

Preparation and Characterization of Biaxially Oriented Polypropylene Film with High Molecular Orientation in the Machine Direction by Sequential Biaxial Stretching

Jun'ichi Masuda, Masatoshi Ohkura

Film & Film Products Research Laboratories, Toray Industries, Inc., 1-1, Sonoyama 1-chome, Otsu, Shiga 520-8558, Japan

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ABSTRACT: Novel approach of applying the ternary polymer blend of long-chain branched polypropylene (LCB-PP), conventional polypropylene (PP), and hydrogenated polydicyclopentadiene (hDCPD) has been employed to tensilize biaxially oriented polypropylene (BOPP) film in the machine direction (MD) by successive sequential biaxial stretching method. It is found that the addition of LCB-PP improves the MD stretchability of the BOPP film of PP/hDCPD blend. Depending on the content of LCB-PP, LCB-PP/PP/hDCPD ternary blend could be biaxially stretched up to the MD stretching ratio (MDX) of 12 without film breakage whereas that of PP (conventional BOPP film) resulted in the MDX up to 6. This excellent MD stretchability enabled to tensilize the BOPP film in the MD, where Young's modulus in the MD could be

increased up to 4.9 GPa, twice higher than that of conventional BOPP film. The orientation of total molecular chains and that of crystalline molecular chains were evaluated by in-plane distribution of refractive indices and wide-angle X-ray diffraction, respectively. The results are discussed from the viewpoint of deformation behavior during stretching process. Moreover, the resultant film had a dimensional stability substantially equivalent to that of conventional one, in spite of the higher stretching ratio, and an improved moisture barrier property. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 4031–4037, 2007

Key words: biaxiality; poly(propylene) (PP); films; orientation; branched

INTRODUCTION

Biaxially oriented polypropylene (BOPP) film is widely used in various applications such as food packaging, electrical insulator, other industrial use because of its advantage of properties, for example, transparency, high stiffness, comparatively low price, excellent electrical properties, high flexibility in converting. On the other hand, a lot of attention has been recently directed on the reduction of wastes and recycling, one of which leads to reducing the thickness of film.

Here almost all of BOPP films are finally converted into secondary products, through processes such as laminating, metallizing, coating, slitting, bag-forming, etc. In those converting processes, processing tension is always applied in the longitudinal direction (e.g., machine direction; MD) of film. To compensate for the reduction of the thickness, we have to improve the durability of the film in the MD at the converting process to prevent sagging, wrinkle formation, or crack formation in the coated or metal-

lized layer on the film, which definitely impair the quality of the resultant products. Therefore, of great importance is to tensilize the BOPP film in the MD.

Most of BOPP films are typically produced by sequential longitudinal-transverse biaxially stretching method. However, BOPP film has been difficult to be tensilized in the MD by this conventional method. That is originated from its inherent deformation behavior during the stretching process in the transverse direction (TD) after the stretching process in the MD. At the initial stage of this TD stretching (up to the TD stretching ratio (TDX) of about 3), MD oriented amorphous chains first reorient in the TD followed by the rapid TD reorientation of crystallites.¹ At the TDX below 3, no BOPP film can be obtained with the uniform thickness nor with the producing cost suitable for practical use. Since the most of crystallites and hence amorphous tie molecules reorient in the TD, the resultant BOPP film has a markedly lower mechanical properties in the MD than that in the TD.

Great efforts have been ever made to tensilize BOPP film in the MD. One of the approaches is to add a petroleum resin such as hydrogenated polydicyclopentadiene (hDCPD), which is the promising way to improve the mechanical properties, moisture barrier property, etc. This is because hDCPD is mis-

Correspondence to: J. Masuda (Junichi_Masuda@nts.toray.co.jp).

cible with the amorphous region of PP to decrease the free volume in the amorphous region, by which the resultant blend exhibits a single and elevated glass transition temperature (T_g).²⁻⁷ But, it was of a problem that the improved mechanical properties of the BOPP film were not enough, and the resultant film tended to get soften above the T_g of hDCPD in addition to the impaired thermal dimensional stability. Alternative approaches were meanwhile employed by modifying its process, for example, simultaneous biaxially stretching process,⁸⁻¹⁰ MD restretching process after sequential stretching,¹¹ etc. Although BOPP film might be modestly tensilized in the MD by these methods, those could remain the unavoidable issue(s) of a vast amount of investment and, additionally for the MD restretching process, an impaired stretchability or thermal dimensional stability. Therefore, there has been no practically effective way reported to obtain the MD tensilized film in terms of modifying the raw materials or the producing process by using a conventional successive sequential biaxial stretching method.

In this study, we focused on tensilizing BOPP film in the MD without substantial deterioration of other properties by ready-made successive sequential MD-TD stretching method. Here we examined the novel technique to obtain a MD tensilized BOPP film by modifying its resin composition and correspondingly stretching condition. Resultant mechanical properties are discussed from the viewpoint of the relations with its orientation behavior in the plane of the film.

EXPERIMENTAL

Materials

Polypropylene (PP) was a commercial grade for a plastic film application with the melt-flow rate (MFR) of 3 g/10 min under the condition of 230°C and 21.18 N. It was purchased from Sumitomo Chemical (Tokyo, Japan). Long-chain branched polypropylene (LCB-PP) was purchased from Basell (Elkton, MD) with MFR of 3 g/10 min at 230°C. Hydrogenated polydicyclopentadiene (hDCPD), also known as a petroleum resin, was purchased from Toei (Tokyo, Japan) with the T_g of 80°C, the bromine number of 3 cg/g, and the hydrogenation rate of 99%, which contains no polar group within its molecular structure. The hDCPD was blended with 50 wt % of PP, melt-mixed with a twin-screw extruder at the temperature of 250°C, and finally cut into chips. Resultant chips were used as a master batch in this study.

Preparation of BOPP film

BOPP film was made by a successive sequential biaxial stretching machine consists of a single-screw extruder, a casting drum with air-knife, longitudinal

roll-type stretching apparatus, transverse stretching apparatus (tenter), and winder. In the casting process, molten polymer extruded from slit die into a sheet with single-screw extruder at the temperature of 260°C was cast on a chill roll with the temperature of 25°C to obtain an unoriented sheet. This sheet was passed through rolls maintained at 135°C, and preheated, and passed between rolls with the temperature of 140°C and the different rotating speed, so that the sheet was stretched to a given MD stretching ratio (MDX). The uniaxially oriented sheet was then immediately cooled to room temperature. The stretched film was next fed into a tenter to be preheated at 165°C, stretched in the TD to the mechanical stretching ratio of about 7 times the initial length at 160°C, and heat-set at 160°C allowing the relaxation in the TD with the ratio of 6%. The film was then cooled and wound so as to obtain a BOPP film with the thickness around 15 μm . The BOPP film was fabricated at the MDX elevated one-by-one up to film breakage. The maximum MDX was hereby evaluated, to which the film could be stretched stably without film breakage at both of the MD and the subsequent TD stretching process. The results are shown in the following manner: if the film breaks at the MDX of 12, the maximum MDX is shown as 11.

Characterization

The stress-strain curves were measured at the temperature of 23°C and the relative humidity of 65% using a Tensilon (AMF/RTA-100) available from Orientech. The Young's modulus, stress at break (tensile strength), and strain at break in the MD and TD were obtained thereby. The specimen dimension was 150 mm in a measuring direction and 10 mm in a direction perpendicular to it. It was stretched at the stretching rate of 300 mm/min from the original length of 50 mm between chucks.

The refractive index was measured at the temperature of 23°C and the relative humidity of 65% using a Abbe refractometer available from ATAGO with the illuminating source of Na-D line ($\lambda = 589 \text{ nm}$), the contact liquid of methyl salicylate ($n = 1.5369$ at 20°C), and the polarizing plate attached at the part of ocular lens. Specimens were cut parallel to each directions of a film, the angle of which was inclined for every 15° from 0° to 90°. Resultant 7 samples were set on a stage of the refractometer so that the inclined direction is parallel to the fixed polarized direction and perpendicular to the direction of the incident light. Obtained data were radar-plotted against the angle between the polarized direction and the MD assuming the symmetry of the in-plane orientation of the BOPP film.

The azimuthal intensity distribution profile was obtained by wide angle X-ray diffraction with a

2 mm ϕ pinhole optical system and a slit system of 1° – 1° using an X-ray generator (4036A2) and goniometer available from Rigaku Corporation. Each film was stacked with its direction aligned in the same way to fabricate the stacked films with the total thickness of about 1 mm, from which a sample was prepared by gluing the edge and cutting into rectangles. It was measured under the condition of 40 kV, 20 mA with the radiation of Cu $K\alpha$. The intensity distribution profile along the azimuthal direction of the diffraction peak for the (-113) plane observed around $2\theta = 43^{\circ}$ was measured rotating the sample in the plane of film, where azimuthal angle, β , corresponds to the angle of the goniometer axis to the MD of the stacked rectangles.

The heat shrinkage ratios at 120°C in the MD and TD were measured using a sample 260 mm in the measuring direction and 10 mm in the perpendicular direction. Each sample was marked at a position corresponding to a length of 200 mm in the measuring direction, that is, the original length L_0 . The samples were heated at 120°C for 15 min, suspended in an oven under the load of 3 g, which would be one of the simplest ways to measure many samples at once without sagging or floating due to the air flow in the oven. After the heat treatment, the sample was immediately cooled into room temperature, the marked length (L_1) of which was measured. The heat shrinkage ratio was calculated by the equation: Heat shrinkage ratio (%) = $100 \times (L_0 - L_1)/L_0$.

The moisture vapor transmission rate (MVTR) was measured at the temperature of 40°C and the relative humidity of 90% using a PERMATRAN-W3/30 available from MOCON/Modern Controls Inc.

RESULTS AND DISCUSSION

Figure 1 shows the effect of MDX on the Young's modulus in the MD (Y_{MD}) as well as the effect of the addition of hDCPD on the stretchability and the Y_{MD} of resultant film. Higher maximum MDX was achieved for the BOPP film of the blend with the composition of 90 wt % of PP and 10 wt % of hDCPD, which is hereafter denoted as 90/10 wt % PP/hDCPD blend, when compared with those of PP (without hDCPD; e.g., conventional BOPP film). This is associated with better stretchability. At the same MDX, higher Y_{MD} was obtained by the addition of hDCPD. These are the major advantages in adding a hDCPD, which is due to its miscibility with the amorphous chain of PP, resulting in the increasing slips among PP chains at the stretching temperature to enable the higher MDX stretching, and the elevation of the glass transition temperature (T_g) of the blend to improve the mechanical properties below the T_g .²⁻⁷ Excess stretching above the maximum

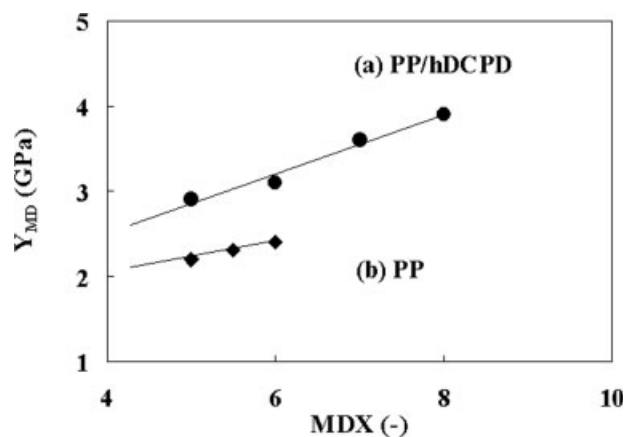


Figure 1 Effect of MDX on Y_{MD} : (a) BOPP film of 90/10 wt % PP/hDCPD blend and (b) that of 100 wt % PP (conventional BOPP film).

MDX ended in the film breakage during the successive TD stretching process for the both cases. This film breakage in stretching above the maximum MDX is believed to be due to the excess fibrillation at the MD stretching process. Nie et al.¹² observed the surface of BOPP films by atomic force microscopy. They reported that a uniaxially oriented strand structure was obtained after the MD stretching process in the film-making process and network-shaped fibril structure after the TD stretching process. Although we could not stably obtain the BOPP film stretched to the MDX of 8 and the TDX of 8 from a conventional PP as they reported (see the data for the conventional BOPP film in Fig. 1; the maximum MDX was 6 under the TDX of about 7), it would be noteworthy in their report that higher MDX leads to the development of more fibrillated structure probably due to more oriented thinner strand structure after the MD stretching process. This result implies that the further higher MDX beyond its maximum MDX may lead to the excessively oriented strand structure after the MD stretching process, which may not propagate the stretching force uniformly over the system to be fibrillated into the network-shaped structure during the subsequent TD stretching process and finally end in the film breakage.

Here we examined a new concept to overcome the aforementioned limitation by a certain modification on the blend component, which would allow the more uniform propagation of the stretching force whole over the highly MD oriented system during the TD stretching process. We then employed a LCB-PP as the alternative blend component, which successfully prevented the film breakage.

Figure 2 shows relationship between the content of LCB-PP to the total PP and the maximum MDX, that is, how the addition of LCB-PP affects on the stretchability of film, which is evaluated with the maximum MDX. The maximum MDXs shown in

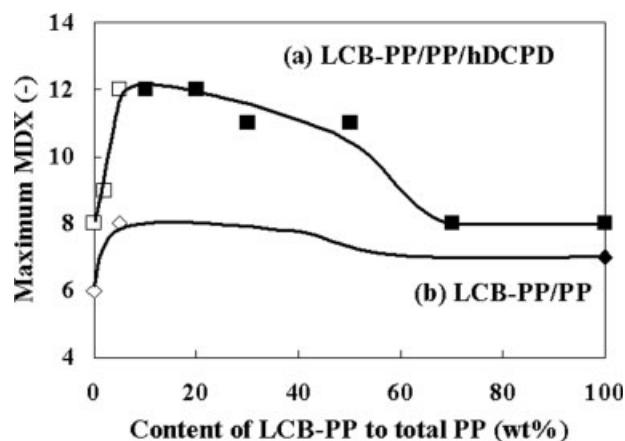


Figure 2 Relationship between the content of LCB-PP to the total PP and the maximum MDX: (a) BOPP film with 10 wt % of hDCPD and (b) that without hDCPD. Open plots and closed plots indicate the film breakage at the TD and MD stretching process, respectively, when biaxially stretched beyond each maximum MDX.

Figure 1 correspond to the plots at the LCB-PP content of 0 wt %, which indicates the effect of adding the hDCPD. The addition of LCB-PP further improved the stretchability of both BOPP films with and without hDCPD blended, which is clearly indicated by the elevated maximum MDX. The LCB-PP/PP/hDCPD ternary blend film obviously showed the optimum content of the LCB-PP around 5–30 wt % to the total PP, which indicates the enhancement of the stretchability by the coexistence of LCB-PP and hDCPD. Of great interest is that each film with the different content of LCB-PP tended to break above the maximum MDX in the different manner. That is, BOPP film with the major content of LCB-PP tended to break during the MD stretching process whereas those with the minor content resulted in the film breakage during the TD stretching process, which is the same behavior as conventional BOPP film, shown earlier.

In the LCB-PP blends, branching points in its molecular chain would be excluded from the crystalline region and hence located in the amorphous region. Those branching points could work as linking points of tie molecules between crystallites, which probably propagates the stretching force more uniformly all over the system, and then results in excellent stretchability during the TD stretching process even at the higher MDX. But, excess addition of the LCB-PP would increase the linking points to the extent of disturbing the deformation into the strand structure during the MD stretching process, which finally leads to the bad MD stretchability. Therefore, the amount of the branching points introduced by the addition of LCB-PP should have an optimum value as shown in Figure 2. Also, different manner of film

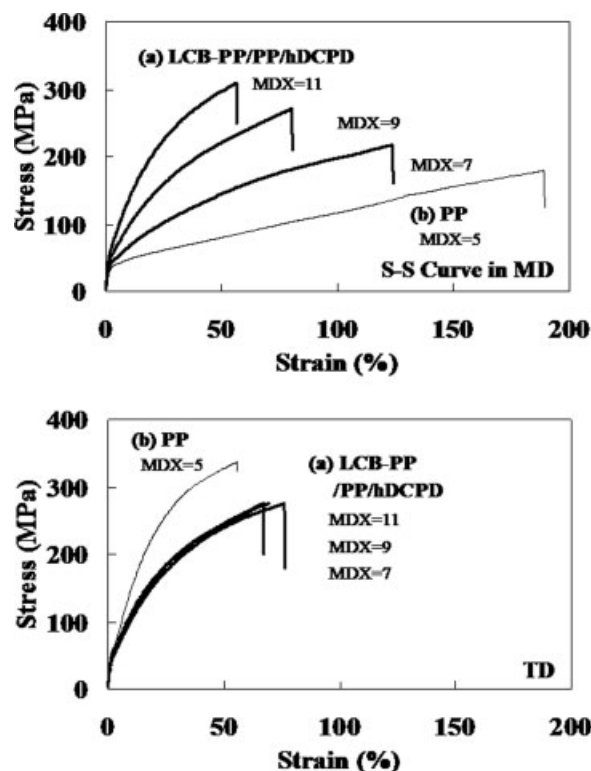


Figure 3 Stress–strain curves in the MD (upper) and TD (bottom): (a) BOPP film of 27/63/10 wt % LCB-PP/PP/hDCPD ternary blend (thick line) and (b) that of 100 wt % PP (thin line). Each caption indicates the MDX.

breakage with the content of LCB-PP is believed to be due to the above effect of the amount of the linking points. This effect by LCB-PP could be further enhanced by the existence of hDCPD in the amorphous phase.

Figure 3 illustrates how the stress–strain curve changes with the elevated MDX for the BOPP film of 27/63/10 wt % LCB-PP/PP/hDCPD blend in addi-

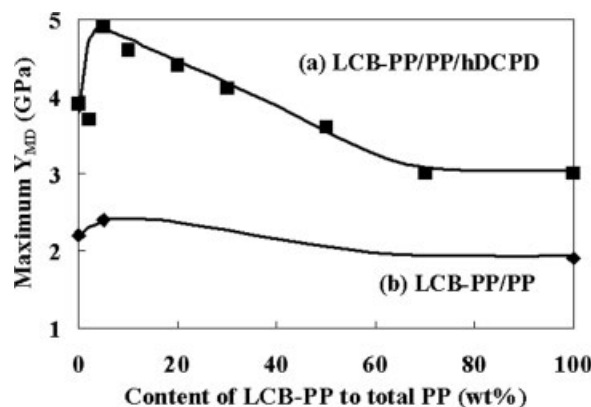


Figure 4 Relationship between the content of LCB-PP to the total PP and the maximum Y_{MD} : (a) BOPP film with 10 wt % of hDCPD and (b) that without hDCPD. Note that every plot indicates the maximum Y_{MD} is that at the maximum MDX.

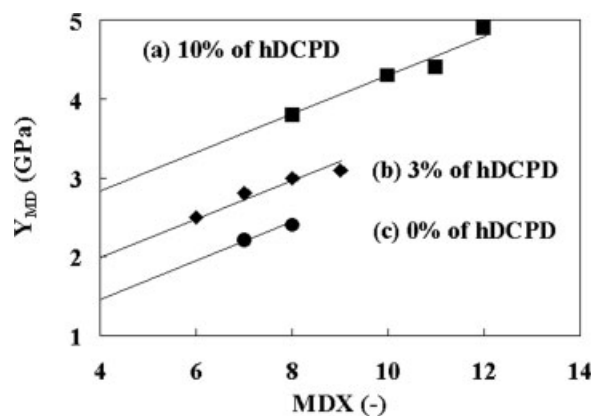


Figure 5 Relationship between the MDX and the Y_{MD} : (a) BOPP film with 10 wt % of hDCPD, (b) that with 3 wt % of hDCPD and (c) that without hDCPD. Each BOPP film contains 5 wt % of LCB-PP to the total PP.

tion to that for the conventional BOPP film. Whereas the resultant stress–strain curve in the TD did not change so much with increasing the MDX, that in the MD dramatically got steepened and tended to fail at earlier stage of the elongation. This is associated with higher Young’s modulus (shown in Fig. 4 later) and stress at break and lower strain at break in the MD, which would be caused by the increasing MD orientation in the plane of film discussed later.

Figure 4 summarizes the effect of the LCB-PP content on the Y_{MD} obtained at the maximum MDX (e.g., maximum Y_{MD}). The content of LCB-PP clearly

had an optimum point of 5 wt % to the total PP, which reflects the trend of the LCB-PP content versus the maximum MDX shown in Figure 2. This optimum content of 5 wt % allows us to stretch the film to the MDX of 12 and fabricate the MD tensilized BOPP film with Y_{MD} of 4.9 GPa, which are twice higher than the MDX and Y_{MD} of conventional BOPP film, respectively. Thus the addition of LCB-PP significantly improved the stretchability of BOPP film by coexistence of hDCPD and hence the mechanical property in the MD without impairing those in the TD.

Figure 5 shows the relationship between the MDX and the Y_{MD} for the LCB-PP/PP/hDCPD ternary blend BOPP film with different content of hDCPD. The higher the content of hDCPD was, the higher the Y_{MD} could be obtained at the same MDX, which is caused by the effect of the elevated T_g described earlier. Furthermore, BOPP film could be stably obtained at a higher MDX due to the aforementioned chain slipping effect by hDCPD, which leads to a further higher maximum Y_{MD} .

Thus, employing the ternary blend of LCB-PP/PP/hDCPD significantly improved its stretchability and mechanical properties in the MD, which was controllable by the blend composition and MD stretching condition. We made a hypothesis that these so-called “MD tensilization” effect would be partly caused by the high orientation of molecular chains to the MD. Then, we evaluated the molecular orientation by refractometry and WAXD to examine

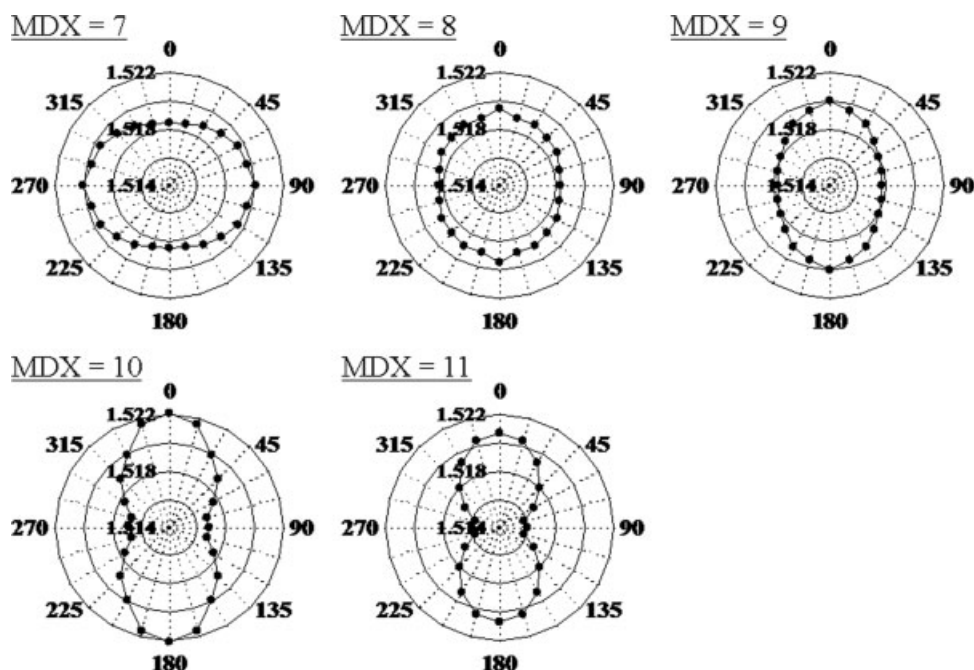


Figure 6 Anisotropy of refractive index for BOPP films of 27/63/10 wt % LCB-PP/PP/hDCPD ternary blend stretched to the various MDX.

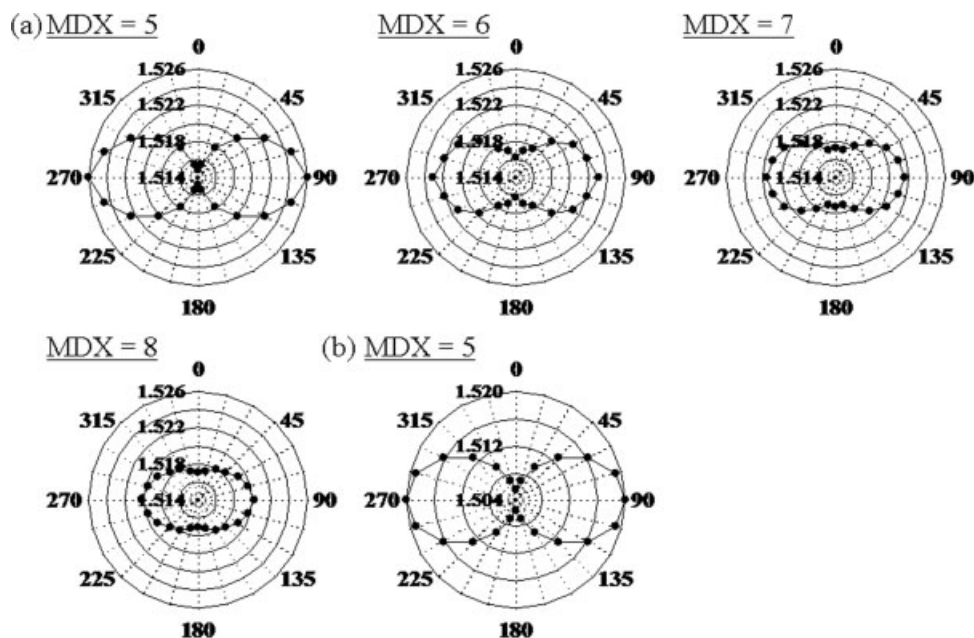


Figure 7 Anisotropy of refractive index of BOPP films stretched to the various MDX: (a) 90/10 wt % PP/hDCPD binary blend; (b) 100 wt % PP.

the effect of the addition of LCB-PP on the relationship between mechanical properties and orientation structure.

The total molecular orientations of the LCB-PP/PP/hDCPD ternary blend film, PP/hDCPD binary blend film, and conventional BOPP film were evaluated with refractive index in each direction and shown in Figures 6 and 7. In each case of the ternary blend film and the binary blend film, whereas the conventional BOPP film could not be stretched stably beyond the MDX of 6, there obtained the elevated refractive index in the MD with increasing MDX, which indicates the elevated molecular orientation in the MD. It is an interesting finding that the addition of LCB-PP has a significant effect on not only improving the stretchability (shown earlier) but controlling the orientation behavior of the resultant film. The ternary blend film exhibited a different distribution of orientation from the binary blend film and conventional BOPP film even at the same MDX and remarkably high orientation in the MD with increasing MDX. This remarkable difference indicates the different molecular deformation between the ternary blend film and the conventional film during the stretching process.

To ensure this, we conducted the azimuthal X-ray scanning where the sample configuration of $2\theta/\theta$ kept fixed in order that the reflection for the (-113) plane could be obtained. We can evaluate the crystalline molecular orientation qualitatively, because this reflection includes the meridional component. The result is shown in Figure 8. Here the peaktops of the intensity distribution at the β of 0° and 180° , and of 90° and 270° correspond to the presence of the orientation

component of crystalline molecular chains in the TD and in the MD, respectively. The peaktops were observed at the β of only 0° and 180° for the conventional BOPP film, indicating the TD orientation of the crystalline molecular chain is dominant. On the contrary, the peaktops were observed at 90° and 270° in addition to 0° and 180° for both ternary blend films stretched to the different MDX, which corresponds to the crystalline molecular orientation in both MD and TD. Moreover, the crystalline molecular chains tended to orient in the MD more with increasing the MDX to 10, illustrated with the elevated intensities of the peaks at 90° and 270° . Therefore, it is clearly confirmed that the addition of LCB-PP and hDCPD could essentially improve its inherent deformation behavior

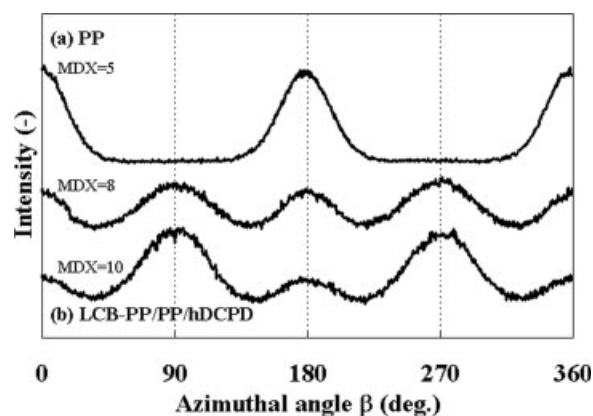


Figure 8 Wide angle X-ray azimuthal diffraction profiles for the (-113) plane of BOPP films: (a) 100 wt % PP and (b) 27/63/10 wt % LCB-PP/PP/hDCPD ternary blend. Each caption indicates the MDX.

TABLE I
Properties of Conventional BOPP Film and MD Tensilized BOPP Film of 4.5/95.5/10 wt %
LCB-PP/PP/hDCPD Ternary Blend

Sample	YMD (GPa)	Stress at break (MPa)	Strain at break (%)	Heat shrinkage ratio (%)	MVTR (g/m ² /d/0.1mm)
Conventional BOPP film 4.5/95.5/10 wt %	2.2/4.5	180/340	190/60	4.0/2.0	1.5
LCB-PP/PP/hDCPD Blend BOPP film	4.9/3.9	340/220	45/100	4.9/2.5	0.48

during the TD stretching process. We consider that this effect would be mainly due to its increasing linking points discussed earlier, which would serve as the work points to propagate the stretching force and hence prevent the crystallites from reorienting in the TD during the TD stretching process. Remaining the MD orientation in the crystalline region would be associated with high MD tensilization due to the high orientation of tie molecules.

Table I shows the properties of the conventional BOPP film and the 4.5/85.5/10 wt % LCB-PP/PP/hDCPD ternary blend BOPP film, which is stretched to the MDX of 5 and 12, respectively. Resultant ternary blend BOPP film in this study exhibited a quite high Y_{MD} and tensile strength in the MD. Heat shrinkage ratio of the ternary blend film is slightly higher than that of the conventional film, which would be caused by the higher internal strain remained after stretching associated with increasing the molecular orientation. But, this might be less important in the practical use assuming that those properties might be controlled by the blend composition and/or the stretching conditions. Moreover, the ternary blend film exhibited an excellent moisture barrier property when compared with the conventional one, reflecting the higher in-plane orientation, especially higher orientation in the amorphous region, which has been recently proved to be due to the tautness of amorphous chains.^{13,14}

CONCLUSIONS

In this study, we employed a novel approach of applying the ternary blend of LCB-PP/PP/hDCPD to obtain the MD tensilized BOPP film. It was found that the addition of LCB-PP into the PP/hDCPD binary blend remarkably improves the stretchability of the film, where the content of LCB-PP exhibits an optimum value. This enabled the MDX to be elevated further, which resulted in the significantly high Y_{MD} by stretching to the higher MDX.

The orientation study of the total and crystalline molecular chains clearly illustrated increasing MD orientation with the elevated MDX. These results have implied that the addition of the LCB-PP modifies its

inherent deformation behavior of the TD reorientation during the TD stretching process, which had been an unsolved problem over the years in tensilizing a BOPP film by sequential biaxial stretching. This remarkable advantage to tensilize BOPP film would be partly due to the controlled number of branching points of the LCB-PP, which would serve as the linking points between crystallites to propagate the stretching force uniformly whole over the system.

Resultant film had the comparable heat dimensional stability and better moisture barrier property when compared with that of the conventional BOPP film. This extraordinary property originated from higher MD orientation could be controlled by the resin composition and the stretching conditions such as MDX. Further study on the hierarchical microstructure and the possibility to apply to other polymer systems would be expected to establish the hypothetical concept of crystallites linking structure discussed here.

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