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ORIENTATION, STRUCTURE AND PROPERTIES OF DOUBLE-BUBBLE ORIENTED LLDPE FILMS

A. L. Bobovitch,^{1,*} S. Elkoun^{2,3} and A. Ajji²

¹*Syfan Saad (99) Ltd., Kibbutz Saad
D.N. Hanegev, 85140, Israel*

²*National Research Council of Canada Industrial
Materials Institute, Quebec, Canada*

³*Université des Sciences et Technologies de Lille
Laboratoire de Structure et Propriétés
de l'Etat Solide, Lille, France*

ABSTRACT: Biaxially oriented linear low density polyethylene (LLDPE) films are produced using the double-bubble process with different machine direction (MD) orientation levels and the same transverse direction (TD) blow-up ratio. Their mechanical behavior is characterized in terms of the tensile strength and tear resistance. The microstructure and orientation are characterized using microscopy, x-ray diffraction (XRD), and Fourier transform infra red spectroscopy (FTIR). The results indicate that MD tensile strength increases with increasing MD stretching (draw) ratio while the TD tensile decreases. Tear resistance remains mainly constant in TD and decreases in MD with increases in draw ratio. Morphology analysis reveals that overstretching lamellae tend to align perpendicular to MD with an increase of their lamellar dimensions. *c*-axis orientation of lamellae in MD increases with draw ratio while *a*- and *b*-axes orient towards normal direction (ND) and TD respectively. A good correlation is observed between *c*-axis orientation and MD tear resistance and tensile strength.

KEY WORDS: morphology, orientation, oriented films, mechanical properties, LLDPE, X-ray diffraction, Fourier transform infrared spectroscopy (FTIR), draw ratio, tear strength, tensile strength.

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*Author to whom correspondence should be addressed. E-mail: arthurB@syfan.co.il
Figures 1, 3 and 4 appear in color online: <http://jpf.sagepub.com>

INTRODUCTION

A MAJOR PORTION of linear low density polyethylene (LLDPE) films are used as flexible packaging; and shrink films occupy a large part of this packaging market. Shrink films use the tendency of an oriented film to try to return to a smaller linear dimension when it is heated above the temperature at which the stretched film was annealed or quenched. The shrink film is snugly wrapped around the product and then heated to provide a tight wrap around a packaged object or group of items.

There are several processes for producing shrink films such as tenter frame or double-bubble processes. In double bubble processes the primary extruded tube is quenched, reheated to a temperature below the melting point and then oriented in both machine direction (MD) and transverse direction (TD) simultaneously. Although stretching occurs simultaneously in the MD and TD, the forces for each are controlled separately. The MD force is applied by the differential speed between the two sets of nip rolls that contain the bubble. The TD force is applied by the pressure of air introduced into the tube. To minimize thickness variations, cooling air is often used outside the inflating tube to shift the stretching to the thicker sections of the tube. The advantage of this technique consists in more balanced properties of the film in both the directions [1]. Biaxially oriented films possess exceptional clarity, superior tensile properties, improved flexibility and toughness, improved barrier properties, and a unique property of engineering shrinkability [2].

In the previous studies the morphology and viscoelastic properties of biaxially oriented films produced by the double bubble process were reported [3–6]. Wide angle x-ray diffraction (WAXD) was applied in order to characterize the influence of orientation ratio on the polymer orientation [7]. However, the Fourier transform infra red spectroscopy (FTIR) was never applied for the study of orientation in such films. Therefore, one of the main goals of this study is to investigate the correlation between the FTIR and WAXD results and to emphasize the effect of machine direction stretching ratio on the orientation, morphology, and properties of the double-bubble oriented LLDPE films.

EXPERIMENTAL DETAILS

The LLDPE monolayer films with density of 0.920 g/cm^3 and thickness of $15\text{ }\mu\text{m}$ were tested. All the films were produced at an

industrial double bubble line ex. Prandi, with a constant orientation ratio (5.2) in the TD and different orientation ratios in the MD. Unstretched primary extruded tube was taken as a reference for some tests.

Mechanical properties of the films were tested using an LRX tensile tester ex. Lloyds according to ASTM 882 method. Tear propagation resistance of the film was measured by an Elmendorf tear tester.

For orientation determination, WAXD and FTIR were used. The FTIR measurements were carried out on a Nicolet 170SX FTIR at a resolution of 2 cm^{-1} with an accumulation of 128 scans. Polarization of the beam was performed using a zinc selenide wire grid polarizer from Spectra-Tech. The details about this method were reported elsewhere [8–10]. For crystalline axes orientations, pole figures of (110) and (200) reflections were obtained using a Bruker AXS X-ray goniometer equipped with a Hi-STAR two-dimensional area detector. The generator was set up at 40 kV and 40 mA and the copper K_{α} radiation ($\lambda = 1.542\text{ \AA}$) was selected using a graphite crystal monochromator. Sample to detector distance was fixed at 8 cm. Hermans orientation functions were derived from (110) and (200) pole figures using the Bruker analytical system software. The (200) Hermans orientation functions give directly the orientation of a -axis. In contrast, b -axis orientation functions were calculated following the Desper et al. method [11]. Finally, the c -axis orientation function was derived from the a - and b -axes using the orthogonality condition of the orthorhombic crystallographic structure.

The lamellar morphology was observed on samples etched for 20 min. using a Hitachi field emission scanning electron microscope [12].

RESULTS AND DISCUSSION

Graphs of Figure 1 show the evolution of the orientation functions related to a -, b -, and c -crystalline axes as a function of MD stretching ratio. The F_M , F_T , and F_N stand for the orientation factors of crystalline axis of interest with respect to MD, TD, and normal direction (ND) respectively. As can be seen, F_M of c -axis increases with drawing ratio while F_T and F_N decrease. This indicates that with increased draw ratio the c -axis tends to orient lamellae preferentially parallel to the MD direction. In contrast, F_M of a - and b -axes decreases as the stretching ratio increases. At the same time, F_T increases for b -axis and decreases for a -axis while the reverse occurs with the orientation

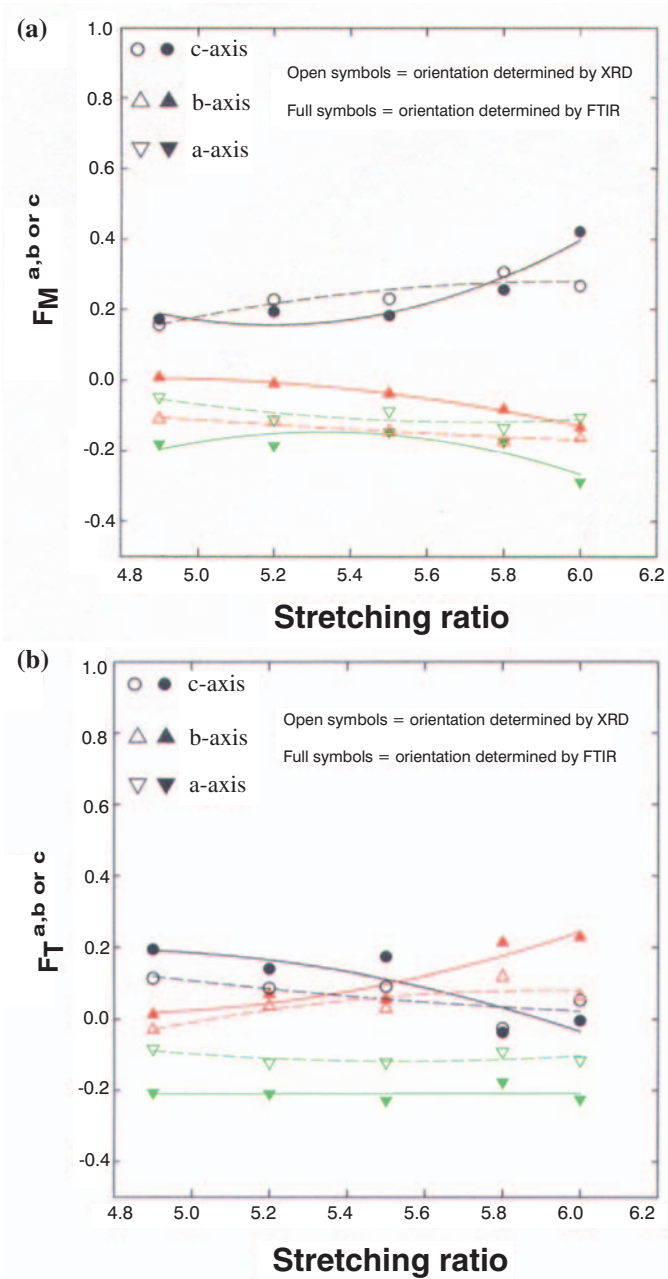


Figure 1. Orientation function, F : (a) F_M (machine direction); (b) F_T (transverse direction); and (c) F_N (normal direction).

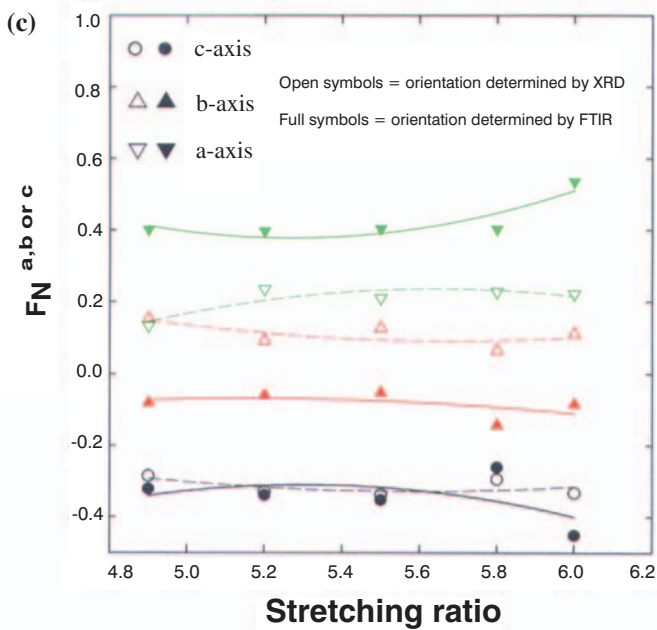


Figure 1. Continued.

towards ND (F_N). These results are contrary to those obtained with c -axis orientation and thus indicate clearly that a - and b -axes tend to orient away from MD and preferentially towards ND and TD respectively. This kind of behavior has already been observed with various PE films subjected to uniaxial stretching towards MD and restricted towards TD [13]. For the sake of comparison, the orientation functions assessed by means of FTIR and X-ray diffraction (XRD) techniques are both depicted in Figure 1. As can be seen, the orientation functions obtained from FTIR and XRD show the same trend. However, the numerical values are somewhat different. This type of result has already been reported in the literature [13,14]. The difference has been ascribed to the calculation procedure and/or the techniques themselves. With FTIR spectroscopy, the orientation of amorphous trans-conformers may contribute to the crystalline orientation factors and eventually yield different values than those obtained from XRD.

Figure 2 shows the micrographs obtained on selected etched films. As can be seen, the primary extruded tube (initial morphology, Figure 2(a)) has a random lamellar structure typical of balanced blown LLDPE films. For samples drawn up to 5.2, the lamellae are

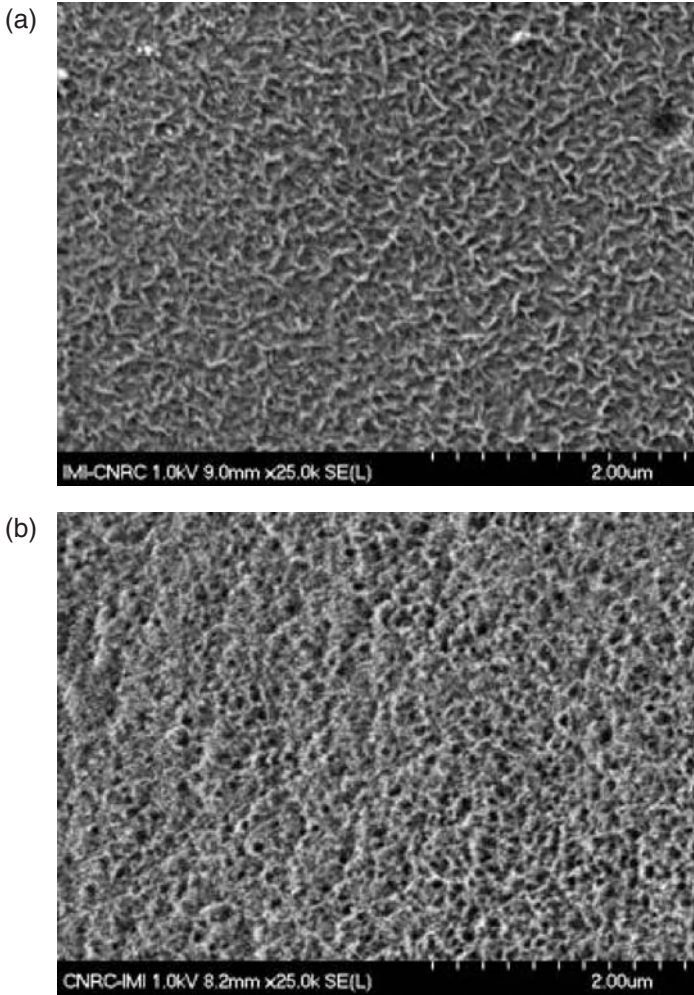


Figure 2. Scanning electron micrographs: (a) unstretched sample (i.e., primary extruded tube), sample stretched at; (b) 5.2; (c) 5.5; and (d) 6.0. MD direction is vertical.

still randomly oriented (Figure 2(b)). In contrast, above that stretching ratio, it was observed that the lamellae thicken, lengthen, and orient perpendicular to the MD (Figure 2(c) and (d)). The lamellar thickening can be accounted for by the occurrence of recrystallization phenomenon in the course of stretching. However, taking into account the results published before [7] one can conclude that the observed thickening

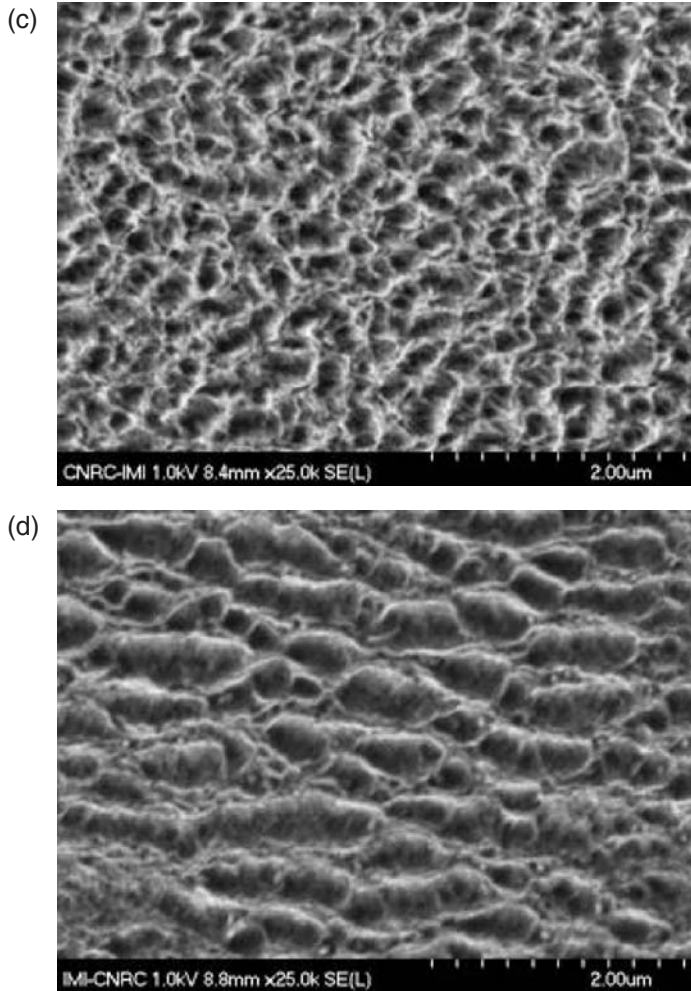


Figure 2. Continued.

of crystalline lamellae is in fact the unetched amorphous phase with very low mobility as a result of orientation below the melting point.

Figure 3 depicts the tensile strength in both machine and transverse direction as a function of c -axis orientation factor obtained from FTIR measurements. It can be seen that MD tensile strength increases and TD strength decreases as c -axis orientation toward MD increases. It is noteworthy that MD tensile strength seems to level off at about 119 MPa for $F_M^c > 0.25$, while the TD strength reaches a minimum of

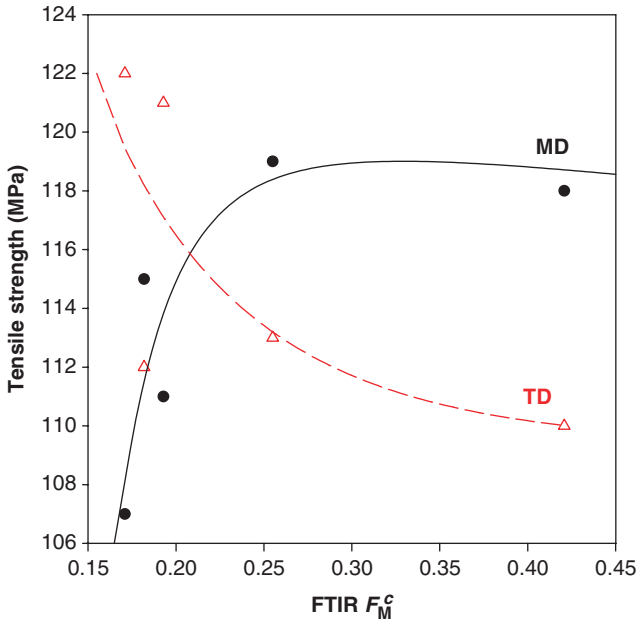


Figure 3. Tensile strength as a function of c -axis orientation towards MD.

about 110 MPa for $F_M^c > 0.40$. These results indicate that above a certain level of c -axis orientation, tensile strength is no longer dependent on the crystalline chain segments orientation. More data are still needed to confirm these results.

Figure 4 presents tear resistance in MD and TD as a function of c -axis orientation. It can clearly be observed that TD tear resistance remains unaffected by the increase of c -axis orientation, while MD tear resistance decreases until reaching a minimum of about 20 g/mil at $F_M^c \approx 0.40$. It is interesting to notice that as long as the F_M^c orientation factor is inferior to 0.2, and accordingly MD stretching ratio is inferior to 5.5, the MD tear resistance is higher than the TD tear resistance. As discussed previously, morphological analysis revealed that below a MD stretching ratio of 5.2, the lamellar arrangement remains somewhat random. In contrast, above that stretching ratio, lamellae tend to align perpendicular to the stretching direction. Consequently, the decrease of MD tear resistance can reasonably be described by this particular lamellar organization induced by the deformation. However, the reasons of why TD tear resistance seems unaffected by the stretching process remain unclear.

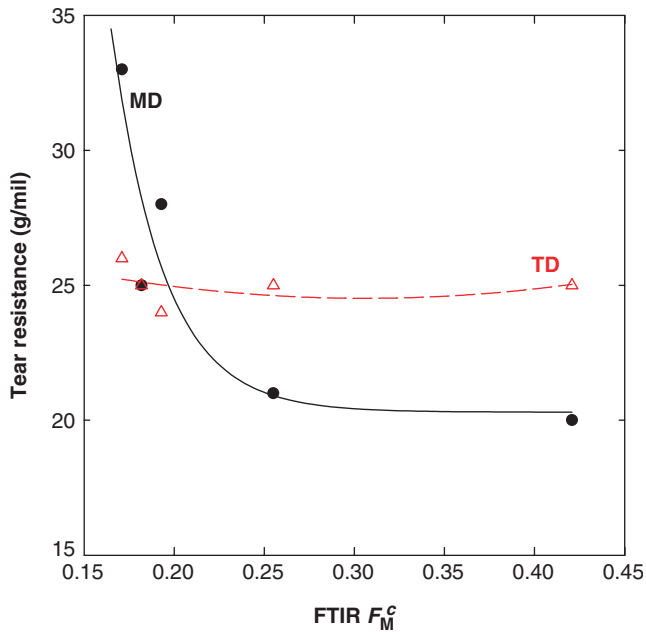


Figure 4. Tear resistance as a function of c -axis orientation towards MD.

CONCLUSIONS

The correlation between FTIR and WAXD results was observed. Despite the fact that the numerical values of orientation functions were somewhat different, the same trend was observed. The correlation between the observed morphology and the tear resistance of the film was also noted. The correlation between orientation function and tensile strength of the film was found. It was shown that the increase of c -axis orientation toward MD leads to the increase of MD tensile strength and to the decrease of TD tensile strength. The significant decrease in MD tear resistance was observed as well. Therefore, one can conclude that the crystalline structure orientation dramatically affects the mechanical properties of oriented films. The observed correlations allow the prediction of the properties of the film when one knows the orientation function. This may provide the possibility to design films with required properties in laboratory conditions by just stretching small samples of LLDPE below melting and investigating the orientation functions.

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BIOGRAPHIES

Arthur Bobovitch

Arthur Bobovitch received his PhD in Materials Engineering from Ben-Gurion University of the Negev in Beer-Sheva in 2005 where he received BSc and MSc degrees in 1993 and 1995 respectively. From 1995 until 1996 he worked in IMI(TAMI) as an engineer in Plastic lab and in 1996 he joined Syfan as a Lab Manager. In 1999 Arthur became Product Manager and in 2001 Vice President responsible for R&D and Quality. His research interests are focused on morphology, mechanical and viscoelastic properties of oriented polymers.

Saïd Elkoun

Dr. Saïd Elkoun received his PhD in Materials Science from the University of Science and Technology of Lille in France (1998). He joined the National Research Council of Canada in 2001 where he worked as a research associate at Industrial Materials Institute for 3 years. Since 2004, he has been Associate Professor at University of Science and Technology of Lille in France. His research topics are mainly focused on processing-structure-property relationships in polymer.

Abdellah Aji

Abdellah Aji earned his MScA and PhD in Chemical Engineering from École Polytechnique de Montreal and worked in research and development on polymers, particularly orientation of polymer films, rheology and blends, for the past 19 years. He is currently a Senior Research Officer at the Industrial Materials Institute of the National Research Council of Canada and has over 75 published articles in scientific journals.