

The Influence of Reactor Conditions, Antioxidant, and Processing on the Degradation of LDPE

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Synopsis

The extrusion of LDPE was simulated under well-defined conditions by using a Brabender Plasti-Corder. The grades tested according to gel formation were synthesized in a modified autoclave reactor. With the basic synthesis conditions the same two different reactor pressures were used and at both pressures, two melt index levels were maintained. The two grades with the lower reactor pressure were synthesized under two-phase conditions. With the Brabender Plasti-Corder the influence of melt temperature, mixing efficiency, mixing time, as well as BHT content was investigated. By studying the torque, the gel content, and the change in molecular weight distribution, the following results were obtained. LDPE synthesized under two-phase conditions is sensitive to gel formation, and this can be more easily seen when the melt index is low. Gel formation was also found to increase with increasing melt temperature and increasing mixing time. The effect of mixing efficiency was minor. When the polymer contained BHT, there was a decrease in torque drop as well as gel content. The Brabender curves had peaks indicating molecular enlargement; and when using more BHT, these peaks developed at a later moment. From the GPC data it can be seen that combination of secondary radicals is typical for the two-phase grades, whereas stripping of LCB predominates for the single-phase grades.

INTRODUCTION

In the extrusion of low-density polyethylene (LDPE), gels or fish eyes sometimes develop. Especially when extruding blown film, gels can be very harmful. The product has a bad appearance, and draw-down deteriorates. The gels are in most cases crosslinked fractions of the polymer and are round spots with diameters usually below 1 mm. Gels can develop in the raw material production line or in the processing extruder. At high temperatures and long delay times, LDPE can form secondary radicals which may combine and form crosslinked molecules. In the presence of peroxide, the generation of radicals accelerates still more and oxygen is often the original cause of gels.¹ Stagnant pockets in the raw material production line and in the processing stage are minimized in order to prevent gel formation. The reactor conditions are also controlled in a way that prevents peroxide initiator and polymer radicals from leaving the reactor with the product. A short-term stabilizing antioxidant is often added to LDPE by the raw material manufacturer in order to terminate radicals and deactivate peroxides. The effect of an antioxidant can however be very different depending on the LDPE grade and the conditions in the raw material production line and in the processing stage. The intention with this study was to obtain

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systematic information about the causes of gel formation and means of preventing it.

EXPERIMENTAL

Materials Investigated

A test run was made with a full-scale modified autoclave reactor in order to get information about the influence of reactor conditions on gel formation in LDPE. Only the influences of two-phase conditions and melt index (MI) were investigated in this study. With all other synthesis conditions the same, two different reactor pressures were used, and the melt indices were controlled with isobutylene as a chain transfer agent.

The difference between the pressures was 200 bars, and the lower pressure caused two-phase conditions. This means that at low pressures and temperatures the big polymer radicals cannot stay in solution any longer but separate as droplets (the polymer-rich phase). The small polymer radicals and molecules stay however in solution (the ethylene-rich phase).² The molecules in the polymer-rich phase are protected from forming long-chain branching (LCB) through intermolecular chain transfer even at high conversions and effective mixing.³ In this way LDPE grades suitable for blown film extrusion can be obtained. A narrow molecular weight distribution (MWD) and a low degree of LCB are necessary if good drawn-down and good optical properties are needed.⁴ The polymer radicals in the polymer-rich phase cannot easily combine but the termination takes place with the radicals in the ethylene-rich phase.^{5,6} Because of the fact that the termination is to some extent hindered, precautions must be taken to ensure that the product leaving the reactor is free of radicals.

The MI levels chosen were 0.35 (heavy-duty film) and 1.6 (general-purpose film), and no additives were added in the raw material production line. In order to minimize degradation, the temperature of the reaction mixture downstream of the reactor was kept as low as possible. The test grades are characterized in Table I. P (in bars) is used as a reference pressure, and the molecular structure data were obtained with gel permeation chromatography (GPC).

A Waters Model 200 GPC was equipped with four Styragel columns (pore sizes 10^7 , 3×10^5 , 3×10^4 , and 10^3 Å) and 1,2,4-trichlorobenzene (TCB) was used as a solvent at 135°C. Polymer solutions, 0.15%, were made and filtered before injected into the GPC. The flow rate was 1 ml/min, and the refractive index of the solution was recorded. The final GPC data were then obtained with a computer assuming the same frequency of LCB in all molecules and using the iterative calculation procedure developed by Drott and Mendelson.⁷ The elution

TABLE I
Characterization of the LDPE Grades

Grade	MI, g/10 min	Reactor pressure, bar	Density g/cm ³	GPC data			
				$\bar{M}_w \times 10^{-3}$	$\bar{M}_n \times 10^{-3}$	R	g'
A	0.36	P	0.919	244	24.5	10	0.39
C	0.30	$P + 200$	0.919	528	23.1	23	0.30
E	1.65	P	0.919	217	19.5	11	0.37
G	1.53	$P + 200$	0.919	384	18.7	21	0.30

times at the starting and the ending of the GPC curve, the height of the curve at every $2\frac{1}{2}$ min, and the intrinsic viscosity of the solution injected were used as inputs for the computer. A linear polyethylene calibration curve (counts vs. molecular weight) was established by running as standards two linear polyethylene grades. The molecular weight range of 10^3 – 5×10^5 was covered by NBS 1475, and the high molecular weight end was extended up to 5×10^6 with a Marlex 6009 sample which has been well characterized by U.S. Industrial Chemicals Co. The calibration curve was also extrapolated above the molecular weight of 5×10^6 . A universal calibration curve (C vs $[\eta]M$) was obtained mathematically by combining the linear polyethylene calibration equation (C vs M) with the Mark-Houwink relation for TCB at 135°C ; $[\eta] = 3.95 \times 10^{-4}M_v^{0.73}$. The calculations were made by a Honeywell GE-635 remote computer using a teletype, and the output of the computer was a plotted molecular weight distribution curve and additional printed information about the molecular structure (weight-average molecular weight \bar{M}_w , number average molecular weight \bar{M}_n , their ratio $\bar{M}_w/\bar{M}_n = R$, and the viscosity ratio $[\eta]_{\text{br}}/[\eta]_{\text{lin}} = g'$).

When testing LDPE containing the antioxidant butylated hydroxytoluene (BHT), dry blends were used. Profiles containing 0.5% BHT were extruded with a Brabender extruder at 150°C , and pellets were cut from the profiles. The appropriate BHT contents were then received from dry blending with the corresponding base resins.

Testing of Degradation

The degradability of the different LDPE grades was tested by melt homogenizing in a Brabender Plasti-Corder under well-specified conditions. The equipment used was of the PL V 151 type with the W 50 EC mixing head. Within a heating jacket there are two counterrotating rotors, and the torque needed for mixing can be studied. In order to get a better simulation of an extruder, the oxygen content was kept as low as possible. Therefore, the mixing was done in a nitrogen atmosphere. The opening of the mixing head was covered, and nitrogen ($\approx 0.001\% \text{O}_2$) was blown through at a rate of 70 ml/min when mixing. The control of the melt temperature was improved by regulating the temperature of the oil bath with a PI regulator instead of the standard ON-OFF regulator, and a thermocouple was measuring the temperature directly from the melt instead of the oil bath. With this arrangement the temperature of the melt could be controlled with an accuracy of $\pm 4^\circ\text{C}$ after a 7-min stabilization period.

The Brabender torque was recorded as a function of mixing time (Fig. 1), and the torque decrease from 7 min to the end of the mixing (A–B) was taken as a measure of molecular size reduction. Also the shape of the curve was studied. In some cases a torque peak develops, and by taking samples for GPC analyses (Fig. 2) the peak was found to be due to formation of big molecules through combination of radicals. Further mixing causes chain scission, but the high molecular weight tail prevails. If the torque peak develops after a short mixing time or the peak is high, it is assumed that there is a high tendency for molecular enlargement and gel formation.

The influence of melt homogenizing on MWD and the degree of LCB was studied with GPC, which was calibrated according to the Drott and Mendelson method.⁷ If the MWD curve for the melt-homogenized polymer revealed mo-

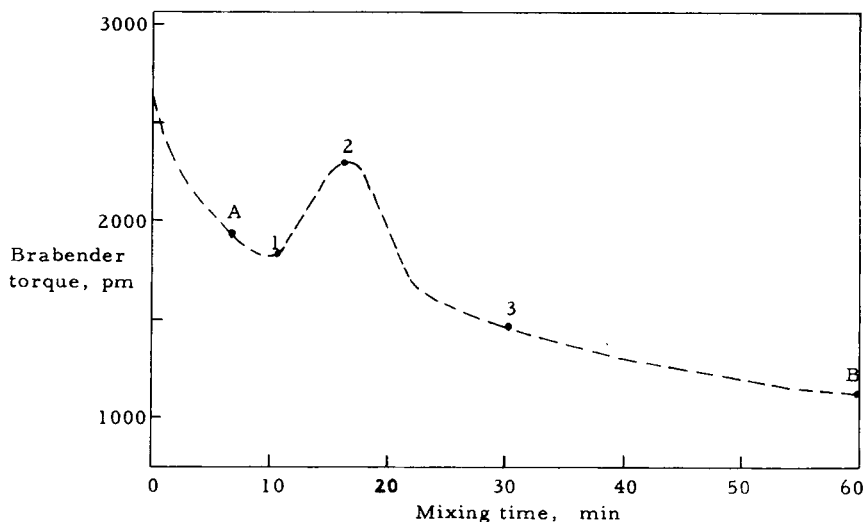


Fig. 1. Brabender torque as function of mixing time; grade A containing 500 ppm BHT and mixed at 220°C melt temperature and 100 rpm rotation speed: (A-B) torque decrease; (1), (2), (3) sampling for GPC analyses.

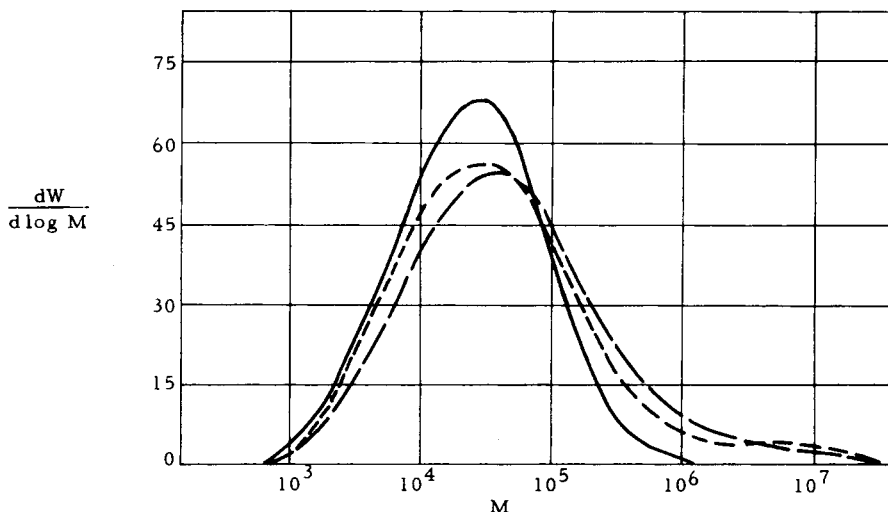


Fig. 2. Molecular weight distribution of grade A (500 ppm BHT) when mixed with the Brabender Plasti-Corder at 220°C melt temperature and 100 rpm rotation speed: (--) sample taken after 11 min mixing time; (—) sample taken after 16.5 min mixing time; (- - -) sample taken after 30 min mixing time.

lecular weights higher than in the original sample, combination of secondary radicals was considered to have taken place. These very big molecules are called microgels in this investigation, and their amount is rated as + or ++. If the high molecular weight part of the MWD curve is unchanged, the rating is 0, and if there is a decrease in molecular weight, the ratings are - or --.

The gel content was determined by Soxhlet extraction with xylene. The polymer was pressed to sheets and four 0.1- to 0.2-g samples were cut and weighed accurately after 1 hr in a desiccator. The sample plaques were put in an ex-

traction thimble having a 10- μ m pore diameter (Macherey-Nagel 645). Glass wool was put between the plaques in order to prevent them from sticking to each other. The extraction was then done with 150-ml xylene for 20 hr, and after that the solution was poured onto 450-ml acetone for complete precipitation of the dissolved polymer. After filtration with a glass filter (Schott-Jena No. 4) the polymer was dried and kept in a desiccator for 1 hr before weighing. The difference in weight between the sample and the precipitation was considered to be due to nondissolvable crosslinked gels staying in the extraction thimble. The gel content was reported as % gel.

RESULTS AND DISCUSSION

When specifically testing the influence of synthesis conditions on degradation and gel formation of LDPE, no antioxidant was added and the melt homogenization was done with the Brabender Plasti-Corder for 60 min with a rotation speed of 100 rpm. The melt temperatures 180 and 220°C were chosen.

From Table II it can be seen that the Brabender torque decreases most when the MI and the temperature are low. Molecular size reduction is more probable when the melt viscosity is high. It can also be seen that the two-phase grades (A, E) are more sensitive to degradation than the single-phase grades (C, G). As can be seen from the presence of gel and microgel, the low-MI two-phase grade has a strong tendency to molecular enlargement and crosslinking through combination of secondary radicals. A high melt temperature seems to enhance this reaction. For the other grades the chain scission reaction dominates at low melt temperature.

From the GPC data it can be seen that at 180°C melt temperature, chain scission took place for all grades. \bar{M}_w and \bar{M}_n decreased and g' increased. The two-phase grades were however less affected because of a simultaneous molecular enlargement reaction. At 220°C melt temperature, the molecular enlargement reaction became more important and dominated especially for the two-phase low-MI grade (A).

TABLE II
Influence of Reactor Conditions on Degradation of LDPE when Melt Homogenized with a Brabender Plasti-Corder for 60 min at 100 rpm

Grade	Melt temp., °C	Brabender torque decrease, pm	Gel, %	GPC data				
				Microgel	$\bar{M}_w \times 10^{-3}$	$\bar{M}_n \times 10^{-3}$	R	g'
A	base resin	—	0	0	244	24.5	10	0.39
A	180	1200	1	0	125	8.1	15	0.55
A	220	1100	2	++	1402	12.5	112	0.14
C	base resin	—	0	0	528	23.1	23	0.30
C	180	820	0	—	48	6.0	8	0.98
C	220	690	0	0	183	7.9	23	0.54
E	base resin	—	0	0	217	19.5	11	0.37
E	180	650	0	—	61	8.6	7	0.86
E	220	570	0	0	108	8.2	13	0.64
G	base resin	—	0	0	384	18.7	21	0.30
G	180	250	0	—	93	10.7	9	0.67
G	220	330	0	0	882	10.0	88	0.21

The GPC data do not correlate very well with the decrease in the Brabender torque. High \bar{M}_w values after melt homogenizing do not necessarily mean that the torque decrease is low. The degree of LCB strongly affects the melt flow behavior of LDPE. It has been reported that lower degrees of LCB cause viscosity enhancement through intermolecular entanglements, whereas higher degrees of LCB cause molecular size reduction and viscosity reduction.⁸ The shear rate also affects the melt viscosity of LDPE. At low shear rates, melt viscosity depends more on the high molecular weight end of the polymer (molecular size and degree of LCB), and the higher the shear rate the bigger the influence of the low molecular weight end. In a Brabender Plasti-Corder there are different shear rates in different parts of the mixing chamber, which makes a correlation between torque and molecular structure parameters still more difficult to obtain. The Brabender torque decrease is nevertheless an easily obtainable indication of net molecular size reduction in melt homogenizing.

Concerning the low-MI grades, the chain scission reaction seems to cause more molecular size reduction for the two-phase grade (high torque decreases), whereas the single-phase grade is more apt to get stripping of LCB (high g' values). For the high-MI grades, there is a correlation between the two types of chain scission. The \bar{M}_w and \bar{M}_n values depend strongly on g' .

When investigating the influence of BHT on degradation and gel formation, the low-MI grades (A, C) were chosen because of their sensitiveness to degradation. By dry blending with masterbatches containing 0.5% BHT, samples with 100, 300, 500, 700, and 1000 ppm BHT were received. The tests with the Brabender Plasti-Corder were also now made with a rotation speed of 100 rpm and a mixing time of 60 min. The melt temperatures were 180 and 220°C.

Grade A is known to have a high tendency to molecular enlargement at 220°C melt temperature, and the influence of BHT on this enlarging reaction can be seen in Figure 3. A torque peak (molecular enlargement) appeared after 15 min of mixing when the sample contained 100 ppm BHT. When higher BHT con-

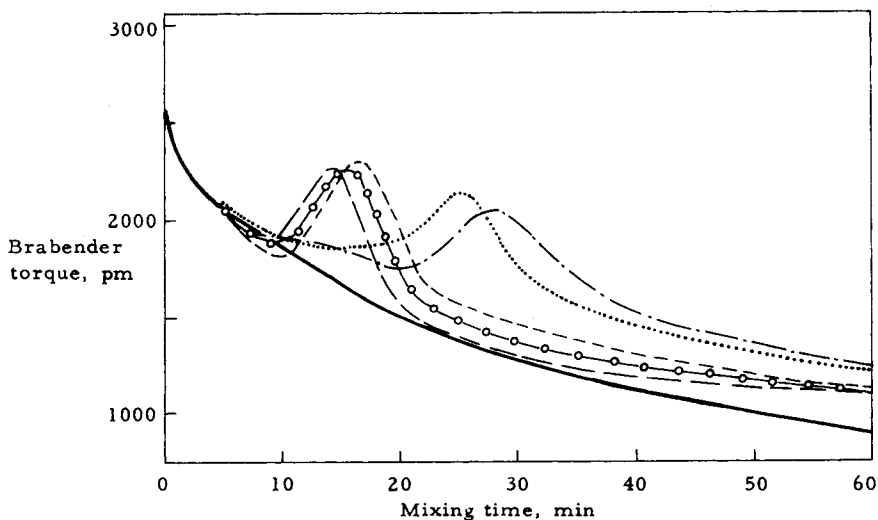


Fig. 3. Brabender torque as function of mixing time; grade A mixed at 220°C melt temperature and 100 rpm rotation speed: (---) no antioxidant; (—) 100 ppm BHT; (—○—) 300 ppm BHT; (---) 500 ppm BHT; (-·-·-) 700 ppm BHT; (-----) 1000 ppm BHT.

tents were used, the torque peak came after a longer mixing time. With 700 ppm BHT, the torque peak came after 28 min; and when the antioxidant content was further increased to 1000 ppm, the peak started to develop earlier again. A high content of BHT keeps the radical concentration low for a longer time, but when the BHT is consumed the radical concentration increases rapidly and molecular enlargement dominates. When the polymer does not contain BHT, however, the torque peak develops after only 7 min, but it is quite low. Molecular scission and enlargement seem to take place simultaneously. The total torque decrease (net molecular size reduction) is however lower when using BHT. The net molecular size reduction is about the same, no matter what the BHT content. The g' value increases and the \bar{M}_n value decreases however with increasing BHT content, indicating less combination of secondary radicals and more stripping of LCB. Grade A should probably contain either no antioxidant or much BHT to produce a good film at these conditions. Small BHT contents produce molecular enlargement at mixing times comparable with the delay time in an extruder. This could cause gels in the final product. Because only a small fraction of the polymer has a very long delay time the molecular enlargement for high BHT contents is not that harmful.

When grade C containing BHT was mixed at 220°C, the mode of the Brabender curves was the same as for grade A. But as can be seen from Figure 4, the torque peaks were much lower. Also the total torque decreases were lower for grade C. It can be concluded that the two-phase grade is more sensitive to molecular enlargement and degradation at high temperatures even when using BHT. From Table III it can be seen that the gel content as well as the microgel content is higher for grade A than for grade C. When using 500 ppm BHT or more, the gel content and the microgel content decrease. When using no antioxidant or small contents of BHT, there is a lot of combination of secondary radicals (\bar{M}_w increases and g' decreases). For grade C the chain scission reactions are predominant for all BHT contents but especially when using high amounts

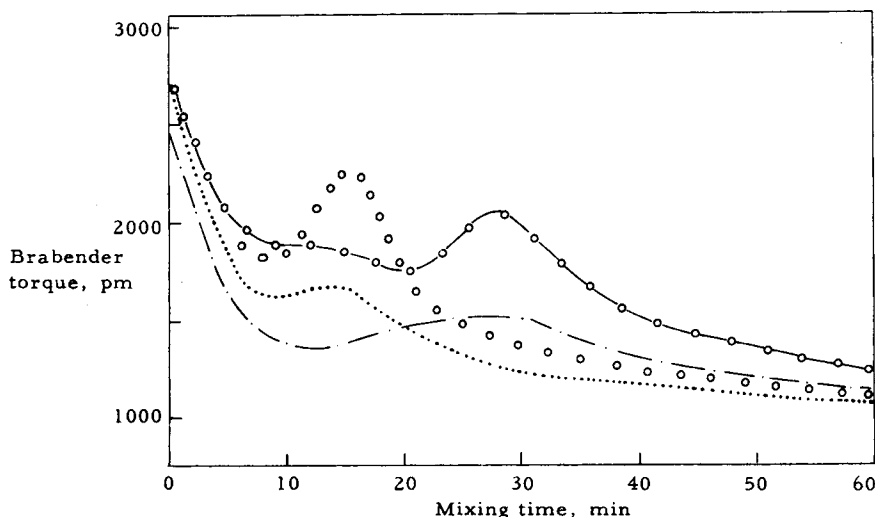


Fig. 4. Brabender torque as function of mixing time; grade A and grade C mixed at 220°C melt temperature and 100 rpm rotation speed: (ooo) grade A, 300 ppm BHT; (—o—) grade A, 700 ppm BHT; (.....) grade C, 300 ppm BHT; (-·-·) grade C, 700 ppm BHT.

TABLE III
Influence of BHT Content on Degradation of LDPE when Melt Homogenized with a Brabender Plasti-Corder for 60 min at 100 rpm and 220°C Melt Temperature

Grade	BHT content, ppm	Brabender torque decrease, pm	Gel, %	GPC data				
				Microgel	$\bar{M}_w \times 10^{-3}$	$\bar{M}_n \times 10^{-3}$	R	g'
A	base resin	—	0	0	244	24.5	10	0.39
A	0	1100	2	++	1403	12.5	112	0.14
A	100	800	3	++	637	11.5	55	0.25
A	300	800	4	++	1132	11.5	99	0.16
A	500	770	0	+	225	10.8	21	0.39
A	700	750	0	0	123	8.4	15	0.64
A	1000	800	0	+	327	9.1	36	0.40
C	base resin	—	0	0	528	23.1	23	0.30
C	0	690	0	0	183	7.9	23	0.54
C	100	490	0	—	85	9.5	9	0.74
C	300	460	0	0	167	10.4	16	0.54
C	500	430	0	0	584	11.1	53	0.26
C	700	360	0	—	48	7.7	6	0.98
C	1000	300	0	—	66	8.4	8	0.86

(700 and 1000 ppm). There is molecular size reduction and stripping of LCB. When using intermediate amounts of BHT (500 ppm), g' decreases somewhat. The single-phase grade C can probably easily be extruded at 220°C without fear of molecular enlargement and gel formation no matter what the BHT content is.

When the melt temperature used was 180°C (Table IV), grade A developed some gels only when containing no antioxidant, but some microgel was also found when using BHT; and with the BHT contents of 700 and 1000 ppm, molecular enlargement was clearly seen. Grade C did not contain any gels at all, and chain

TABLE IV
Influence of BHT Content on Degradation of LDPE when Melt Homogenized with a Brabender Plasti-Corder for 60 min at 100 rpm and 180°C Melt Temperature

Grade	BHT content, ppm	Brabender torque decrease, pm	Gel, %	GPC data				
				Microgel	$\bar{M}_w \times 10^{-3}$	$\bar{M}_n \times 10^{-3}$	R	g'
A	base resin	—	0	0	244	24.5	10	0.39
A	0	1200	2	0	125	8.1	15	0.55
A	100	500	0	—	54	8.8	6	0.98
A	300	280	0	+	315	17.8	18	0.38
A	500	300	0	+	272	15.2	18	0.42
A	700	160	0	+	392	21.0	19	0.30
A	1000	230	0	+	537	24.0	23	0.25
C	base resin	—	0	0	528	23.1	23	0.30
C	0	820	0	—	48	6.0	8	0.98
C	100	300	0	—	24	7.8	3	0.99
C	300	320	0	—	43	10.2	4	0.91
C	500	190	0	—	37	9.2	4	0.99
C	700	190	0	—	140	15.2	9	0.66
C	1000	120	0	0	261	18.1	14	0.45

scission was the predominant reaction. At 180°C melt temperature BHT decreased the molecular size reduction reaction very much, whereas the LCB stripping reaction was very effective, especially for grade C.

In order to prevent molecular enlargement and gel formation in extrusion, 500 ppm BHT would be appropriate for grade A, and grade C could probably be used without antioxidant.

When extruding a polymer with a screw extruder, one can assume that the delay time of the polymer is approximately inversely proportional to the rotation speed of the screw. In order to get a high production rate, the screw is normally run as fast as possible; but when considering the quality of the product, it is important to know the influence of delay time and mixing efficiency. These two parameters can also be controlled separately when designing the extruder. The influence of delay time and mixing efficiency on the degradation of grades A and C was studied with the Brabender Plasti-Corder. Using the melt temperatures 180° and 220°C and a critical BHT content of 200 ppm, the product of rotation speed and mixing time was kept constant at 6000 revolutions. The following combinations were used: 60 rpm, 100 min; 80 rpm, 75 min; 100 rpm, 60 min; 120 rpm, 50 min; 140 rpm, 43 min.

When mixing at 220°C melt temperature, it can be seen from Table V that the torque decrease is about the same for all rotation speed–mixing time combinations. The torque decrease is however higher for the two-phase grade A than for the single-phase grade C. Also the combination of secondary radicals (microgel, high \bar{M}_w , and low g') is for grade A quite independent of the rotation speed–mixing time combinations. The combination of secondary radicals for grade C however increases with increasing mixing efficiency. For both grades the gel content increases with increasing mixing time, and grade A is more sensitive to gel formation than grade C. The reduction in molecular size is very high (high Brabender torque decreases) even if the combination of secondary radicals is quite significant (low g' values).

It appears that for grade A at 220°C melt temperature the molecular en-

TABLE V
Influence of Rotation Speed and Mixing Time on Degradation of LDPE when Melt Homogenized with a Brabender Plasti-Corder at 220°C Melt Temperature and Using 200 ppm BHT

Grade	Rotation speed, min ⁻¹	Mixing time, min	Brabender torque decrease, pm	Gel, %	GPC data				
					Microgel	$\bar{M}_w \times 10^{-3}$	$\bar{M}_n \times 10^{-3}$	R	g'
A	base resin	—	—	0	0	244	24.5	10	0.39
A	60	100	1030	6	++	1600	14.4	111	0.13
A	80	75	1000	3	++	1673	13.2	127	0.12
A	100	60	940	3	++	1130	12.0	94	0.16
A	120	50	890	0	++	1587	14.9	107	0.13
A	140	43	960	1	++	1504	14.5	104	0.15
C	base resin	—	—	0	0	528	23.1	23	0.30
C	60	100	570	3	+	463	12.1	38	0.30
C	80	75	500	2	+	492	10.2	48	0.29
C	100	60	530	1	++	915	13.0	70	0.25
C	120	50	480	1	++	1332	12.8	104	0.14
C	140	43	520	0	++	4479	13.0	346	0.06

TABLE VI
Influence of Rotation Speed and Mixing Time on Degradation of LDPE when Melt Homogenized with a Brabender Plasti-Corder at 180°C Melt Temperature and Using 200 ppm BHT

Grade	Rotation speed, min ⁻¹	Mixing time, min	Brabender torque decrease, pm	Gel, %	GPC data				
					Microgel	$\bar{M}_w \times 10^{-3}$	$\bar{M}_n \times 10^{-3}$	R	g'
A	base resin	—	—	0	0	244	24.5	10	0.39
A	60	100	1040	1	+	316	14.1	22	0.42
A	80	75	570	0	—	68	10.4	7	0.97
A	100	60	690	1	—	78	11.2	7	0.91
A	120	50	390	0	—	44	9.9	4	0.99
A	140	43	230	0	—	169	19.2	9	0.51
C	base resin	—	—	0	0	528	23.1	23	0.30
C	60	100	200	0	—	71	11.4	6	0.97
C	80	75	200	0	0	281	19.3	15	0.41
C	100	60	200	1	0	291	19.0	15	0.41
C	120	50	120	0	0	311	19.7	16	0.39
C	140	43	80	0	0	303	18.6	16	0.39

largement continues only to a certain level (the microgel level) after which crosslinking (gel formation) occurs as a function of mixing time. High shear might also prevent gel formation when high rotation speeds are used.

Grade C mixed at 220°C melt temperature develops gel at a lower microgel level when using low rotation speeds, and the molecular enlargement can go very far without crosslinking when using high rotation speeds.

When using 180°C temperature (Table VI), the dominating reaction is chain scission. Grade A is more affected than grade C. The torque decrease is higher for grade A than for grade C, and these values increase with increasing mixing time. Molecular enlargement occurs only when mixing grade A for 100 min at 60 rpm. For grade C the stripping of LCB increases with increasing mixing time. In both cases gel formation is minor.

CONCLUSIONS

The results described above indicate that two-phase synthesis conditions make LDPE more sensitive to degradation and gel formation when extruded. When the melt index is low, this tendency is accentuated. A high melt temperature and a long delay time in an extruder are apt to increase the gel content in melt homogenized LDPE. The mixing efficiency is of minor importance concerning development of gels. For two-phase grades, the BHT content is important and specifications must be made separately for each grade. Low BHT contents make the polymer more sensitive to gel formation than if there is no antioxidant. The single-phase grades, on the other hand, are not so much affected by the antioxidant content. In this investigation the single-phase grades worked quite well without antioxidant, but even they should be carefully specified according to stabilization. The analysis methods used in this project give in some cases conflicting results, but they are all useful when predicting the development of gels in blown film extrusion. The chain scission reaction, the molecular enlargement reaction, and the crosslinking reaction take place to different degrees

under different conditions, and the proportion of these reactions taking place change over time. In real extrusion, the melt temperature and the mixing efficiency is different in different parts of the extruder; and there is also, depending on the extruder design and the extrusion conditions, a quite broad delay time distribution. The base resin and the antioxidant type and content have to be chosen in such a way that a great variety of extrusion conditions can be used without fear of gel formation.

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