

Thermal and Mechanical Modification of LDPE in Single-Screw Extruder

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ABSTRACT: The effect of processing history in a single-screw extruder on molecular characteristics was studied by employing commercially available low-density polyethylene with no additives. Generation of long-chain branch, which is responsible for the neck-in phenomenon and draw resonance, is indicated by nonlinear viscoelastic properties of the extruded samples. Consequently, the processed samples show higher level of elastic property than the original pellet. However, thermal analysis revealed that there is no change

in the distribution of short-chain branch. Moreover, both chain scission and cross-linking take place, and the chain scission is predominant above 320°C. Furthermore, processing history at low temperature depresses the melt elastic nature, although primary molecular structure is unchanged. This would be attributed to shear modification phenomenon. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 1462–1470, 2009

Key words: polyethylene; extrusion; degradation; rheology

INTRODUCTION

Extrusion is an important step operation in various polymer processings, such as film-casting, film-blowing, and extrusion coating. During the operation, polymer pellets are heated, deformed, and melted in the extruder by conductive heat transfer and shear action between a barrel and a rotating screw, which leads to thermal and/or mechanical modification. In particular, thermal modification is quite important for extrusion coating, because the processing is generally performed at high temperature.

Extrusion coating is the principal technique to manufacture milk cartons to coat polymer film on a paperboard substrate.¹ Currently, low-density polyethylene (LDPE), is synthesized by radical reaction using the autoclave process which has long-chain branch (LCB) and broader molecular weight distribution (MWD) than other types of polyethylene (PE), and is predominantly employed for the extrusion coating. During the processing, a molten LDPE film is pulled down from a T-die and adhered to paperboard; then, the laminate is pressed and cooled between a nip roll and a chill roll. In order to enhance the adhesion between the film and the substrate, melt temperature, die opening, air gap, and chill roll temperature should be controlled properly. Further, the oxidation of a polymer during process-

ing, which is promoted at high temperature, yields polar groups on the film surface, leading to a strong bonding with the substrate.² Because oxidation occurs in the air gap, resin temperature, air gap, and the line speed influence the degree of oxidation. Furthermore, the extrusion coating often employs antioxidant-free or antioxidant-reduced polymers for promotion of surface oxidation. As the drawback of such high-temperature processing, however, some oxidized substances were found both in the smoke from extruded films³ and also in the films.⁴ The oxidized compounds lead to an "off-flavor" that affects the taste of products in the food package.^{5,6}

In regard to productivity, both drawability and neck-in are important processing parameters. The drawability, often called "drawdown," is determined by the velocity difference of extrudate between the die exit and the chill roll. The film ruptures if the drawability is not adequate, especially at high speed, which limits the productivity. The neck-in is defined as the lateral reduction of the width of the extruded film, leading to thicker edges, called "edge bead," and thus narrower film width. The thicker edge has to be trimmed before winding the product.

The influences of some polymer properties, i.e., melt flow rate (MFR), density, MWD, and degree of LCB, on extrusion coating processability have been reported.⁷ Studies have discussed these polymer characteristics to describe the rheological properties, because the viscoelastic properties directly affect the neck-in and drawability. The pioneering work on processability considering rheological properties was

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carried out by Dobroth and Erwin. They explained that the predominant cause of edge beads is the edge stress effect.⁸ According to them, strain-hardening behavior in elongational viscosity is responsible for the degree of neck-in. The strain-hardening behavior also improves the flow stability of the drawn film at high draw ratio, known as "draw resonance."⁹ Therefore, LDPE showing strain-hardening in elongational viscosity is preferably employed. Furthermore, based on the theoretical approach by Dobroth and Erwin, some numerical simulations of the film-casting process by means of finite element method for Newtonian or viscoelastic fluids were preformed,¹⁰⁻¹⁴ assuming that viscoelastic properties are unchanged during processing.

As mentioned previously, thermal and oxidative reactions take place in LDPE during actual processing, especially at high temperature with prolonged residence time,¹⁵ leading to changes of molecular weight, polydispersity, and branch structure. It is said that PE tends to cross-link to increase molecular weight by degradation, whereas poly(propylene) exhibits chain scission to decrease molecular weight.¹⁶ The difference stems from the structural dissimilarity, i.e., existence of tertiary carbon atom in the backbone. However, the sequence of tertiary carbon and stereoregularity influence the thermal durability.¹⁷ Rideal and Padget proposed a mechanism in which alkyl radical diffuses to react with oxygen to generate peroxy radical, and the radical abstracts hydrogen from an adjacent polymer chain to create a branch in high-density PE.¹⁸ The rheological change due to thermal and oxidative reactions has to be taken into consideration, because the processability, such as drawdown and neck-in, must be modified. Zahavich et al. suggested that rheological properties are changed by repeated extrusion.¹⁹ Further, Satoh et al. indicated that the discrepancy between the film casting simulations and the experimental result can be attributed to the viscoelastic change during processing.¹⁴ Rybnikar showed that extrusion history affects the crystallization of PE.²⁰ However, the details of the rheological and structure changes of PE by extrusion processing are still unknown and must be clarified for the control of processability and mechanical properties of the products. In this study, influence of extrusion temperature, from 170 to 350°C, on structure and rheological properties of LDPE were investigated by employing commercial LDPE. The changes in rheological properties in the linear and non-linear viscoelastic regions, where the MWD, polydispersity index, and especially, higher molecular weight fractions are involved, are discussed as a function of the extrusion temperature. Thermal analysis was also conducted to investigate the number and distribution of short-chain branch (SCB) after extrusion.

EXPERIMENTAL

Materials and processing history

Two types of autoclave LDPE (LDPE-A: MFR, 8.0 g/10 min; density, 920 kg/m³; and LDPE-B: MFR, 3.0 g/10 min; density, 924 kg/m³) were used. No additives were compounded in the material.

Extrusion tests were carried out with a laboratory single-screw extruder (Laboplast mill; Toyo Seiki Seisaku-sho, Japan). The extruder has a 20-mm diameter screw and $L/D = 24$ cylindrical body, with a circular strand die having two 3-mm diameter holes mounted on the head. The barrel temperature was controlled in three zones (Zones 1, 2, and 3) from the hopper to the die. The temperature of Zone 3 and the die varied from 170 to 350°C in increments of 30°C; as a consequence, seven different extrusion temperatures, i.e., 170, 200, 230, 260, 290, 320, and 350°C, were employed. The output rate was 10 g/min. The extruded strands were trapped and quenched in a water bath placed 20 cm under the die.

In this paper, the numbers in the parentheses represent the extrusion temperature, and P denotes the original pellet, e.g., LDPE-A (P) and LDPE-B (170) stand for LDPE-A pellet and LDPE-B extruded at 170°C, respectively.

Measurements

The molecular weight and the MWD of the pellets and extruded samples were obtained by the gel permeation chromatography (GPC) as a linear PE standard. The measurement was carried out at 140°C by dissolving polymers with 1,2,4-trichlorobenzene by high temperature GPC (HLC-8121GPC/HT; Tosoh Corp., Japan). In order to evaluate SCB and chemical structure, the Fourier Transform Infrared (FTIR) spectra were measured by using Nicolet 470 FTIR (Thermo Fisher Scientific). The samples were compressed into a sheet of 1-mm thickness at 130°C. Additionally, the number of SCB per 1000 carbon atoms was calculated from the chemical shift of each SCB up to 5 carbons and that of chains having 6 or more carbons in the ¹³C-nuclear magnetic resonance (NMR) spectra. The frequency of 100.40 MHz was applied at 130°C by GSX-400 (JEOL).

In regard to the thermal analysis, Differential Scanning Calorimetry (DSC) measurements were carried out by Perkin-Elmer Diamond DSC. In addition to conventional DSC measurements, a thermal fractionation called Successive Self-nucleation and Annealing (SSA) was performed. The SSA executes stepwise isothermal crystallization from an initial temperature to lower temperatures at constant intervals for polymer segregation, and features repeated cooling and heating between the isothermal stages.

After repeating all the steps, a final temperature scan was carried out to obtain the thermal fractionation distribution of the polymer. In this study, the holding time for isothermal crystallization was 10 min, and the temperature interval of 5°C was applied, with cooling and heating rates of 20°C/min between each crystallization step. Figure 1 demonstrates the whole temperature profile in the SSA treatment of LDPE-A. Prior to the isothermal crystallization, the polymer was kept at 190°C for 3 min to erase its thermal history, and then cooled. The first crystallization temperature was set at 107°C. After holding for 10 min, it was cooled down to -30°C, allowing the rest of the polymer to crystallize, kept for 1 min at -30°C, and then heated up to the next crystallization temperature, which was 5°C lower than the previous one. The heating and cooling rate was 20°C/min. In this way, the stepwise isothermal crystallization was repeated down to 32°C. Finally, a temperature scan was carried out to obtain a fractionated DSC curve.

The frequency dependence of the oscillatory shear responses in the molten polymers was measured at 160°C by a cone-and-plate type rheometer (MR500; Rheology). The drawdown force measurement was also carried out at 160°C by a capillary rheometer (Capilograph 1D; Toyo Seiki Seisaku-sho). The drawdown force is defined as the force needed to uniaxially stretch an extruded polymer strand at the drawing. The overall diagram is illustrated in Figure 2. The molten polymer in a vertically installed $D = 9.55$ mm cylinder reservoir was plunged into a die of $D = 2.095$ mm, $L = 8$ mm, and the incident angle of 90°, at a plunger speed of 10 mm/min at 160°C. The extrudates were drawn by a pair of pulling wheels. The drawdown force measurement was carried out under constant drawing rates of 5, 10, and 15 m/min. Further, evaluation of drawability was conducted by accelerating the drawing speed at a rate of 20 m/min² from the initial 1 m/min drawing until the rupture of strand. The rotation torque of

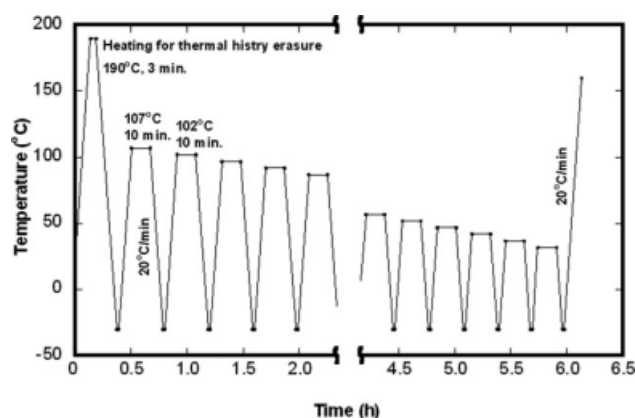


Figure 1 SSA temperature profile for LDPE-A.

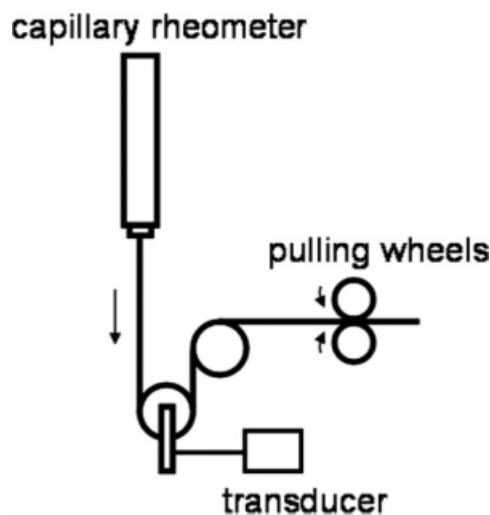


Figure 2 Diagram of drawdown measurement.

the pulley was detected by a transducer. The swell ratio D_e/D was obtained by measuring the diameter of the extrudates, D_e without drawing. The molten samples were extruded and entrapped in a specific water/ethanol solution, whose density is controlled to cancel the gravity force by buoyancy.

RESULTS AND DISCUSSION

Characterization

The average molecular weights were measured for the original pellet and some extruded samples. As shown in Table I, the molecular weights vary randomly with the extrusion temperature. However, the M_w/M_n ratio, referred to as polydispersity index, is the largest for the samples extruded at 320°C, indicating that the extruded LDPE at 320°C has the broadest MWD owing to both cross-linking reaction, which leads to branching, and chain scission reaction. The branching is responsible for high M_z , which greatly affects the elastic nature in the molten state.²¹ Further, it is shown that average molecular weights of the samples extruded at 350°C are lower than those of other temperatures for both polymers. Chain scission of cross-linked branching could take

TABLE I
Average Molecular Weights of LDPE-A and LDPE-B

LDPE	M_n	M_w	M_z	M_w/M_n
LDPE-A (P)	1.75×10^4	1.37×10^5	5.69×10^5	7.9
LDPE-A (260)	1.67×10^4	1.40×10^5	6.35×10^5	8.4
LDPE-A (320)	1.53×10^4	1.37×10^5	6.56×10^5	8.9
LDPE-A (350)	1.33×10^4	1.11×10^5	5.35×10^5	8.3
LDPE-B (P)	1.64×10^4	1.34×10^5	5.14×10^5	8.2
LDPE-B (260)	1.76×10^4	1.42×10^5	5.94×10^5	8.1
LDPE-B (320)	1.64×10^4	1.39×10^5	6.04×10^5	8.5
LDPE-B (350)	1.43×10^4	1.14×10^5	5.01×10^5	8.0

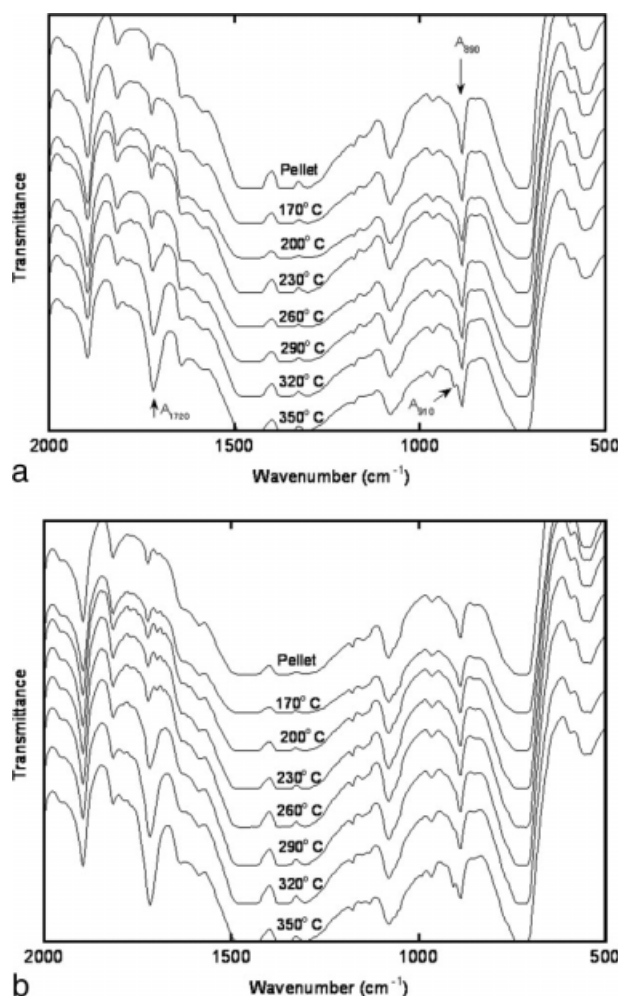


Figure 3 (a) FTIR spectra of LDPE-A pellet and extruded samples. (b) FTIR spectra of LDPE-B pellet and extruded samples.

place at high temperature. That is the reason why the polydispersity at 350°C is lower than that at 320°C. The result indicates that chain scission is predominant at 350°C.

Figure 3(a,b) shows the FTIR spectra of LDPE-A and LDPE-B, respectively. The intensity of the 1720 cm^{-1} absorption peak, which is assigned to carbonyl group, is pronounced at 290°C or higher extrusion temperature. The figures are not shown, but the carbonyl index, defined as the absorbance ratio of 1720 cm^{-1} /reference (1380 cm^{-1}),²² is stable until 260°C extrusion and then it increases in both LDPE-A and LDPE-B. This suggests that oxidation occurs remarkably at higher temperature. Further, a small peak appears at 910 cm^{-1} on the shoulder of the 890 cm^{-1} peak when LDPE is extruded at 350°C. This small absorption peak, assigned as terminal vinyl group created by chain scission reaction,²³ is not detected in the samples extruded at lower temperatures. It is found that the peak intensity of the absorption peak at 890 cm^{-1} , attributed to propyl

and longer branches,²⁴ is not affected by extrusion temperature. This indicates that the SCB structure is not affected by thermal degradation.

The number of SCB per 1000 carbon atoms, which was calculated from the ^{13}C -NMR peak intensity and classified by the length of the chain, is shown in Table II. Although each extruded LDPE has different MWD, as seen in Table I, there are not significant differences in the number of SCB and their distribution. This indicates that the degradation reactions take place at backbone of PE, and thus the SCB is not involved in the cross-linking reaction and chain scission reaction. This corresponds to the result of FTIR measurements. Further, in Table II, LDPE-A (P) seems to contain more branches than other LDPE. The reason is not obvious; however, one of the possible interpretations is that low-molecular-weight species, which have relatively higher content of the SCB per unit length, were lost during the extrusion.

The DSC heating curves of LDPE-A and LDPE-B measured at a heating rate of 10°C/min are shown in Figure 4(a,b), respectively. All the DSC curves in LDPE-A show that the melting peak is located at 106°C, and the shapes of the curves are independent of the extrusion temperature. The same results are obtained for LDPE-B, with the peak top temperature of 110°C. This indicates that the melting point of LDPE is not influenced by the extrusion temperature.

For further investigation, thermal fractionation was carried out with the SSA method, and the result is shown in Figure 5 for LDPE-A. Some thermal fractionation technologies, which use DSC for segregation, have been developed.²⁵ These types of thermal fractionation have great advantages, because the fractionation can be carried out in a short time by means of DSC without investing in any particular equipment, as compared with conventional fractionation technologies, such as Temperature Rising Elution Fractionation (TREF) and Crystallization Analysis Fractionation (CRYSTAF). The SSA method was developed by Müller et al., aiming to characterize linear LDPEs.²⁶ It is known that the SSA gives better molecular segregation than Step Crystallization. Further, in regard to the fractionation distribution, SSA provides qualitative distribution as good

TABLE II
Number of Short-Chain Branch in LDPE-A
(per 1000 Carbon Atoms)

LDPE	C2	C4	C5	C6+
LDPE-A (P)	1.7	8.2	2.9	3.4
LDPE-A (260)	1.3	7.3	2.4	2.8
LDPE-A (320)	1.3	7.4	2.3	2.8
LDPE-A (350)	1.5	7.3	2.5	3.3

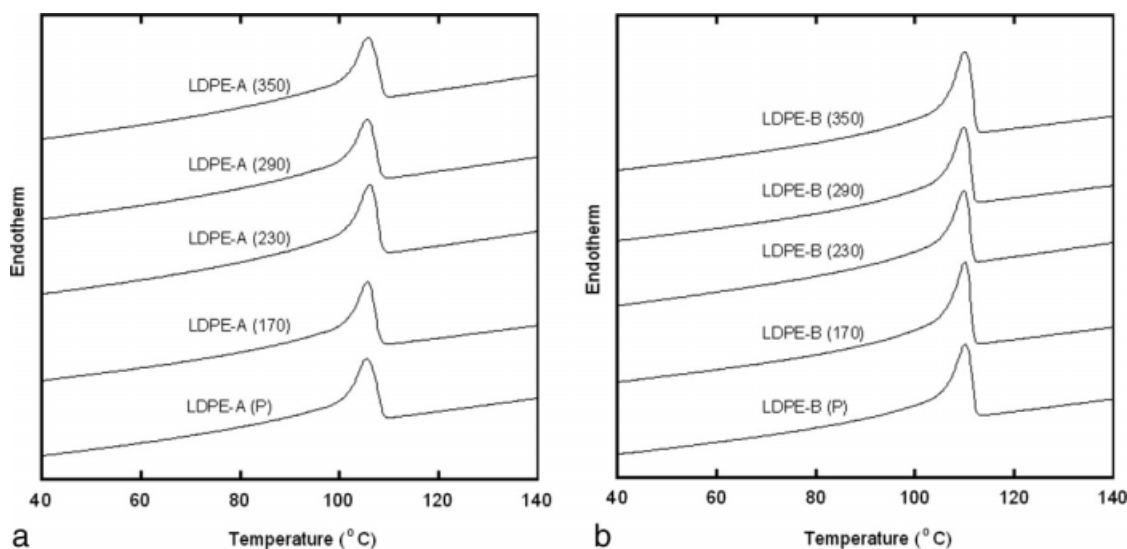


Figure 4 (a) DSC curves of LDPE-A at a heating rate of 10°C/min. (b) DSC curves of LDPE-B at a heating rate of 10°C/min.

as TREF, although a certain downward temperature shift is observed in the SSA.²⁵ Each peak in the bumpy DSC curve represents the melting point of the crystallites that grew during the corresponding crystallization step. As seen in Figure 5, the peak at the right end with the peak top at 111°C was ascribed to the crystallites grown in the initial step of crystallization at 107°C. Further, the largest peak is located at 107°C, suggesting that the main fraction of this polymer crystallizes at 102°C. Moreover, it should be noted that the relative peak intensity is similar in all of the samples. In the SSA, the heat of fusions are 118, 116, 119, 115, and 117 J/g for LDPE-A (P), LDPE-A (170), LDPE-A (230), LDPE-A (290), and LDPE-A (350), respectively. The mass crystallinity, which is determined by supposing 293 J/g for heat of fusion of crystalline PE,²⁷ is in the range of 39.2 to 40.6%. This indicates that the thermal behavior of LDPE is the same as that of the original pellet, regardless of the extrusion temperature and consequent molecular alteration.

Viscoelastic properties

The angular frequency dependence of the storage modulus G' and the loss modulus G'' measured at 160°C are shown in Figure 6(a,b) for LDPE-A and in Figure 7(a,b) for LDPE-B. Apparently, both moduli are almost independent of the processing history, except for the sample extruded at 350°C. When extruded at 350°C, the moduli drop far below those of the original pellets, suggesting that chain scission occurs predominantly, as shown in Table II.

Figure 8(a,b) is the van Gurp-Palmen plot,²⁸ i.e., phase angles δ [$=\tan^{-1}(G''/G')$] plotted against the absolute values of shear complex modulus $|G^*|$, of LDPE-A and LDPE-B, respectively. García-Franco

et al. proposed a method to quantitatively evaluate the frequency of LCB in PEs based on the van Gurp-Palmen plot. According to them, the curve is located lower when the material has more LCB.²⁹ In Figure 8, there is little difference between the plots for the original pellet and for the extruded samples, for both LDPEs. This indicates that linear viscoelastic measurement is not sensitive enough to describe the change of LCB state in the extruded LDPE.

During the drawing process of a molten polymer, the polymers show nonlinear viscoelastic response, which is obvious at high strain rate. The uniaxial elongational viscosity is, in many cases, evaluated with a uniaxial elongational viscometer by stretching a molten polymer at a constant strain rate under isothermal condition. Although the drawing of molten

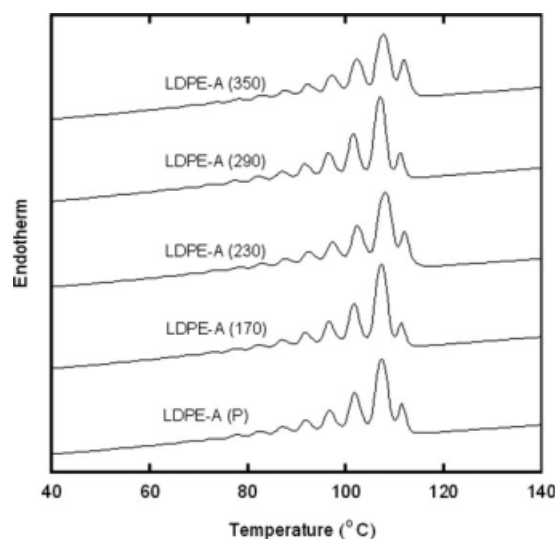


Figure 5 Fractionated DSC curves of LDPE-A at a heating rate of 20°C/min.

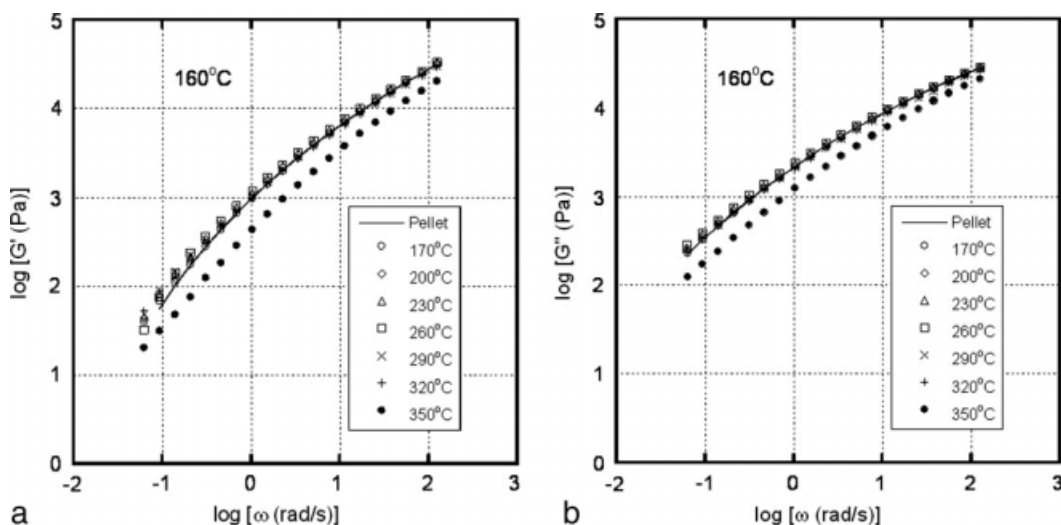


Figure 6 (a) Storage modulus of LDPE-A at 160°C, pellet (solid line), 170°C (open circle), 200°C (diamond), 230°C (triangle), 260°C (square), 290°C (cross), 320°C (plus), and 350°C (filled circle). (b) Loss modulus of LDPE-A at 160°C, pellet (solid line), 170°C (open circle), 200°C (diamond), 230°C (triangle), 260°C (square), 290°C (cross), 320°C (plus), and 350°C (filled circle).

polymers out from a capillary rheometer is not performed at isothermal process, the response provides very important information, because it has a close relation to elongational viscosity, as discussed by Bernat.³⁰ Further, the response should be considered seriously because conventional polymer processing is performed under nonisothermal condition.

The drawdown force under constant drawing speed is shown in Table III. The swell ratio, calculated by the diameter of extrudate samples without drawing, is also shown. In the table, the blank represents that the experiment was not performed because of the rupture of the strand. As seen in the

table, the drawdown force increases with the drawing speed in this experiment. Further, the samples processed at high temperature show poor drawability. Furthermore, it should be noticed that nonlinear rheological responses under uniaxial flow, such as drawdown force, drawability, and swell ratio, are quite sensitive to the applied processing history. It is found that the swell ratio drops when LDPE is extruded at lower temperatures. The swell ratio of LDPE-A decreases until 230°C and then it increases at 260°C. On the other hand, the swell ratio of extruded LDPE-B is smaller than that of original pellet at 170 and 200°C extrusion, and then it recovers

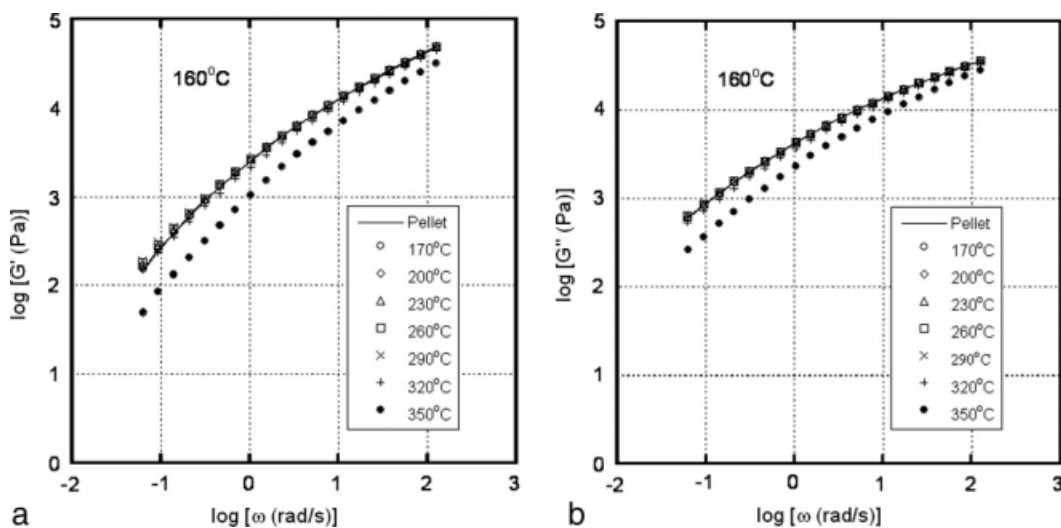


Figure 7 (a) Storage modulus of LDPE-B at 160°C, pellet (solid line), 170°C (open circle), 200°C (diamond), 230°C (triangle), 260°C (square), 290°C (cross), 320°C (plus), and 350°C (filled circle). (b) Storage modulus of LDPE-B at 160°C, pellet (solid line), 170°C (open circle), 200°C (diamond), 230°C (triangle), 260°C (square), 290°C (cross), 320°C (plus), and 350°C (filled circle).

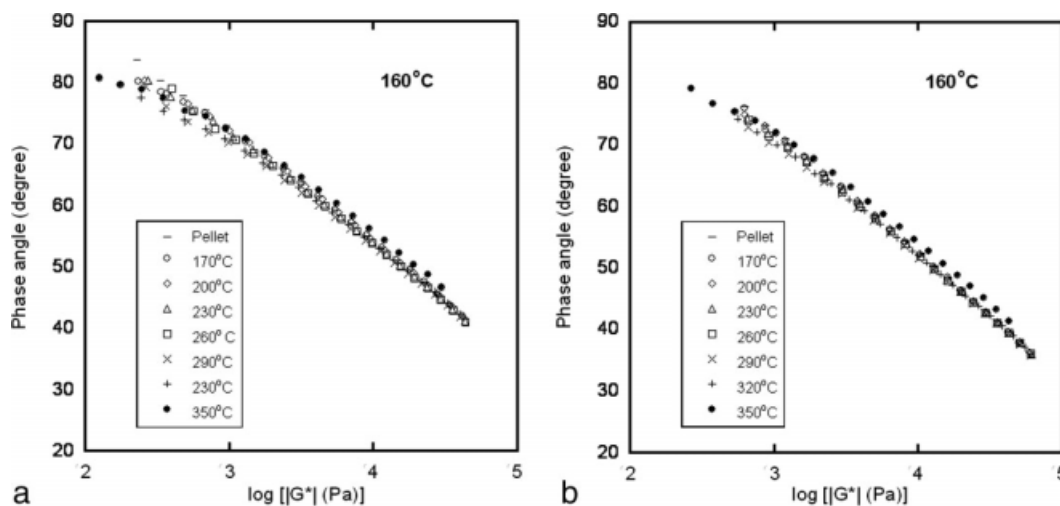


Figure 8 (a) van Gurp-Palmen plot of LDPE-A, pellet (solid line), 170°C (open circle), 200°C (diamond), 230°C (triangle), 260°C (square), 290°C (cross), 320°C (plus), and 350°C (filled circle). (b) van Gurp-Palmen plot of LDPE-B, pellet (solid line), 170°C (open circle), 200°C (diamond), 230°C (triangle), 260°C (square), 290°C (cross), 320°C (plus), and 350°C (filled circle).

at 230°C. Although precise reason of the difference is unknown, LDPE-A may have well-developed branch structure. As a result, rheological properties of LDPE-A are greatly affected by the applied processing history. It is also found that the drawdown force drops to the lowest level for the samples extruded at 170°C, and then it increases greatly with extrusion temperatures. As for the samples extruded at 230 and 260°C, the drawdown force is higher than that of the original pellet. However, the drawdown measurement was not possible in samples extruded at 290°C or higher temperatures, even at 5 m/min for both LDPE-A and LDPE-B. Moreover, it is found that LDPE-B shows similar drawdown behavior as LDPE-A; however, LDPE-B has nearly double the drawdown force and is more susceptible to rupture of the strand due to drawing speed.

The reduction of the swell ratio and the drawdown force at relatively low extrusion temperature from 170 to 200°C could be attributed to the shear modification, which is known as physical modification due to the reduction of entanglement density associated with LCB.³¹ As a result of the reduced entanglement couplings, elastic nature, such as strain-hardening in elongational flow and drawdown force, is reduced by applied shear viscosity.³² Because the magnitude of shear modification is determined by the shear stress and the residence time in a flow,³³ the shear modification, affecting extrudate's swell, drawdown force, and so on,³² is more prominent at low-temperature processing owing to high shear stress.³⁴ This phenomenon has been well known for LCB polymers, especially LDPE produced by autoclave process.³⁵ The increases in the swell ratio and the drawdown force seen at extrusion temperatures of

230°C or higher are attributed to strain-hardening in elongational viscosity.

The maximum drawing speed and the drawdown force at rupture, i.e., the speed and the drawdown force at the rupture of the strand, were recorded. The result for LDPE-A is shown in Figure 9. The maximum drawing speed of the extruded samples is lower than that of the original pellet. Further, it decreases with increasing extrusion temperature up to 290°C, after which it slightly increases at higher temperatures. Considering that a polymer melt with low viscosity shows better drawability, the decrease in drawability suggests that the extrusion processing results in increased elongational viscosity. Because no remarkable difference was detected by the linear viscoelastic measurements, the elongational viscosity

TABLE III
Swell Ratio and Drawdown Force at 160°C

	Swell ratio	Drawdown force (mN)		
		5 m/min	10 m/min	15 m/min
LDPE-A (P)	1.63	65	72	75
LDPE-A (170)	1.60	57	64	67
LDPE-A (200)	1.55	62	67	70
LDPE-A (230)	1.51	83	89	
LDPE-A (260)	1.66	118	127	
LDPE-A (290)	1.88			
LDPE-A (320)	1.78			
LDPE-A (350)	1.68			
LDPE-B (P)	1.66	126	130	131
LDPE-B (170)	1.58	114	119	
LDPE-B (200)	1.59	117	124	
LDPE-B (230)	1.66	134	138	
LDPE-B (260)	1.76	174		
LDPE-B (290)	1.73			
LDPE-B (320)	1.79			
LDPE-B (350)	1.71			

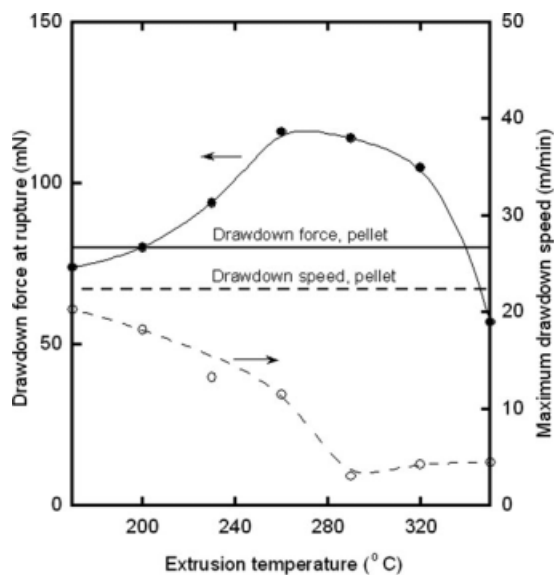


Figure 9 Drawdown properties of LDPE-A at 160°C; drawdown force at rupture (filled circle); and maximum drawdown speed (open circle).

in the linear region is assumed to be unchanged. Thus, the increase in the drawdown force at rupture is owing to the strain-hardening in the elongational viscosity. This is very important for extrusion coating because the intensity of strain-hardening determines the degree of neck-in.³⁶ Further, the draw resonance would also be diminished by the increase of strain-hardening.

The enhancement of the elongational viscosity may be attributed to the generation of higher molecular weight fraction, including branch structure. Andersson et al. indicated that cross-linking occurs predominantly during extrusion.⁴ They also reported that the melt viscosity of LDPE decreases by an extrusion process at 325°C, indicating the chain scission. According to our experiments, the structure change takes place even at 170°C extrusion, because the maximum drawing speed is lower than that of the pellet. Further, the slight recovery of the maximum drawing speed observed at 320 and 350°C in Figure 9 indicates that the chain scission increases along with increase of extrusion temperature.

On the other hand, the drawdown force at rupture once drops and then turns to increase as the extrusion temperature rises. This tendency is partially found in the case of constant drawing (as shown in Table III), but not for all the extrusion temperatures. Figure 9 shows that, after showing the highest peak at 260°C, the drawdown force at rupture declines again and there is a steep drop between 320 and 350°C. This behavior does not synchronize with the viscosity observation above. However, considering the nonlinear response of the drawn polymer and

thermal degradation relating to the extrusion temperature, the initial decline of the drawdown force would be associated with predominant shear modification. With increase of cross-linking, the decline of the drawdown force becomes prominent at higher extrusion temperature. However, the decrease of the drawdown force at extrusion temperature of 320°C indicates that the excessive heating simultaneously causes chain scission reaction. The steep drop of drawdown force at 350°C implies evolution of vigorous chain scission.

CONCLUSION

Processing history in the single-screw extruder alters the structure and properties of LDPE by the applied shear and thermal history. The oxidation of LDPE, indicated by FTIR as absorption of carbonyl group at 1720 cm^{-1} , is explicitly shown when extrusion is performed at high temperature. The generation of terminal vinyl group as the result of the chain scission, which corresponds with GPC measurements, is also identified in the samples extruded at 350°C. Further, various experiments, such as FTIR, NMR, and DSC including SSA technique, suggest that the number of SCB are unchanged by the applied extrusion process.

Moreover, rheological properties are studied in detail, and it is found that the linear viscoelastic properties are less sensitive to structure change by processing, except for the samples extruded at 350°C. However, the nonlinear rheological properties, which directly correlate with the processability at actual extrusion coating, are affected by the extrusion process to a great extent. The decrease in the maximum drawdown speed as a measure of drawability indicates that cross-linking reaction occurs even at relatively low extrusion temperature of 170°C. At the same time, shear action in the extruder enhances the alignment of LCB along the backbone and results in the reduction of the swell ratio and the drawdown force. However, the influence of shear on the rheological properties was not noticeable at higher extrusion temperatures, whereas the cross-linking led to further decrease in the maximum drawdown speed as well as increase in the drawdown force, which is responsible for the neck-in and draw resonance. Under extremely high extrusion temperatures of 320°C or higher, the maximum drawdown speed increases and the drawdown force decreases, indicating that chain scission is predominant. Finally, it is concluded that the evaluation of the nonlinear viscoelastic properties of the processed sample is necessary to predict processability, especially for extrusion coating.

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