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RESEARCH PAPER

Effects of Cast Extrusion Line Speed on the Crystallinity of LLDPE Stretch Films

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ABSTRACT

In this study, the influence of line speed on the crystallinity of linear low-density polyethylene (LLDPE) stretch films manufactured in a cast extrusion line was examined using differential scanning calorimetry (DSC) and wide-angle X-ray diffraction (WAXD). The multilayer LLDPE films were prepared at a wide range of line speeds. The DSC results showed that there was an increase in the crystallinity of films at higher line speeds. The crystallinity increased from 24.5 to 39.8 % while the line speed changed from 200 to 1000 m/min. Evaluating melting endotherms showed that the size of crystals was more uniform as the line speed increased. The crystallinity of films obtained from WAXD analysis exhibited the similar trend of DSC results, though their values were different. Additionally, there was a reduction in the crystal size calculated from WAXD data upon increasing the line speed. The observed increase in crystallinity and decrease in crystal size were due to the enhanced flow induced crystallization (FIC) as a result of greater shear stresses the polymer melt encountered at higher line speeds.

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1. INTRODUCTION

Polyethylene films are widely used in packaging applications due to their mechanical performance, barrier properties and low cost [1, 2]. An extensive packaging application of polyethylene films is stretch wrapping which is the most common method of load unitization to increase the handling efficiency during distribution [3]. Stretch films are essentially used to wrap/stretch around the palletized group of items to hold together and protect them during the transportation and warehousing [4, 5]. Linear low-density polyethylene (LLDPE) possesses high strength and stretchability and also superior tear resistance due to the introduction of short chain branches [6]. Therefore, LLDPE is the most accepted polymer used for the stretch wrapping packaging [2, 7].

Cast film extrusion and film blowing are the most common techniques for film manufacturing. However, LLDPE is prone to film instabilities in blown film extrusion that consequently affects the final film properties [8, 9]. Therefore, to avoid such instabilities the rate of film production is to be limited [8]. On the other hand, the cast

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film extrusion provides high line speeds for film processing which is of great importance from industrial point of view [10]. The processing parameters of cast extrusion including melt temperature, air gap, haul-off rate and also line speed influence the properties of the extruded film. Greater film extensibility and lower load retention are observed at higher melt temperatures, larger air gaps, and slower line speeds [11].

Anisotropic tensile behavior of trilayer extruded stretch films was investigated and the results showed a clear difference in machine and transverse direction mechanical properties [12]. Uniaxial deformation of LLDPE cast film at very fast stretching speed caused visible crazes in the film [13]. Castellani et al. who investigated the adhesive properties of LLDPE stretch films found that adhesion energy is related to LLDPE viscoelastic behavior [5]. Different LLDPE blends were used to prepare stretch films using blown film extrusion to obtain the suitable tearing properties [14].

Furthermore, the mechanical properties of extruded films such as modulus, strength and stretchability are affected by the crystallinity and crystal structure of the films which are determined by processing parameters [1, 15]. In addition to processing variables, the crystallinity and mechanical performance of cast LLDPE stretch films are also greatly influenced by chain structure, comonomer type and melt flow index (MFI) [2, 16]. Moreover, the crystallization during film processing influences the viscoelastic behavior of the molten polymer [17]. During the film processing, shear or extensional flow fields enhance the nucleation rate and the crystallization is accelerated [17–20]. Besides, during the crystallization and solidification of the molten extrudate, the rheological and relaxation behaviors change; as a result, oriented structures are developed in the final film [17, 19]. Thus, the ability to comprehend the details of crystal structures in film processing is an essential requirement.

Evaluating the effects of applying high-line speeds in cast extrusion of LLDPE cast films on their properties is lacking in the literature. In our earlier studies, the mechanical properties and chain orientation of multi-layered LLDPE stretch films prepared at high values of line speeds were investigated in detail [10, 21]. Therefore, as an extension of our previous studies, the present study aims at the evaluation of the crystallinity of five-layered LLDPE films manufactured using a cast film line operated at low to high line speeds.

2. EXPERIMENTAL SECTION

2.1. Materials

Film-grade linear low-density polyethylene (LLDPE) resins were supplied by Braskem Petrochemical Company to prepare multi-layered stretch films. Table 1 lists the density and melt flow index (MFI) values of the used LLDPE resins in addition to the percentage of each layer in the five-layered film. The LL-D grade was used as one of the surface layers (Figure 1) to achieve the cling properties.

Table 1: LLDPE properties and each layer percentage in the film

Resin (LLDPE)	Each layer percentage (wt %)	Density (g/cm^3)	MFI 190 °C/2.16 kg (g/10 min)
LL-A	14	0.918	3.5
LL-B	2×29	0.912	4.5
LL-C	14	0.919	2.7
LL-D	14	0.906	4.3

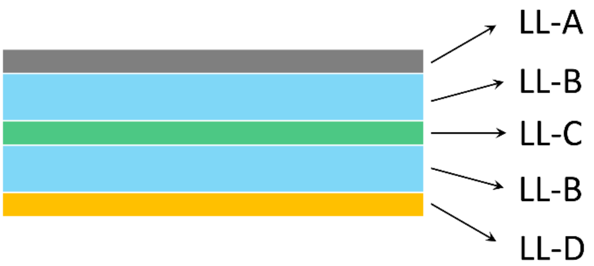

Figure 1: Composition and the stacking sequence of LLDPE layers (five layers) in the film

MFI values correlate with the processability and properties of LLDPE films. A lower MFI corresponds to higher head pressure, larger die gaps (to prevent melt fracture), and running at higher melt temperatures. However, a low MFI results in a higher tensile strength [22].

2.2. LLDPE film preparation

Five-layered films were prepared using an SML cast film line (SML Maschinengesellschaft mbH, Austria). The line included four extruders and a feedblock was used to produce five-layered cast films based on the composition listed in Table 1. The molten polymer exited the die vertically and subsequently contacted a chill roll with 1600 mm of diameter. A vacuum box web pinning and an electrostatic edge pinning were utilized for a close contact of the film with the chill roll. The conditions of the cast film extrusion were based on a procedure described previously [10, 21]. The thickness of the multi-layered LLDPE films was set to 12 µm. Various line speeds of 200, 600 and 1000 m/min were applied for the film preparation. Figure 1 shows the sequence of stacking layers of the film.

2.3. Characterization

2.3.1. Differential scanning calorimetry (DSC)

The thermal behavior of the films was characterized using a differential scanning calorimetry DSC1 STARe SW 13.0 system from Mettler Toledo, at a heating rate of 10 ºC/min. In the first heating run, 5 mg of samples were heated up from room temperature to 220°C. The reported percent degree of crystallinity results was obtained from the first heating scans using a heat of fusion of 290 J/g for a fully crystalline polyethylene [23].

2.3.2. Wide angle X-ray diffraction (WAXD)

The WAXD experiments were conducted using a D/Max Rapid II diffractometer with a Cu anode. The scans were recorded in the range of 2θ values from 5 to 45°. The percent degree of crystallinity (X_c) was calculated using the following equation based on the method of Hermans and Weidinger [24, 25]:

$$X_c(\%) = \frac{A_c}{A_c + A_a} \times 100 \tag{1}$$

A_c and A_a are crystalline and amorphous areas of the corresponding fitted peaks, respectively. Fityk program was used for the deconvolution of the WAXD data and peak fitting with Pseudo-Voigt functions.

3. Results and Discussion

In order to evaluate the effects of line speed on the crystallinity of LLDPE films, DSC analysis was conducted on the films. The DSC thermograms in Figure 2 indicate the melting endotherms exhibit greater area as the line speed increases from 200 to 1000 m/min. In addition, a sharper peak appeared in the melting curve for the highest line speed (1000 m/min). The quantitative data obtained from DSC experiments are listed in Table 2.

Comparing the endotherms (Figure 2) and the crystallinity values (Table 2) indicates that increasing the line speed leads to the crystallinity enhancement of the LLDPE films.

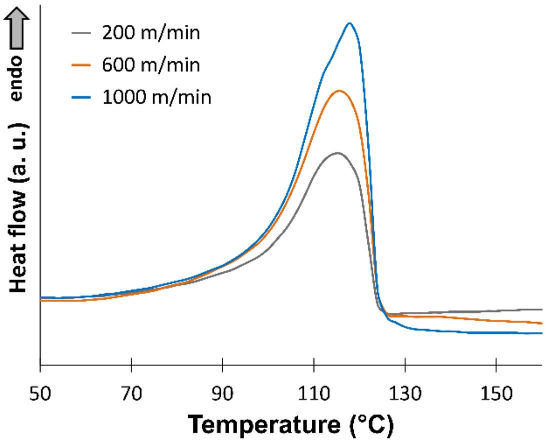

Figure 2: DSC thermograms of LLDPE films prepared at different line speeds

In addition, increasing the line speed enhances shear stress values experienced by the molten polymer in the die land and also reduces the time scales for the extrudate while exiting the die and reaching the cast roll to be relaxed before the crystallization. Consequently, the crystallinity of LLDPE cast films increases as a result of flow induced crystallization (FIC) which decreases the entropic barrier for the crystallization [17]. It is worth mentioning that since both the line speed and chill roll rotating speed increase correspondingly, to keep the film thickness constant, elongation forces applied to molten polymers are practically similar for the different line speeds. There is an increase in the melting temperature (T_m) of LLDPE film prepared at the line speed of 1000 m/min (Table 2), which might be due to the emerging aligned crystalline structures (shish-like) as the molten polymer encountered higher stress values at the line speed of 1000 m/min.

The values of full width at half maximum (FWHM) decrease and the height values of melting curves increase as the line speed increases from 200 to 1000 m/min (table 2) indicating a narrower melting curve for the higher line speed. This narrower melting endotherm shows a more uniform crystal size for the films prepared at the higher line speeds [23], which is in agreement with the results obtained from AFM micrographs illustrated in our previous article (not shown here) and indicates a more uniform and smaller crystal lamellae in the LLDPE films prepared at a high line speed [10].

Table 2: Data obtained from DSC results

Line speed (m/min)	Crystallinity (%)	T_m (°C)	FWHM (°C)	Peak height (W/g)
200	24.5	116.7	19.4	2.2
600	28.6	116.8	17.6	3.1
1000	39.8	118	17.7	4.2

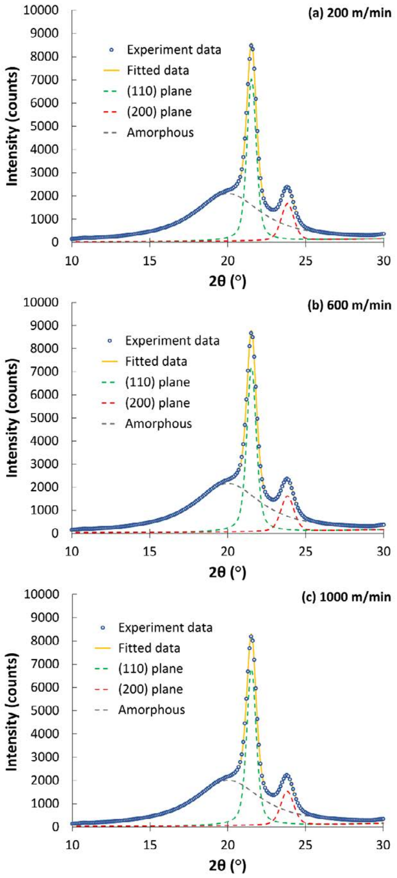

Figure 3: WAXD diffractograms obtained for LLDPE films at line speeds of (a) 200 m/min, (b) 600 m/min, (c) 1000 m/min, with curve decompositions using Pseudo-Voigt function fits

WAXD analysis was carried out for the cast films to further evaluate the crystalline structure of the films. The WAXD patterns and the decomposed crystalline peaks and amorphous halo are illustrated in Figure 3. As the figure shows, the line speed does not change the crystalline modification of LLDPE films and the (110) and (200) crystal planes representing the orthorhombic crystal structure are clearly seen in the WAXD patterns [26, 27].

The crystallinity of films calculated from peak areas of crystalline and amorphous regions as well as full width at half maximum (FWHM) of crystalline planes and the corresponding mean crystal sizes are presented in Table 3. Similar to DSC results, there is a trend in the crystallinity enhancement as the line speed increases; however, the crystallinity values obtained from DSC analysis differ from those of WAXD experiments. This discrepancy may arise from the different techniques used for the crystallinity measurements. In addition, since the films are composed of different LLDPE layers to prepare multilayer films, applying different methods to calculate the crystalline content may lead to dissimilar results.

Table 3: Data obtained from WAXD results

Line speed (m/min)	Crystallinity (%)	FWHM (110) (°)	FWHM (200) (°)	L (110) (nm)	L (200) (nm)
200	32.8	0.663	0.87	12	25
600	33.4	0.662	0.95	12	24
1000	35.2	0.725	1.043	11	23

The crystal sizes along the (110) and (200) planes calculated from FWHM values by using Scherrer equation [28] indicate that increasing the line speed results in a reduction in crystal sizes. This observation is in accordance with the DSC results which indicated that a more uniform crystal size is obtained as the line speed increases. As it was discussed previously in this article, increasing the line speed enhances the flow induced crystallization (FIC). Therefore, the crystallinity of the films increases and the crystal sizes decrease due to FIC effects [18, 19].

4. CONCLUSIONS

In this study, the crystallinity of LLDPE films prepared in cast film extrusion process in a wide range of line speeds was evaluated using DSC and WAXD measurements. The DSC results showed that increasing the line speed enhances the crystallinity of cast films. In addition, the shape of melting curves in terms of FWHM and peak heights are narrower at higher line speeds showing a more uniform crystal structure. The WAXD data also confirmed that increasing the line speed leads to higher crystallinity of LLDPE films, however, the values of crystallinity obtained from the DSC and WAXD experiments were dissimilar. Furthermore, crystal size along (110) and (200) planes decreases as the line speed increases. The higher crystallinity and smaller crystal size observed at higher line speeds were due to greater shear stresses experienced by the molten polymer in the die land and lower time scales for the molten polymer for relaxation before crystallization which enhanced the flow-induced crystallization.

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REFERENCES

[1] S. Auksornkul, S. Soontaranon, C. Kaewhan, P. Prasassarakich. “Effect of the blow-up ratio on morphology and engineering properties of three-layered linear low-density polyethylene blown films”. *J. Plast. Film Sheeting*, vol. 34, pp. 27–42, 2018.

[2] C.M. Small, G.M. Mcnally, G. Garrett, W.R. Murphy. “The Characteristics of Polyethylene Film for Stretch and Cling Film Applications”. *Dev. Chem. Eng. Miner. Process*, vol. 12, pp. 5–20, 2008.

[3] J. Singh, E. Cernokus, K. Saha, S. Roy. “The Effect of Stretch Wrap Prestretch on Unitized Load Containment”. *Packag. Technol. Sci.*, vol. 27, pp. 944–961, 2014.

[4] P.M. German, C.B. Johnson, M.G. Williams. “Polyethylene Stretch Film”. US 9,388,306 B2, 2016. https://patents.google.com/patent/US9388306B2/en, 2016.

[5] L. Castellani, A. Castiglioni, D. Ferri, A. Baraldi, L. Martinelli, S. Rotunno. “Rate effects on adhesion energy between polyethylene films and different substrates”. *Eng. Fract. Mech.*, vol. 149, pp. 387–401, 2015.

[6] S. Feng, Y. Lin, W. Yu, O. Iqbal, J.C. Habumugisha, W. Chen, L. Meng, A. Lu, L. Li. “Stretch-induced structural transition

of linear low-density polyethylene during uniaxial stretching under different strain rates". *Polymer (Guildf)*, vol. 226, pp. 123795, 2021.

[7] M. Rennert, S. Fiedler, M. Nase, M. Menzel, S. Günther, J. Kressler, W. Grellmann. "Investigation of the migration behavior of polyisobutylene with various molecular weights in ethylene/α-olefin copolymer blown stretch films for improved cling properties". *J. Appl. Polym. Sci.*, vol. 131, pp. 40239, 2014.

[8] H. Zhao, Q. Zhang, S. Ali, L. Li, F. Lv, Y. Ji, F. Su, L. Meng, L. Li. "A real-time WAXS and SAXS study of the structural evolution of LLDPE bubble". *J. Polym. Sci. Part B Polym. Phys.*, vol. 56, pp. 1404–1412, 2018.

[9] M. Niaounakis, E. Kontou. "Effect of LDPE on the thermomechanical properties of LLDPE-based films". *J. Polym. Sci. Part B Polym. Phys.*, vol. 43, pp. 1712–1727, 2005.

[10] H. Bayazian, A. Yadegari, V. Schöppner. "Probing tensile properties of LLDPE stretch films prepared in cast extrusion process". *Polym. Bull.*, pp. 1–14, 2021. https://doi.org/10.1007/s00289-021-03599-9

[11] J.A. Degroot, A.T. Doughty, K.B. Stewart, R.M. Patel. "Effects of cast film fabrication variables on structure development and key stretch film properties". *J. Appl. Polym. Sci.*, vol. 52, pp. 365–376, 1994.

[12] M.I. Babaghayou, A.H.I. Mourad, N. Cherunurakal. "Anisotropy evaluation of LDPE/LLDPE/PIB trilayer films". 2020 Advances in Science and Engineering Technology International Conferences, ASET 2020. *Institute of Electrical and Electronics Engineers Inc.* (2020). https://doi.org/10.1109/ASET48392.2020.9118263

[13] W. Du, Y. Ren, Y. Tang, Y. Shi, X. Yao, C. Zheng, X. Zhang, M. Guo, S. Zhang, L.Z. Liu. "Different structure transitions and tensile property of LLDPE film deformed at slow and very fast speeds". *Eur. Polym. J.* vol., 103, pp. 170–178, 2018.

[14] D. Nagy, K. Belina, E. Kókai. "Research and Manufacture of Stretch Films using LLDPE blends". IOP Conference Series: Materials Science and Engineering. pp. 012064. *Institute of Physics Publishing* (2018).

[15] V. Compañ, L.F. Del Castillo, S.I. Hernández, M.M. López-González, E. Riande. "On the crystallinity effect on the gas sorption in semicrystalline linear low density polyethylene (LLDPE)". *J. Polym. Sci. Part B Polym. Phys.*, vol. 45, pp. 1798–1807, 2007.

[16] G.M. McNally, C.M. Small, W.R. Murphy, G. Garrett. "The Effect of Polymer Properties on the Mechanical Behavior and Morphological Characteristics of Cast Polyethylene Film for Stretch and Cling Film Applications". *J. Plast. Film Sheeting.*, vol. 21, pp. 39–54, 2005.

[17] M. Andreev, D.A. Nicholson, A. Kotula, J.D. Moore, J. den Doelder, G.C. Rutledge. "Rheology of crystallizing LLDPE." *J. Rheol.*, vol. 64, pp. 1379–1389, 2020.

[18] S.H. Tabatabaei, P.J. Carreau, A. Ajji. "Effect of processing on the crystalline orientation, morphology, and mechanical properties of polypropylene cast films and microporous membrane formation". *Polymer (Guildf)*, vol. 50, pp. 4228–4240, 2009.

[19] S. Yakovlev, D. Fiscus, P. Brant, J. Butler, D.G. Bucknall, K.H. Downing. "Mechanism of stress induced crystallization of polyethylene". *Polymer (Guildf)*, vol. 175, pp. 25–31, 2019.

[20] H. Zhao, Q. Zhang, L. Li, W. Chen, D. Wang, L. Meng, L. Li. "Synergistic and Competitive Effects of Temperature and Flow on Crystallization of Polyethylene during Film Blowing". *ACS Appl. Polym. Mater.*, vol. 1, pp. 1590–1603, 2019.

[21] V. Schöppner, H. Bayazian, A. Yadegari, H. Haddad. "Orientation in LLDPE cast films manufactured under different processing parameters". AIP Conference Proceedings. pp. 020022. *American Institute of Physics Inc.* (2020).

[22] K.G. Schurzky. "Design Parameters for LLDPE Film Resin Selection". *J. Plast. Film Sheeting.*, vol. 1, pp. 142–151, 1985.

[23] A. Yadegari, J. Morshedian, H.A. Khonakdar, U. Wagenknecht, G. Heinrich, M. Malanin, K.J. Eichhorn, D. Fischer. "Correlation of crystal alignment with interphase content in oriented high density polyethylene cast films". *CrystEngComm.*, vol. 18, pp. 2337–2346, 2016.

[24] P.H. Hermans, A. Weidinger. "On the determination of the crystalline fraction of polyethylenes from X-ray diffraction". *Die Makromol. Chemie.*, vol. 44, pp. 24–36, 1961.

[25] P.P. Kundu, J. Biswas, H. Kim, S. Choe. "Influence of film preparation procedures on the crystallinity, morphology and mechanical properties of LLDPE films". *Eur. Polym. J.*, vol. 39, pp. 1585–1593, 2003.

[26] Y. Takahashi, T. Ishida, M. Furusaka. "Monoclinic-to-orthorhombic transformation in polyethylene". *J. Polym. Sci. Part B Polym. Phys.*, vol. 26, pp. 2267–2277, 1988.

[27] H. Uehara, M. Kakiage, T. Yamanobe, T. Komoto, S. Murakami. "Phase Development Mechanism during Drawing from Highly Entangled Polyethylene Melts". *Macromol. Rapid Commun.*, vol. 27, pp. 966–970, 2006.

[28] S.J.S. Qazi, A.R. Rennie, J.K. Cockcroft, M. Vickers. "Use of wide-angle X-ray diffraction to measure shape and size of dispersed colloidal particles". *J. Colloid Interface Sci.* vol. 338, pp. 105–110, 2009.

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مقاله تحقیقاتی

بررسی اثر سرعت خط فرایند اکستروژن بر بلورینگی فیلم های استرچ پلی اتلین سبک خطی

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چکیده

در این مطالعه، آثار سرعت خط تولید فیلم بر بلورینگی فیلم‌های استرچ پلی اتیلن سبک خطی (LLDPE) تهیه شده در فرایند اکستروژن با استفاده از گرما سنجی روبشی تفاضلی (DSC) و پراش اشعه ایکس با زاویه باز (WAXD) مورد بررسی قرار گرفته است. فیلم‌های چندلایه LLDPE در بازه‌ی وسیعی از سرعت خط تهیه شدند. نتایج DSC نشان دادند که با افزایش سرعت خط، بلورینگی فیلم بیشتر می‌شود و اندازه بلور نیز یکنواخت‌تر می‌گردد. به طوری که با افزایش سرعت خط از ۲۰۰ به ۱۰۰۰ m/min، بلورینگی نیز از ۲۴/۵ به ۳۹/۸ درصد افزایش می‌یابد. بلورینگی به دست آمده از آزمون WAXD نیز، همانند نتایج DSC، روند صعودی بلورینگی با سرعت خط را نشان دادند، هرچند که مقادیر بلورینگی به دست آمده از این دو آزمون تفاوت داشتند. اندازه‌گیری ضخامت بلور نشان داد که اندازه بلور در سرعت‌های بالاتر خط کاهش می‌یابد. افزایش بلورینگی و کاهش اندازه بلور فیلم‌ها در اثر تبلور القا شده با جریان (FIC) در نتیجه‌ی افزایش تنش برشی تحمل‌شده توسط مذاب پلیمری با افزایش سرعت خط بوده است.

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