Study of the Relationship Between Shear Modification and Melt Fracture in Extrusion of LDPE

YOUN CHEOL KIM, KYOUNG SUN YANG, CHANG-HYUN CHOI

Compounds & Application R & D Team, Research and Development Center, Samsung Chemical Group, 103-6 Moonji-Dong, Yusong, Taejon 305-380, Korea

ABSTRACT: Successive passes through an extruder can modify the melt morphology of low-density polyethylene (LDPE) by applying a shearing process. The major effects of shear modification are to decrease the elastic properties, as evidenced by the decrease in extrudate swell at the exit of a capillary and in melt viscosity at a low-frequency region. The effect of shear modification is also shown by the delay in the onset of melt fracture upon extrusion. The critical shear stress resulted from extrudate appearance, and apparent discontinuity in the flow curve of LDPE shows a similar value with polypropylene rather than those of LLDPE and HDPE. The shearing histories experienced by these materials did not result in any measurable change in molecular weight, so that the chemical modification process such as degradation and crosslinking may be ruled out. These behaviors were also confirmed to the fact that the extrudate swell was fully reversible by annealing in a molten state. The effects of shear modification on rheological properties could be explained by the changes in melt morphology owing to the disentanglement of temporary couplings between long branches. Also, a reduction in melt elasticity by shear modification of LDPE can be used as an effective tool to improve the surface roughness of extrudates in the cable-making process. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 2187–2195, 1998

Key words: shear modification; LDPE; melt elasticity; melt fracture; extrudates

INTRODUCTION

Low-density polyethylene is extensively used in plastic markets using extrusion process such as films, electrical insulation material, and so on.[1,2] Of these applications, high-voltage power cables containing extruded polymeric insulation especially require insulation material that exhibits good surface roughness. There are several causes for surface roughness in extrusion process. An irregular dimensional change in the molten polymer is the main cause of the melt fracture after it exits the die in the extrusion process. The dimensional change is due to an inhomogeneous elastic response of the melt to the flow fields it encounters.

Polymer modification by a special shearing history is becoming a more widely accepted and studied method of altering polymer properties, such as a reduction in melt viscosity and elasticity, and a delay in the onset of melt fracture during extrusion. This is the reason that the relationship between shear modification and rheological behavior of polymers is a topic of long-standing interest.[3–6] The shearing process has been attributed to the disentanglement of polymeric chains in the melt, which does not cause any disruption of primary bonds. This fact is further supported by extrudate swell results that the original entan-

gled structure could be re-formed by heat treatment. For a reduction in melt viscosity and elasticity, it was confirmed by some researchers that the phenomenon could be explained by a decrease in entanglement density as the polymer becomes more highly sheared.[3,5]

Recently, Prooyen and his co-workers[5] have studied the physical changes taking place during shear modification of LDPE using the Carr–Purcell–Meiboom–Gill spin-echo technique. The results of the experiment showed that as the number of extrusion passes is increased, the spin–spin relaxation time of the slowest relaxing region (the most entangled component) decreases from 0.25 to 0.17 s, which indicates that entangled component is being converted to less constrained species. It could be explained that the result is an evidence of a decrease in entanglement density and side-chain alignment along the backbone due to shear modification.

The most important feature in the properties affected by shearing is a delay of melt fracture (distortion of surface smoothness) during extrusion. A principal problem in the extrusion of LDPE is the phenomenon of extrudate distortion commonly known as melt fracture. Although there has been considerable interest in rheological behavior and physical changes taking place during shear modification of LDPE, little progress has been made in elucidating the shear modification–melt fracture relationships as one of the most important factors in extrusion process of LDPE.

The present study was carried out to determine the effects of shear modification on melt fracture and rheological properties of LDPE. Shear modification was accomplished in this study with a laboratory-scale single-screw extruder, and a systematic study was made on the effects of extrusion temperature and the number of passes through the extruder. The surface roughness of extrudates was measured by scanning electron microscopy (SEM). To analyze the effect of shear modification on the surface roughness of the end product, rheological properties and surface roughness of curing materials with 2.0 wt % dicumyl peroxide (DCP, Nippon Oils) were also examined.

EXPERIMENTAL

Materials

Polyethylene used in this study was a tubular process LDPE from Samsung General Chemicals of Korea with a melt index = 2.0 (190°C, 2.16 kg) and a density = 0.920. Two kinds of samples were prepared for testing after a one and three times pass through a single-screw extruder (Shinwha Indus., SE40-03V). Extrusion was done with the temperatures set at 150, 170, and 210°C. The head pressure did not change during these steps, and there was very little, if any, melt fracture. Antioxidant (Irganox 1010, Ciba Geigy), 0.1 wt % was added to prevent chemical degradation during extrusion.

Measurements

Molecular weight analyses were carried out with a high temperature gel permeation chromatograph (GPC, Waters-150C). The samples were analyzed at a temperature of 140°C in 1,2,4-trichlorobenzene (TCB) solvent.

Melt viscous and elastic parameters were monitored by using Rheometrics Dynamic Spectrometer (RDS, Instec-RDS II) in a parallel plate type of geometry (12.5 mm in radius and 1.0 mm in gap size). The disk-shaped samples were molded at a temperature of 180°C for neat LDPE and 125°C for LDPE containing 2.0 wt % DCP by a laboratory hot press under about 10 metric tons, and dried in a vacuum oven for 24 h before the test. The samples had the diameter of 25 mm and the thickness of 3 mm. The gap between the plates was 2 mm. Recoverable elasticity (die swell) was measured by using melt-flow indexer (Ceast-6542). Recoverable elasticity was observed by measuring extrudate diameter at the exit of the die.

Onset of melt fracture was simply determined by observation of the extrudate appearance (the surface roughness of extrudate). The surface of the extrudate was measured by using scanning electron microscopy (SEM, ZEOL-JSM 6300). Measured surfaces were coated with gold for the microscopy.

Recovery after shear modification was performed by heat treatment (annealing). For an annealing, the polymer was pressed into plaques on a heat press at 150°C. These plates were kept in an oven under nitrogen atmosphere at 150°C for 8 h.

The flow properties of the samples were measured by using a capillary rheometer (Rosand, RH7-15, L/D = 16, D = 2 mm).

The samples containing 2.0 wt % DCP were compounded by using a mixer (Moriyama, D3-7.5) at 130°C. The torque change of the samples containing 2.0 wt % DCP was monitored by a Haake Mixer at 130°C.

Figure 1 Gel permeation chromatographs for the samples after shearing (a) with extrusion pass at constant temperature, and (b) with temperature at constant extrusion pass.

RESULTS AND DISCUSSION

Effect of Shear Modification on Melt Fracture of LDPE

Figure 1 and Table I show the molecular weight of

Table I   Molecular Characterization Data and Die Swell Data of LDPEs

Items	Base	S_{150-1}	S_{150-3}	S_{170-1}	S_{170-3}	S_{210-1}	S_{210-3}	SA_{150-3} [a]
Extrusion temperature (°C)	—	150	150	170	170	210	210	150
Number of extrusion	—	1	3	1	3	1	3	3
Melt Index (g · 10 min^{-1}) (180°C, 2.16 kg)	1.96	2.07	2.14	2.07	2.09	1.96	1.96	2.04
Density (g · cm^{-3})	0.9209	0.9208	0.9209	0.9208	0.9208	0.9210	0.9209	0.9209
GPC								
$M_w \times 10^{-5}$ [a]	1.80	1.85	1.80	1.79	1.74	1.76	1.75	1.80
MWD [b]	7.5	7.8	7.6	7.7	7.4	7.7	7.9	7.6
Diameter of extrudate [c]	3.84	3.72	3.65	3.80	3.72	3.80	3.82	3.85

[a] Weight average molecular weight.
[b] Molecular weight distribution.
[c] Diameter of extrudate at 1 cm from die exit of melt indexer (130°C, 10 kg).
[d] Heat treatment with N$_2$ at 150°C for 8 h.

the samples before and after shearing. It was shown that the molecular weights were little changed upon extrusion, and it was concluded that the extrusion processes employed did not result in detectable chemical degradation of LDPE. This conclusion was further supported by extrudate swell results, which showed that the extruded material annealed at 150°C gives the same value as the swell of base polymer. In Table I, values of melt index and extrudate swell for the base and $SA_{150\text{-}3}$[4] are presented. It can be seen that melt index and swell revert to the values of the original material. These observations are in accord with earlier reports[3–4] and industrial experience that the effects of shear modification of polyethylene are only slowly reversible. From the above discussion it is concluded that the changes in the various polymer properties discussed later can be attributed to shear modification alone. Table I shows the effects of shear modification at three temperatures (150, 170, and 210°C), as evidenced by the change of the apparent extrudate swell measured at the melt flow indexer of 10 kg and 130°C. The decrease in melt elasticity of the sample after shearing at 150°C is remarkable in the case of three passes, and reduces progressively with decreasing of the number of extrusion pass. One may also note that shearing at lower temperature entails higher efficiency in the reduction of swell. The higher efficiency in the reduction of elastic property at lower temperature agrees with the results of Maxwell,[7] but contradicts other works.[3,8] The temperature dependence of LDPE is associated with higher shear energy because of the higher value of viscosity (shear stress) at low temperature. The effects of shear modification on melt elasticity could be explained by structural change (physical modification) owing to the disentanglement of temporary couplings between long chain branches. Long chain branching has been demonstrated[9–11] to have significant effects on the rheological behavior, physical properties, and environmental stress cracking of polyethylene. Generally, the increasing of long-chain branches increases melt viscosity at a low shear rate and shear sensitivity of melt viscosity, reducing the average melt viscosity in processing very effectively. Bersted[9] reported on the relationships between viscous behavior and branching level, which has been introduced by peroxide decomposition, thermal-mechanical degradation, or free radical polymerization. There was good evidence to show that the melt viscosity

at a low rate is shown to increase considerably with the branching level.

Dynamic data (frequency response in the linear viscoelastic region) of shearing samples were obtained from dynamic rheometer in the parallel-plate mode at 150°C. The results of complex viscosity are shown in Figure 2. The complex viscosity in a low frequency increased upon extrusion temperature, whereas it decreased with increasing number of extrusion passes for the samples after shearing, as expected from the results of the extrudate swell. In Figure 2, the results of the samples after shearing show a slight decrease in the slopes of the flow curves, demonstrating the tendency toward more Newtonian-like flows as an evidence for the decreasing effect of the long-chain branch. The zero rate viscosity of the samples were measured and given in Table II. The values decreased upon extrusion pass and increased upon extrusion temperature. The fact that the complex viscosity at a low frequency decrease with extrusion could be explain by the effect that the shearing process might lead to more linear-like structure, inducing a decrease in entanglement density and side-chain alignment along the backbone.

The loss and storage moduli of the samples before and after shearing at 150°C are shown in Figure 3. It is well known that loss modulus is related to molecular weight property, and storage modulus is related to the elastic property. In Figure 3, the viscous behavior, as expressed by the dynamic loss modulus, do not show a change, but the decrease of the storage modulus becomes apparent. The decrease of dynamic moduli with extrusion at a low frequency suggests that the shearing process has influences on the elastic properties of LDPE, owing to the re-formation of the original entangled structure.

Following reports by Han[12] and Ritzau,[4] an attempt was made to correlate the measured values of the storage modulus with the loss modulus. In Figure 4, these values are plotted for the base and $S_{150\text{-}3}$ samples. Because the decrease in the values of the storage moduli due to shear modification is greater than the decrease in the values of the loss moduli, the log G' over log G'' curve moves toward the right for a low frequency. This result, of course, indicates a reduction in the elasticity for the $S_{150\text{-}3}$ sample.

Melts of linear polymers exhibit an extrusion instability,[13] known as "melt fracture," in which there are two critical stresses. The first critical stress is characterized by the visual appearance

Figure 2 Complex viscosity of the samples after shearing (a) with extrusion pass at constant temperature, and (b) with temperature at constant extrusion pass.

Table II   Zero Shear Viscosity of the Samples After Shearing

Sample	$\eta_0 \times 10^{-5}$ (Zero Shear Viscosity, Poise)
Base	4.0973
$S_{150\text{-}1}$	3.9134
$S_{150\text{-}3}$	3.8873
$S_{170\text{-}1}$	3.9623
$S_{170\text{-}3}$	3.8938
$S_{210\text{-}1}$	3.9987
$S_{210\text{-}3}$	4.1020
$SA_{150\text{-}3}$	4.0764

$\eta_0 = \lim_{\omega \to 0} \eta^*.$

served that there is a sudden transition from a smooth extrudate to a grossly distorted one (wavy fracture) without the observation of sharkskin. For polyethylenes[14] such as linear low-density polyethylene (LLDPE) and high-density polyethylene (HDPE), fine-scale surface distortion (sharkskin) usually occurs before wavy melt fracture. However, this type of melt fracture does not occur in the case of polypropylene, and the transition from a smooth surface to a wavy fracture one is rather abrupt.[15]

From several studies,[14–16] the onset of wavy fracture was detected to occur at critical apparent

of regular fine-scale surface distortions, and is known as "sharkskin." At the second critical stress there is an apparent discontinuity in the flow curve, sharkskin disappears, and the extrudate becomes wavy or distorted; this transition is known as "wavy fracture" or "gross melt fracture."

Figure 5 shows the extrudate for the samples before and after sharing at 150°C. It can be ob-

Figure 3 Dynamic moduli of the base and $S_{150\text{-}3}$.

Figure 4 Storage modulus versus loss modulus plot for the base and S_{150-3}.

shear stresses in the range of 0.3–0.4 Mpa for linear polyethylene (LLDPE and HDPE), and in the range of 0.1–0.2 MPa for polypropylene. Figure 6 shows the apparent flow curves obtained by using a capillary rheometer (Rosand, RH7-1C, L/D = 16, D = 2 mm) with the samples before and after shearing at 150°C. From the results of apparent discontinuity in the flow curve and SEM photos of extrudate, the onset of wavy melt fracture was detected to occur at critical apparent shear stresses in the range of 0.09–0.11 MPa, as shown in Figure 6. These results indicate that the onset behavior of LDPE used in this study shows more similar patterns with polypropylene rather than those of LLDPE and HDPE. Moreover, the onset of wavy fracture shows a trend towards appearing at a higher apparent shear rate for the sample after the shearing of three passes at 150°C.

Prooyen et al.[5] certified the fact that the melt fracture was present at the lowest shear rate for the LDPE system, even though the critical apparent shear stress was not calculated from the experimental results. Kim and his co-workers[11] also reported the fact that the onset of wavy fracture was detected to occur at a critical apparent shear stress of 0.1 MPa for branched low-density polyethylene. Although a more precise estimate of

shear rate for onset of melt fracture could not been obtained due to the limitations on the shear rate increments on the rheometer, the onset for extruded material was delayed around 60 s^{-1}, as shown in Figure 5.

Effect of Shear Modification on the Melt Fracture of LDPE Containing DCP

An example of the expected improvement on the end-product properties due to shear modification is in the high-voltage cables as insulation materials. Apparently, the end-product qualities of insulation materials are governed by extrusion and curing process. To analyze the curing properties, LDPEs containing 2.0 wt % DCP were compounded using mixer at 130°C. The properties are shown in Table III. The results show the similar values in both case of before and after shearing. Considering crosslinking process for wire and cable insulation, an estimation of scotch time is generally accepted as an important factor. The torque changes in mixer maintained at 130°C are shown in Figure 7. The starting point of torque

Figure 5 SEM pictures from LDPE extrudates of base and S_{150-3} in capillary rheometer.

Figure 6 Apparent viscosity of LDPE as a function of apparent (a) shear rate and (b) shear stress.

Table III   The Properties After Curing the Samples with 2.0 wt % DCP

Sample	Gel Content[a] (%)	Delta Torque[b] ($kg_f \cdot cm$)	Diameter of Extrudate (mm)
Base	77.3	7.0	3.67
$S_{150\text{-}3}$	75.8	6.8	3.49

Press sheet molding condition: 180°C × 15 min.
[a] Two hours in boiling xylene.
[b] Measured by using conical disk rheometer (Model 1000, Toyo Seiki).

weight distribution, and number of long chain branch.

In Figure 8, viscoelastic results are presented for the base and $S_{150\text{-}3}$ with 2.0 wt % DCP. Shear modification is found to result in a drop in the values of storage modulus, and to lesser degree, of loss modulus in the range of low frequency. SEM photos of extrudates for the curing samples are shown in Figure 9. The photographs show the same trend with the samples without DCP. Because the newly formed structure does not immediately revert to its original state due to the long relaxation time in highmolecular-weight polymer, viscoelastic results of the curing material after

changes accepted usually as scotch time has a higher value for the sample after shearing at 150°C. This change is, however, not big enough to affect the final insulation material properties. The fact that shear modification of LDPE is not effective for the curing process or reaction could explain that the shearing process might lead to the change in melt morphology but not chemical modification, such as molecular weight, molecular

Figure 7 Torque changes in mixer of the samples before and after shearing with 2.0 wt % DCP.

having thermal history in mixer were showing a similar trend with the base resin without DCP. From the above results it could be concluded that LDPE should be shear modifiable, and this affects rheological properties such as die swell, flow curve, and critical shear stress, owing to the decrease of entanglement density and the chain alignment along the backbone. Particularly, a reduction in melt elasticity by shear modification of LDPE can be used as an effective tool to improve the surface roughness of insulation materials in the cable-making process.

CONCLUSION

The effect of shear modification for LDPE was examined by varying the process parameters such as temperature and number of extrusion pass. The effectiveness of shearing increased with the increase of extrusion pass and with the decrease of extrusion temperature. After shearing, the samples exhibited a decrease in melt elasticity, as measured by extrudate swell, in dynamic storage modulus and in critical shear stress. The wavy fracture of LDPE was detected to occur at critical apparent shear stresses in the range of 0.09–0.1 MPa. The observed changes in rheological properties can be attributed to changes in melt mor-

$30sec^{-1}$ $60sec^{-1}$ $120sec^{-1}$

$(S_{150-3} + 2.0wt\% \; DCP)$

$30sec^{-1}$ $60sec^{-1}$ $120sec^{-1}$

$(Base + 2.0wt\% \; DCP)$

Figure 9   SEM pictures from LDPE extrudates of base and S_{150-3} with 2.0 wt % DCP in capillary rheometer.

phology by shear modification alone, without significant changes in molecular weight. The initial properties were recovered by heat treatment as a further evidence of no change in the molecular weight. The changes in melt morphology could be explained by the fact that the shear modification process might lead to the decrease of entanglement density and the chain alignment along the backbone. From the results of curing materials, it was concluded that the shearing process of LDPE could be used as an effective tool to improve the surface roughness of insulation materials.

Figure 8   Dynamic moduli and complex viscosity of the samples with 2.0 wt % DCP.

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