Figure 2, significant amounts of γ-form crystals are apparent along with α-form when the ethylene content is greater than or equal to 2.5 % by weight. It is noted that there is a large difference between WAXS and DSC measurement of the relative β-crystallinity of the random copolymer having 2.5 % ethylene by weight. Such a difference may be attributed to the differences in the cooling rate between DSC measurement and the sample preparation for WAXS, especially when the formation of β-form and γ-form is competitive. It can also be caused by the transformation of β- to α-form during DSC scan. Above 2.5 % ethylene by weight of the random copolymer, however, it appears that the γ- and α-forms are the dominant crystalline forms regardless of cooling rate for the sample preparation. However, for an impact copolymer that is composed of homopolymer matrix and ethylene-propylene copolymer dispersed phase, the β-crystallinity is governed by the homopolymer matrix regardless of the overall ethylene content of the polymer.

Orientation at conventional temperatures for BOPP (biaxially oriented polypropylene) film: Clear film

The performance of BOPP film grade materials on a commercial biaxial orientation process is often evaluated by determining the T. M. Long yield stress at a given stretch temperature and stretch ratio. In general, a lower T. M. Long yield stress as well as the shallow slope of the yield stress vs. temperature curve is preferred for better processability (16). The T. M. Long yield stress increases with increasing crystallinity of iPP and decreases with increasing stretching temperature at a given crystallinity and strain rate (14). Therefore, either an iPP having a low isotacticity or a random copolymer provides a material with a low T. M. Long yield stress. Although a random copolymer exhibits lower yield stress than a homopolymer, it is rarely employed as the core layer in commercial BOPP a film, especially when the ethylene content is greater than 0.5 % by weight, due to the poor properties of the resultant film (17).

In this work, pieces from an extruded cast-sheet of 0.508 mm thick were stretched simultaneously at various temperatures using a 6 x 6 (MD x TD) stretch ratio, where MD and TD stand for machine direction and transverse direction, respectively. Table II gives the polymers stretched at conventional temperature and the properties of the resultant film while Figure 3 depicts T. M. Long yield stresses with respect to the stretch temperature. In Figure 3, the iPPs A and B are a homopolymer and a random copolymer having 0.5 % ethylene by weight, respectively, which are commercially used in BOPP films. Sample C iPP is an random copolymer containing 2.5 % ethylene content by weight and is not used in commercial BOPP film, but evaluated for comparison. The β-crystalline iPP employed here is a homopolymer (Bepol™ B022SP).

As shown in Figure 3, despite the similar densities of the sheet stock, the T. M. Long yield stress for β-iPP homopolymer is significantly lower than that for conventional BOPP film grade materials (A and B) but higher than the random copolymer having 2.5 % ethylene by weight (C). The lower melting temperature of the β-crystalline phase is responsible for such a low yield stress. Since the β-crystals start to melt around 125°C as seen in Figure 1, the β-iPP is partially in a molten state at a stretching temperature 138°C and higher. As a result, the density of the cast sheet becomes significantly lower at the stretching temperature, thereby lowering the yield stress.

The film properties of β-iPP homopolymer are comparable to those of conventional BOPP film grade materials, as given in Table II. As mentioned earlier, the tensile properties of the random copolymer having 2.5 % ethylene by weight are worse compared to the other samples tested. Based on the information reported elsewhere (16), it may be concluded that β-iPP provides a wide processing window without sacrificing the properties of oriented film.

Orientation at low temperatures: Opaque film

Using the various β-crystalline iPP products, unoriented, extruded cast-sheets of 0.254 mm thick were stretched into films at various conditions below the conventional stretching temperature typically used for BOPP film. Table III gives the stretching conditions and appearance of the resultant films. Below 138°C, it was not possible to stretch a conventional homopolymer BOPP film grade iPP using the T. M. Long without tearing the resulting film.

In comparison, Bepol™ homopolymer is stretchable even far below the conventional stretching temperatures, i.e., 138°C vs. 104°C, and actually becomes opaque when stretched at or below 116°C. Stretchability at low temperature is again attributed to the presence of the lower melting β-crystalline phase. When the overall crystallinity of iPP was reduced by employing an impact modifier as in impact copolymers, the β-iPP was even uniaxially stretchable using the T. M Long stretcher even at 49°C at the given strain rate without tearing the film.

It is known that the β-form crystals turn into α-form upon application of external force (8). When the material is stretched, the β-crystalline phase undergoes a physical transformation to the α-crystalline phase. Such a transformation causes the formation of voids or pores in the vicinity of the crystalline lattice. As a result, the stretched film becomes opaque. The degree of opacity of the film depends on the relative β-crystallinity of the extruded sheet as well as the stretching temperature. Thus, it is worthwhile to understand the processing factors affecting the relative β-crystallinity of the extruded sheet.

The effect of cast roll temperature on the relative β-crystallinity of the extruded sheet is demonstrated in Table IV while the effect of stretching temperature on the opacity of the resulting film is quantitatively demonstrated in Table V by measuring haze and % light transmittance of the resultant film. As given in Table IV, the β-crystallinity increases with increasing the roll temperature for casting. Therefore, a roll temperature higher than 90°C is preferred for the extruded sheet to have sufficient β-crystallinity for opacity after orientation. As given in Table V, when the extruded sheet having the K value of 0.90 was stretched at a temperature higher than 127°C, the resultant film became translucent. In order to obtain an opaque film using the T. M. Long stretcher, a stretch temperature below 116°C is preferred. Figure 4 illustrates the transformation of β-crystals in the cast-sheet to α-crystals upon stretching 0.254 mm thick sheet at 3 x 3 ratio at 90°C.

The biaxially stretched film was observed via scanning electron microscope as shown in Figure 5. Numerous pores are seen throughout the film.

Conclusions

In this study, a variety of β-crystalline iPP products and their applications to oriented film were investigated. The amount of formation of the β-crystalline form in the presence of β-nucleator depends on both the polymer architecture and cooling rate. Either clear or opaque film from b-crystalline iPP can be obtained from β-crystalline iPP depending upon the stretching temperature. In a clear film application at higher stretching temperature, significantly improved processability is expected based on relatively low T. M Long yield stress in comparison to conventional BOPP grade materials. In an opaque film application, both the cast-roll temperature for the extruded sheet and the stretching temperature are very important. The opaque film produced from β-crystalline iPP contains numerous voids or pores throughout the surface and matrix. As a result, good permeability is expected.

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Keywords

β–crystalline polypropylene, oriented film

Table I
β-crystallinity and thermal characteristics of various products

iPP	homo	random	random	random	random	impact	impact
% C_2	0	0.5	2.0	2.5	2.7	2.5	8.6
K- WAXS	0.88	0.84	0.84	0.06	0	0.89	0.92
K- DSC	0.85	0.80	0.72	0.58	<0.05	0.84	0.84
T_m (°C) – β	152	147	138	135	-	151	149
T_m (°C) – α	168	164	157	147	148.0	168	167
T_c (°C)	122	117	108	107	114	120	120
% Xc	55	52	41	41	43	51	42

Table II
Polymers oriented at conventional temperature and properties of film oriented at 138°C

iPP	Homo	random	random	BEPOL™
% C_2	0	0.5	2.5	0
Density[a]	0.8987	0.9007	0.8957	0.8987
Tensile stress (MPa)	192	197	151	189
Tensile strain (%)	73.4	71.0	59.9	62.8
Modulus (MPa)	2586	2710	2503	2731

[a] sheet stock

Table III
Various Bepol™ products stretched with TM Long Stretcher

	STRETCH TEMP. (°C)	STRETCH RATIO (MD X TD)	APPEARANCE
Conventional iPP (K= 0)	138	2.5 x 2.5	transparent
	<138	NA	-
Bepol™ Homo (K= 0.83)	138	2.5 x 2.5	transparent
	125	2.5 x 2.5	translucent
	116	2.5 x 2.5	opaque
	104	2.5 x 2.5	opaque
Bepol™ ICP (K= 0.92)	93	3.5 x 3.5	opaque
	49	x 2.5	opaque

Table IV
Temperature dependence of β-crystal formation in the extruded sheet

CAST ROLL TEMPERATURE (°C)	K (WAXS)
60	0.35
90	0.78
104	0.85

Table V
Effect of stretching temperature on haze and light transmittance of 25.4 μm film stretched from an extruded sheet (K = 0.92)

STRETCH TEMP. (°C)	% TRANSMITTANCE	HAZE	APPEARANCE
132	70.1	36.7	translucent
127	49.6	48.5	translucent
116	9.7	93.3	opaque
90	0.3	100	opaque

Figure 1
DSC Thermograms of various β-crystalline polypropylene

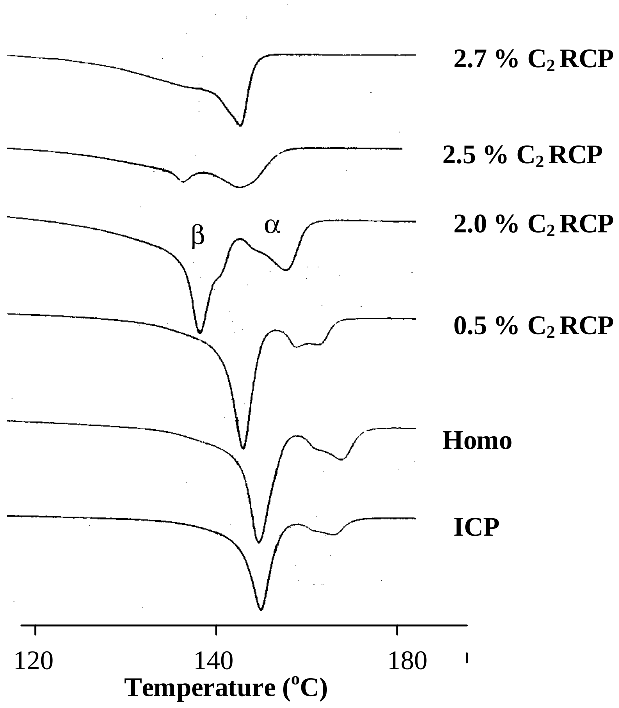

Figure 2
WAXS scans of various β-crystalline polypropylene in comparison to α-crystalline polypropylene

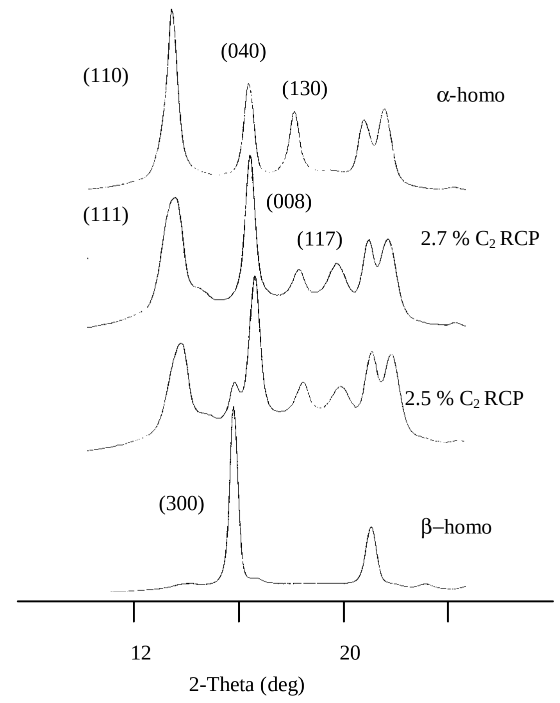

Figure 3
T. M. Long yield stress at various temperatures

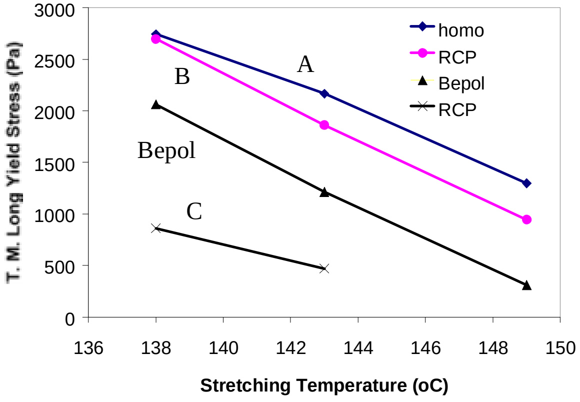

Figure 4
WAXS scans for cast sheet and MDO and TDO film

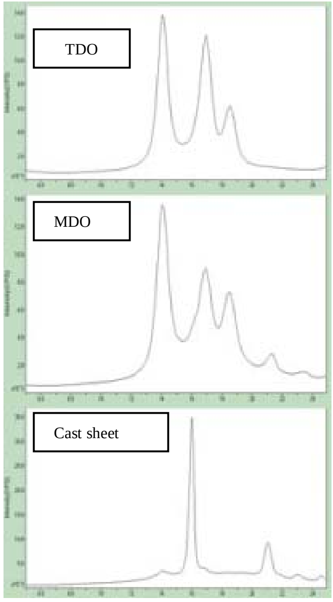

Figure 5
Scanning Electron Micrographs of stretched film