Effects of Melt-Extension and Annealing on Row-Nucleated Lamellar Crystalline Structure of HDPE Films

Sang-Young Lee,[1] Soon-Yong Park,[2] Heon-Sik Song[2]

[1]Batteries R&D, LG Chem, Yusong-gu, Daejon 305-380, Korea
[2]Information and Electronic Materials R&D, LG Chem, Yusong-gu, Daejon 305-380, Korea

ABSTRACT: The row-nucleated lamellar crystalline structure of high-density polyethylene (HDPE) films was prepared by applying elongation stress to HDPE melt during T-die cast film extrusion and subsequently annealing the extruded films. This unusual crystalline structure was analyzed in terms of lamellar crystalline orientation, long-period lamellar spacing, crystallite size, and degree of crystallinity. The contribution of melt-extension represented by draw-down-ratio (DDR) to the overall orientation was found to be most noticeable than other processing variables. Meanwhile, the long-period lamellar spacing, the crystallite size, and the degree of crystallinity were influenced predominantly by the annealing temperature. Finally, the processing (melt extension and annealing temperature) – structure (lamellar crystalline structure) – property (hard elasticity) relationship of HDPE films was investigated. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 3326–3333, 2007

Key words: HDPE; crystallization; annealing; lamellar; structure–property relations

INTRODUCTION

Over the past years, "hard elastic" polymers have attracted much attention because of their possible applications to precursor films for preparing microporous membranes.[1–18] They are characterized by high modulus of elasticity, reversible deformation, energetic retractive force, and constant cross-sectional area during deformation. These unusual properties are believed to be due to their "row-nucleated lamellar crystalline" structures that comprise rows of crystalline lamellae arranged preferentially normal to draw direction and connected by tie chains. The lamellar crystalline structure can be formed when polymers having high degree of crystallinity are melt-extruded with experiencing elongation stress and then recrystallized, which is called as stress-induced crystallization.[1–9]

When the hard elastic polymer is annealed and extended in the orientation direction, the portions of crystalline lamellae that are not connected by tie chains move apart, which leads to the bending of crystalline lamellae and the formation of micropores between them.[10–14]

Therefore, to have a comprehensive understanding of the microporous membrane formation, a more

Correspondence to: Dr. S.-Y. Lee (syleeq@lgchem.com).

quantitative analysis on the processing–structure–property relationship of hard elastic precursor films should be preceded. In this study, the effects of processing variables such as the screw rpm and the take-up speed (during T-die cast film extrusion) and the annealing on the row-nucleated lamellar crystalline structures in the high-density polyethylene (HDPE) films were examined. The row-nucleated lamellar crystalline structures were analyzed in terms of lamellar crystalline orientation, long-period lamellar spacing, crystallite size, and degree of crystallinity. Finally, the relationship between the lamellar crystalline structure of HDPE films and their hard elastic properties was investigated.

EXPERIMENTAL

Preparation of HDPE films

A commercial grade of HDPE resin [melt index (g/10 min, 190°C, 2160 g) = 0.35] was used. The HDPE resin was melt-extruded through a T-die under controlled processing conditions (Fig. 1). During the T-die extrusion, the uniaxial (machine direction, MD) stretching was applied to the HDPE melt, which results in the oriented crystalline structures.[19–21] The melt flow rate at die exit and the degree of melt extension were varied by controlling either the velocity of melt outflow from die exit or the rotation velocity of take-up roll (chill roll). The degree of
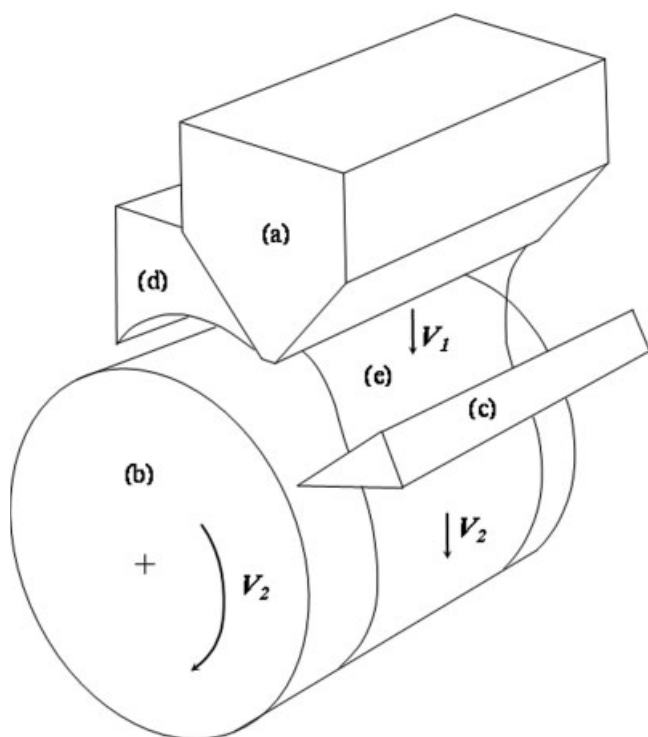
Figure 1 Schematic representation of T-die cast film extrusion. (a) T-die; (b) Take-up roll; (c) Air knife; (d) Vacuum box; and (e) HDPE melt.

melt extension was described as draw-down-ratio (DDR) $= V_2/V_1$, where V_1 is the velocity of melt outflow from die exit and V_2 is the linear velocity of rotation of take-up roll. Another factor influencing the structural rearrangement of HDPE films, i.e., annealing temperature, is controlled by annealing the extruded films for 1 h at various temperatures (from 95°C to 125°C) in a hot oven. The detailed processing variables for preparation of the HDPE films were summarized in Table I.

Analysis

The birefringence (BR) of HDPE films was measured on a polarizing microscope using N and K analyzer1200 (N and K Technology, USA) with varying orders of retardation. The melting peak temperature and the heat of fusion of HDPE films were recorded from the DuPont Thermal Analyst 2000 model differential scanning calorimeter (DSC) at a heating rate of 10°C/min. The lamellar thickness and its distribution were calculated by applying the DSC experimental results to the Thomson equation.[22,23] The elastic recovery (ER) of HDPE films was determined from a stress–strain curve during cyclic loading of samples by using a Zwick 1100 tensile tester (Zwick, Germany), which can be used as an index for representing

the structural arrangement and the hard elasticity of lamellar crystalline structure. The initial length of test samples was 50 mm, the strain rate was 100%/min, and the maximum tensile strain was 100%. After the sample is extended to 100% strain, jaws of the apparatus are reversed at the same speed until the distance between them becomes the same as at the start of the test, i.e., the original gauge length. The jaws are again immediately reversed and are stopped as soon as the stress begins to increase from zero point. The ER is then calculated using eq. (1)[6,7,10–13]:

$$
\begin{aligned}
\text{Elastic Recovery (ER, \%)} = 100 \\
\times \{(\text{total length when extended}) \\
- (\text{final distance between jaws})\}/ \\
\{\text{length added when extended}\} \quad (1)
\end{aligned}
$$

The lamellar crystalline morphology of HDPE films was observed from a JSM-6340F (JEOL, Japan) field emission scanning electron microscopy (FE-SEM).

RESULTS AND DISCUSSION

The crystalline structures and the properties of HDPE films were investigated as a function of melt flow rate at die exit (V_1), DDR, and annealing temperature. Figure 2 shows that the BR of HDPE films tends to increase with V_1, DDR, and annealing temperature. The BR measurement is known to be an effective way for characterizing the overall orientation of hard elastic materials.[8,14] The high BR is possibly attributed to the lamellar crystalline and molecular orientation. The influence of V_1, DDR, and annealing temperature on the BR was quantitatively examined. In Figure 2, from the slopes, $\Delta(\text{BR} - V_1) = 0.005$, $\Delta(\text{BR} - \text{DDR}) = 0.025$, and $\Delta(\text{BR} - T_{\text{ann}}) = 0.018$ were obtained, respectively. This presents

TABLE I
Processing Variables for Preparing Hard Elastic HDPE Films

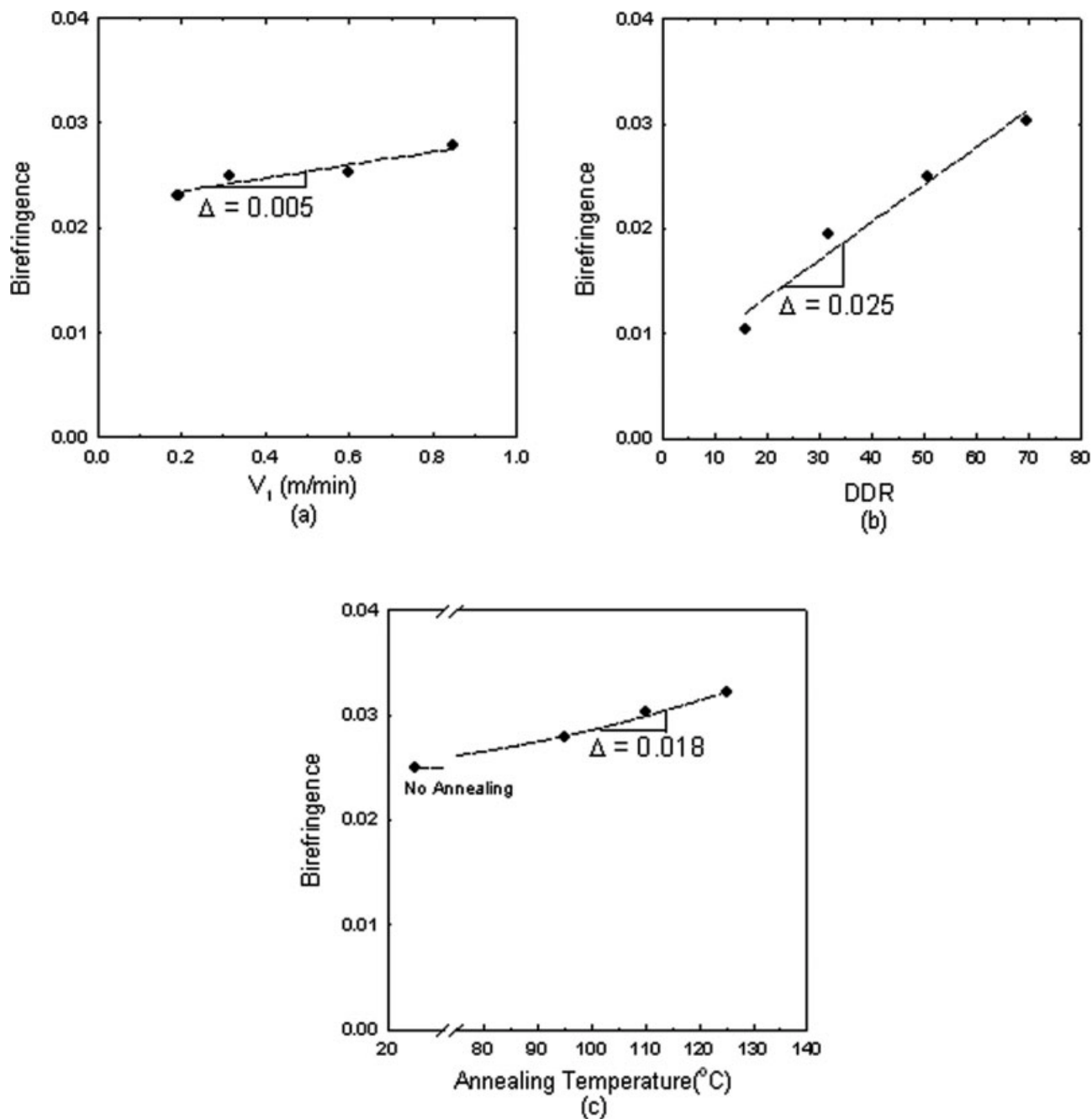| Sample no.	V_1 (m/min)	DDR	Annealing temperature (°C)
V_1-1	0.193	51.9	None
V_1-2	0.316	50.6	None
V_1-3	0.600	48.3	None
V_1-4	0.847	49.6	None
DDR-1	0.316	15.8	None
DDR-2	0.316	31.6	None
DDR-3	0.316	50.6	None
DDR-4	0.316	69.6	None
Anneal-1	0.316	50.6	None
Anneal-2	0.316	50.6	95
Anneal-3	0.316	50.6	110
Anneal-4	0.316	50.6	125

Figure 2 Effects of melt flow rate at die exit (V_1), degree of melt extension (DDR), and annealing temperature (T_{ann}) on birefringence (BR) of HDPE films. (a) BR versus V_1. (b) BR versus DDR. (c) BR versus T_{ann}.

that the DDR is most effective in increasing the overall orientation of HDPE chains.

Meanwhile, the effect of processing variables on the overall tendency of apparent lamellar thickness of HDPE films was examined by measuring the melting peak temperature ($T_{m, peak}$) and the heat of fusion (ΔH_m) from the DSC results. It is suggested that at a given temperature, for a sample of molten polymer, the rate of heat consumption is

proportional to the fraction of crystalline lamellae. The apparent lamellar thickness could be estimated by considering Thomson equation,[22,23] $T_m = T_m^0(1 - 2\sigma_e/\Delta H_m^0 \mathscr{L})$, though this equation is considered to hold some simple assumptions, where T_m is the observed melting point of lamellae of thickness $\mathscr{L}$, T_m^0 is the equilibrium melting point of an infinite crystal ($T_m^0 = 415$ K for polyethylene[22]), σ_e is the surface free energy of the basal
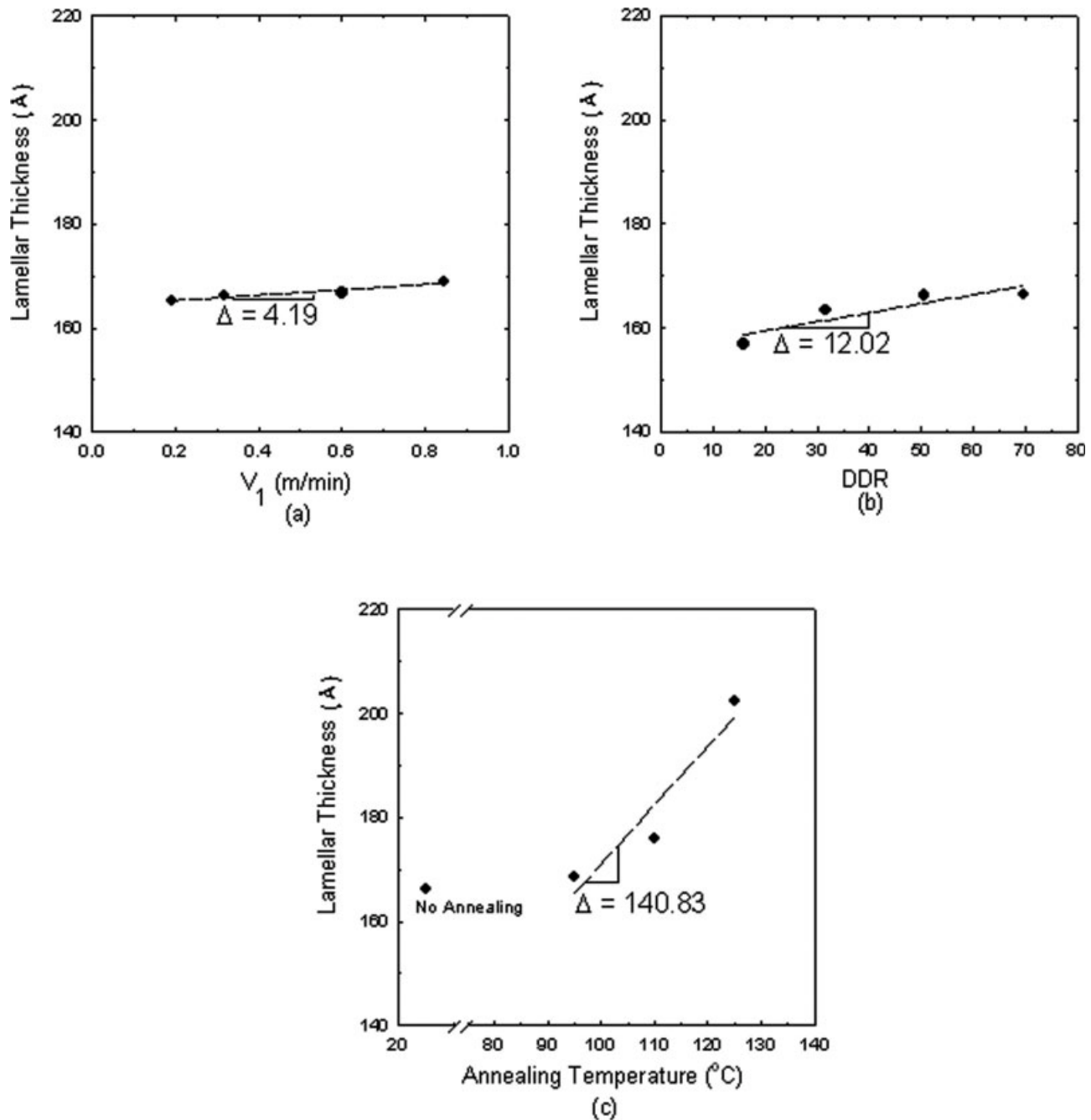
Figure 3 Effects of melt flow rate at the die exit (V_1), degree of melt extension (DDR), and annealing temperature (T_{ann}) on apparent lamellar thickness ($\mathscr{S}_{app}$) of HDPE films. (a) $\mathscr{S}_{app}$ versus V_1. (b) $\mathscr{S}_{app}$ versus DDR. (c) $\mathscr{S}_{app}$ versus T_{ann}.

plane ($\sigma_e = 6.09 \times 10^{-2}$ J/m^2 for polyethylene[22]), ΔH_m^0 is the enthalpy of fusion per unit volume ($\Delta H_m^0 = 2.88 \times 10^{-8}$ J/m^2 for polyethylene[22]), and $\mathscr{S}$ is the lamellar thickness. The calculated lamellar thickness and its overall tendency are summarized in Figure 3, which shows that the apparent lamellr thickness is influenced noticeably by the annealing temperature than by other processing variables.

To have a more detailed understanding of the effect of annealing process on the crystalline structure, the changes of T_m and ΔH_m are investigated as a function of the annealing temperature. Figure 4(a) exhibits that as the annealing temperature increases to 125°C from room temperature, the T_m changes from 131°C to 133°C. In contrast, the ΔH_m was observed to increase from 190.9 to 222.0 J/g, which reveals that compared with the crystal perfectness
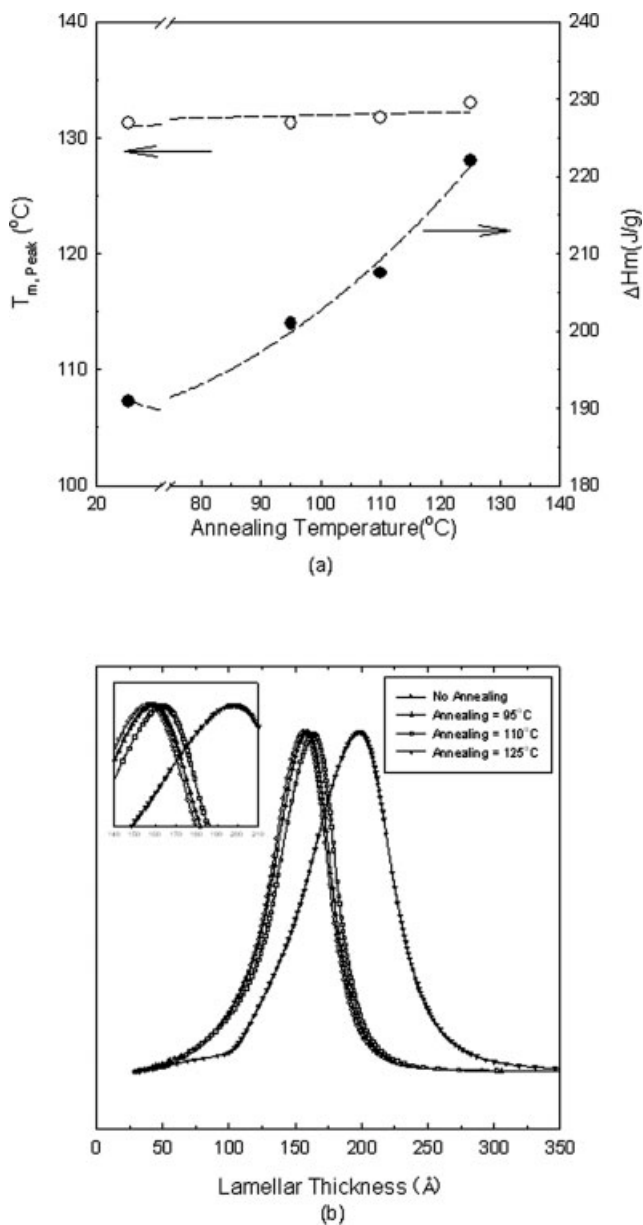
Figure 4 Effects of annealing temperature (T_{ann}) on melting peak temperature ($T_{m, peak}$) and lamellar thickness distribution ($\mathscr{S}$) of HDPE films. (a) $T_{m, peak}$ versus T_{ann}. (b) $\mathscr{S}$ as a function of T_{ann}.

(reflected by T_m), the overall degree of crystallinity (reflected by ΔH_m) was significantly affected by the annealing temperatures. The lamellar thickness distribution was calculated by using the Thomson equation. Figure 4(b) exhibits the distribution of lamellar thickness annealed at various temperatures. As the annealing temperature increases, the lamellar thickness tends to be larger and its distribution becomes broad. It is possibly expected that under high annealing temperature, involving the segments of loose tie chains into the crystallites is probably induced, which may result in the increase

of lamellae thickness (i.e., long-period lamellar spacing) and the increase in the overall degree of crystallinity. Chen et al.[14] suggested that by employing small-angle X-ray scattering (SAXS) analysis, long-period lamellar spacing increases with annealing temperature up to melting peak temperature.

The ER can be used as an indicator for characterizing the elastic deformation properties of lamellar crystalline structures.[6,7,10–13] An ideal model of hard elastic material presents its structure as a combination of stacks of lamellae arranged perpendicular to melt flow direction.[1–5,15–17] In Figure 5, it is shown that the ER becomes larger as V_1, DDR, and annealing temperature increases. Considering the slope of ER against V_1 and DDR, it is also observed that the ER appears to be more dependent on the DDR rather than the V_1, which is consistent with our previous results on the BR. Besides the stress conditions, the annealing temperature is also found to largely influence the ER [Fig. 5(c)]. Rosova et al.[7] suggested that as the annealing temperature increases, the length of polymer chain folds starts to increase and the chain segments in the amorphous region are drawn into the crystallites, yielding the narrower length distribution of tie chains and the larger number of stretched tie chains. Within interlamellar regions containing a high concentration of stretched tie chains, these tie chains remain intact and function as crosslinks, which may be responsible for the elastic character of lamellar bending.

This elastic recoverable nature of HDPE films is also evidently observed from the FE-SEM images that indicate the anisotropic lamellar crystalline structures (Fig. 6). It is seen that when the high elongation stress was applied, the crystalline lamellae tilted toward preferential alignment with respect to stretching direction and the lamellar twisting hardly occurred, resulting in a well-developed stacked lamellar structure [Fig. 6(a,d)]. Meanwhile, the annealing temperature was observed to affect the lamellar thickness rather than the alignment direction of the crystalline structure [Fig. 6(e,f)], which is consistent with the previous DSC results (Fig. 4) on the lamellar crystalline structures.

Finally, by summarizing the results of this study, we can figure out the processing (DDR and annealing temperature) – structure (lamellar crystalline alignment) – property (ER) relationship. The preferential lamellar crystalline alignment with respect to the stress direction (governed mainly by the DDR) and the larger long-period lamellar spacing, i.e., the larger number of stretched tie chains (governed mainly by the annealing temperature) are observed to have a significant influence on the increase of the ER.
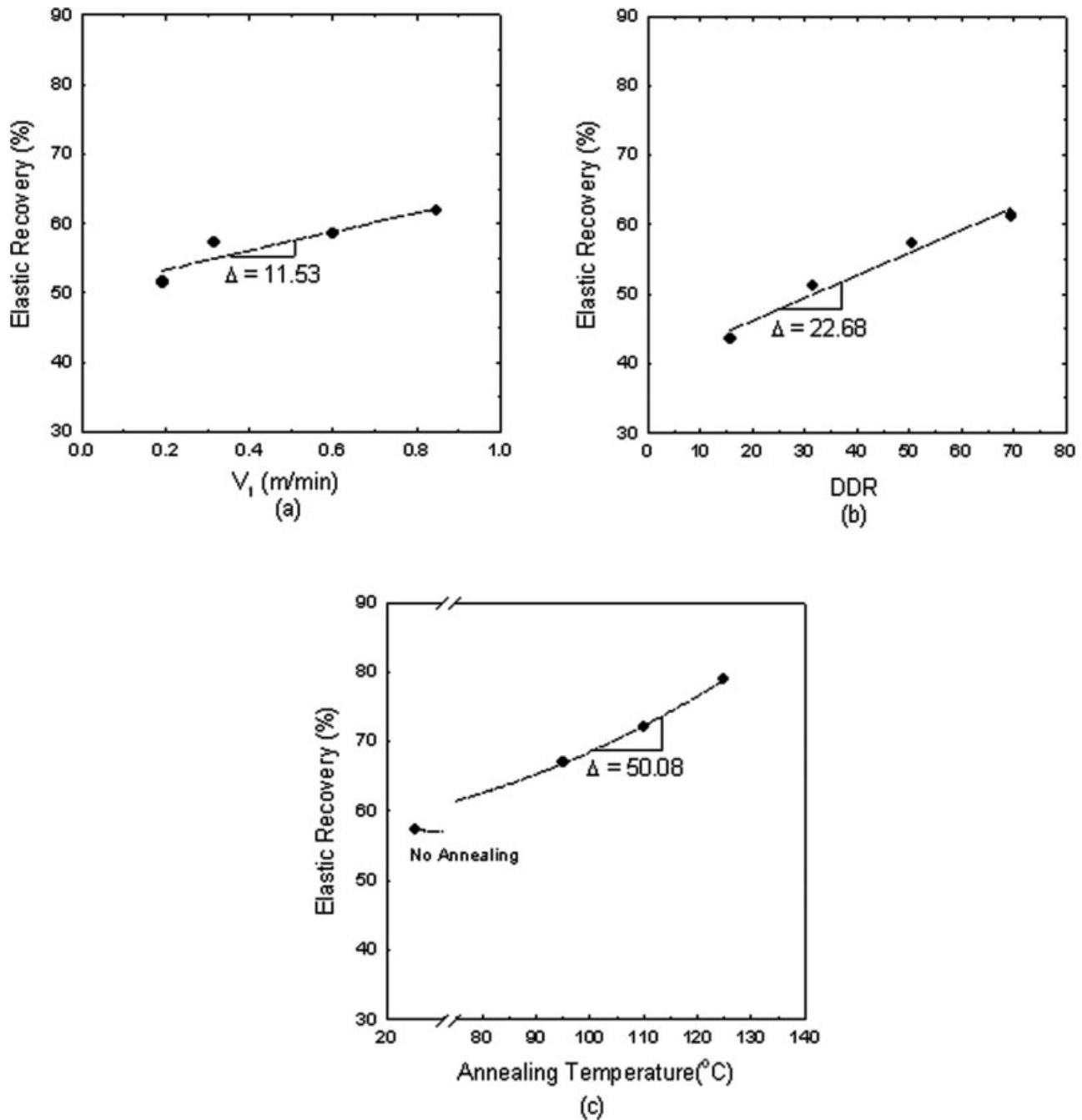
Figure 5 Effects of melt flow rate at die exit (V_1), degree of melt extension (DDR), and annealing temperature (T_{ann}) on elastic recovery (ER) of HDPE films. (a) ER versus V_1. (b) ER versus DDR. (c) ER versus T_{ann}.

CONCLUSIONS

In this study, the effects of the stress-induced crystallization during T-die cast film extrusion and the subsequent annealing process on the structure and the properties of HDPE films were investigated. The row-nucleated lamellar crystalline structure of HDPE films was quantitatively analyzed in terms of the lamellar crystalline orientation, the long-period lamellar spacing, the crystallite size, and the crystallinity.

The contribution of DDR to the overall orientation was found to be most noticeable than other processing variables. Meanwhile, the long-period lamellar spacing, the crystallite size, and the degree of crystallinity were influenced predominantly by the annealing temperature. The relationship between the lamellar crystalline structure of HDPE films and their hard elastic properties represented by the ER was investigated, which reveals that the well-oriented lamellar crystalline structure and the larger
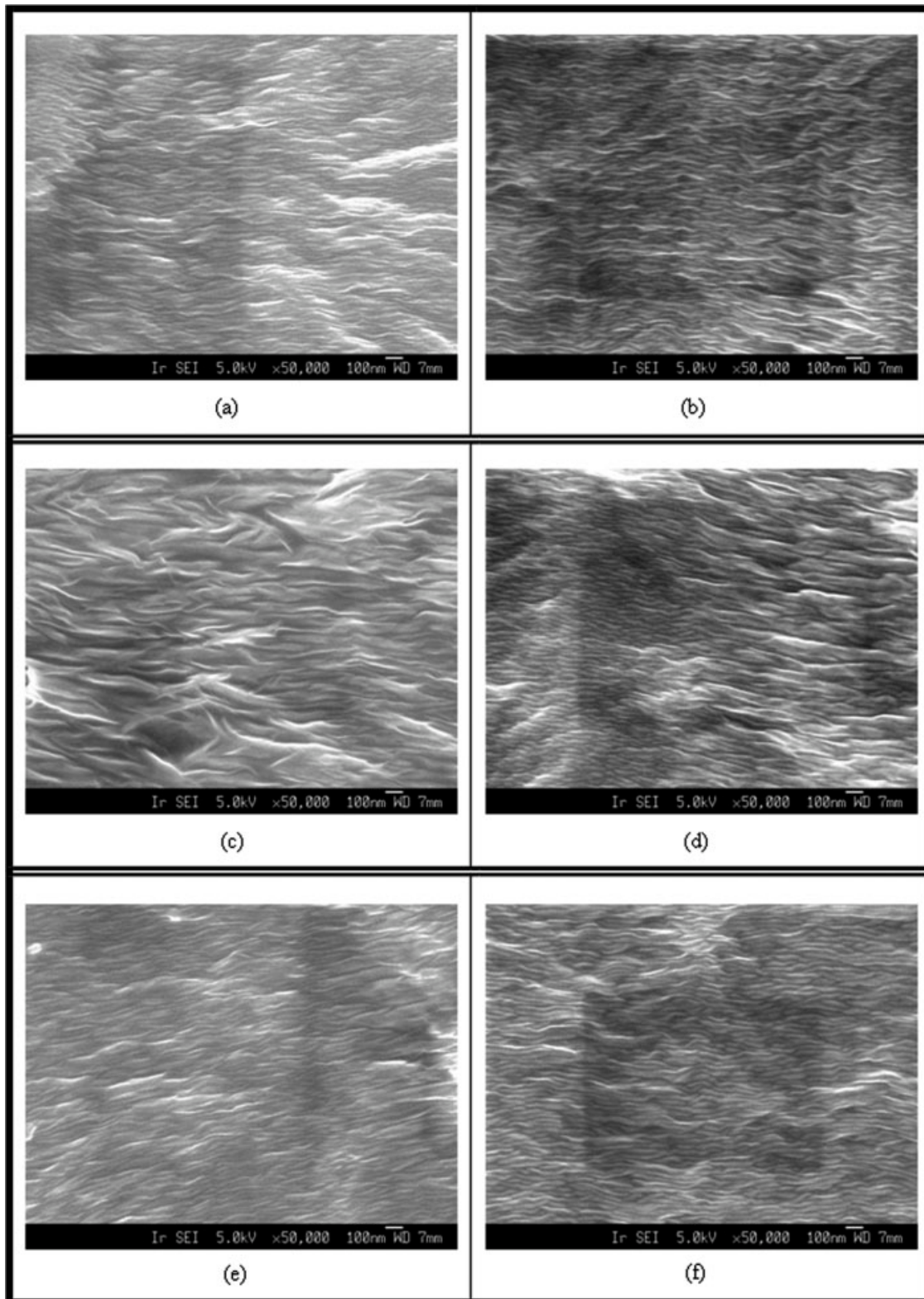
Figure 6 FE-SEM photomicrographs of HDPE films as a function of melt flow rate at die exit (V_1), degree of melt extension (DDR), and annealing temperature (T_{ann}). (a) V_1−1 (= 0.193 m/min); (b) V_1−4 (= 0.847 m/min); (c) DDR-1 (= 15.8); (d) DDR-4 (= 69.6); (e) Anneal-1 (= None); (f) Anneal-4 (= 125°C).

number of stretched tie chains contribute to the high modulus of elasticity and the reversible deformation of HDPE films. Future works will be focused on the effect of hard elasticity of HDPE precursor films on the microporous structure formation and its air permeability property.

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