

Two-Step Degradation of High-Density Polyethylene During Multiple Extrusion

EDINA EPACHER,^{1,2} JÁNOS TOLVÉTH,^{1,2} KLAUS STOLL,³ BÉLA PUKÁNSZKY^{1,2}

¹ Technical University of Budapest, Department of Plastics and Rubber Technology, H-1521 Budapest, P.O. Box 92, Hungary

² Institute of Chemistry, Chemical Research Center, Hungarian Academy of Sciences, H-1525 Budapest, P.O. Box 17, Hungary

³ Polymer Additives, Clariant Huningue SA, 68331 Huningue CEDEX, BP 149, France

Received 18 November 1998; accepted 24 March 1999

ABSTRACT: Ensuing our recent studies on polyethylene stabilization,^{1,2} further multiple extrusion experiments were carried out with a high-density polyethylene (HDPE) polymer containing various amounts of a sterically hindered phenolic antioxidant. Discoloration, thermoxidative stability, and melt flow index (MFI) retention were measured by standard techniques; the functional group content of the polymer was determined by Fourier transform infrared (FTIR) spectroscopy, and rheological, as well as mechanical properties, were also measured. The results indicated that degradation and stabilization reactions take place according to two different mechanisms in the first and subsequent processing steps, respectively. Color development could be described well by the simple first-order overall reaction kinetics proposed earlier, and color change could be related to the stability of the polymer. The existence of general correlations among the properties proved that all chemical reactions are interrelated. The reactions of the stabilizer lead to color development, while those of the polymer to a modification of its molecular architecture, which determines the rheological and mechanical characteristics of the product. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 1596–1605, 1999

Key words: high-density polyethylene; multiple extrusion; thermal degradation; weak sites; stability; oxidation induction time; discoloration; film properties

INTRODUCTION

During the processing of polyethylene (PE), numerous reactions take place, which lead to changes in the structure of the polymer produced in the polymerization process.^{3–7} The extent and direction of these reactions are deter-

mined by the inherent properties of the polymer, processing conditions, and technology, for example, melt temperature, shear rate, the amount of oxygen being present,⁸ the amount and type of stabilizers and catalyzer residues.^{4,9,10} The processing stability of polyethylene has been extensively studied in the past, and considerable knowledge was accumulated.^{3–5,11} However, due to the complicated interrelation of the great number of reactions taking place in the melt during processing, numerous contradictions exist in the literature about processing stability of polyolefins, and many questions remain unex-

Correspondence to: B. Pukánszky.
Contract grant sponsor: National Science Research Fund of Hungary; contract grant number: F023065.

Journal of Applied Polymer Science, Vol. 74, 1596–1605 (1999)
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plained. The processes are even more complicated in a stabilized polymer; thus, stabilization remains an important technical and economical challenge.

Previously, an interesting correlation of several properties was observed in the course of an optimization study directed towards the development of an additive package for a film-grade, high-density polyethylene (HDPE).^{1,2} An analysis of the data and additional experiments indicated that all chemical reactions are related to each other. The reactions of the stabilizer lead to color development,¹²⁻¹⁷ and that of the polymer leads to changes in its molecular structure, which, on the other hand, determine the rheological properties of the granulates^{11,18,19} and the mechanical characteristics of the films blown from them.^{20,21} However, the general validity of the correlations was in doubt because of the industrial character of the project. Besides two phenolic antioxidants, the package contained a phosphonite costabilizer, as well as zinc stearate, while the stabilizer content changed in a relatively narrow range.

The main goal of the present study was the further verification of the validity of previous observations. In order to simplify the system and the relationships, various amounts of a single phenolic antioxidant, Irganox 1010, was added to the same polymer used in the previous series of experiments. This article reports the most important results of the study, points out the correlations of general validity, and calls attention to the facts that are in contradiction with former conclusions. Some new observations are also reported, which indicate that degradation of polyethylene proceeds in two subsequent steps during processing.

EXPERIMENTAL

The polyethylene used in the study was the Phillips-type Tipelin FA 381 of TVK, Hungary, with a melt flow index (MFI) of 0.28 g/10 min (190°C, 2.16 kg), a density of 0.938 g/cm³, and a nominal 1-hexene content of 3–5%. The phenolic antioxidant {tetrakis [(3,5-di-tert-butyl-4-hydroxyphenyl)propionate] methane, Irganox 1010 Ciba-Geigy, Switzerland} was introduced at six different concentrations, that is, at 0, 0.025, 0.05, 0.10, 0.15, and 0.25 wt %. No other additives were added to the polymer. The PE powder and the additives were homogenized in a Baker Perkins high-speed fluid mixer for 3 min. The polymer

was extruded six times on a Rheomex $\frac{3}{4}$ " extruder attached to a HAAKE Rheocord EU 10 V driving unit. The temperature of all zones was set to 260°C during the degradative extrusions. Films for mechanical testing were blown on a Tanabe VS 30 extruder having a 24 L/D screw of 30 mm in diameter. The films were prepared with a blow ratio of 1 : 4 at 40 rpm and 175, 190, 190, and 190°C set temperatures.

The MFI of the samples produced by multiple extrusion was determined according to ASTM D 1238-79 at 190°C with 2.16 kg load in a Zwick MFI tester. The color of the samples was measured on a Colourgard System 2000 (URAI) apparatus. The determination was carried out on 3.0-mm-thick compression-molded plates prepared on a Fontijne SRA 100 machine at 170°C. Thermoxidative stability was characterized by the oxidation induction time (OIT) measured by a Perkin-Elmer differential scanning calorimeter (DSC 2) at 200°C. Chemical changes in the structure of the polymer were determined by Fourier transform infrared (FTIR) spectroscopy. FTIR spectra of the samples were registered on ~120- μ m-thick films on a Mattson Galaxy 3000 apparatus. The relative concentration of methyl ($-\text{CH}_3$), vinyl ($-\text{CH}=\text{CH}_2$), vinylene ($-\text{CH}=\text{CH}-$), and vinylidene ($>\text{C}=\text{CH}_2$) groups were determined at 1376, 908, 965, and 890 cm⁻¹ wave numbers, respectively.

The following mechanical characteristics of the films were measured: propagation tear resistance by the pendulum method according to ASTM D 1922 (Elmendorf test), impact resistance by the free falling dart method (ASTM D 1709, dart test), and pendulum impact resistance (ASTM D 3420, Spencer test); tear resistance was determined both in parallel and perpendicular direction to that of the extrusion. Also tensile strength and elongation-at-break of the films were measured in both directions on a Zwick 1445 tensile tester at 200-mm/min crosshead speed and 50-mm gauge length.

RESULTS AND DISCUSSION

The color and the MFI of the polymer produced in the polymerization process is routinely measured in production plants; in fact, the quality control of the product includes the results of these measurements. Color must not exceed a certain value, while changes in MFI lead to processing problems and the deterioration of the properties of the final

product. The close correlation of these quantities to each other and to all processes taking place during the extrusion of HDPE is shown in the following paragraphs.

Color Development

In our previous article,¹ a simple first-order overall kinetics of discoloration was presented, which described color development well during multiple extrusion in all studied cases. The approach was based on the assumption that discoloration is primarily caused by the reaction of the phenolic antioxidant during its stabilization reactions. Colored products, mainly quinones, form in these reactions, which usually give a yellow tint to the polymer, although other colors from pink to green have been also observed. The final correlation describing the kinetics of discoloration was the following

$$YI = YI_0 + Ac_0[1 - \exp(-k_1n)] \quad (1)$$

where YI is the actual color of the sample; YI_0 is a hypothetical color before any processing history; c_0 is the initial amount of stabilizer added; n is the number of extrusions, representing time dependence here; k_1 is the overall rate constant of discoloration; and A is the proportionality constant converting the stabilizer concentration to color. We also assumed that YI_0 , the initial color, should be the same in all cases since the same PE powder was used in each run, and the small amount of stabilizer, which is white anyway, should not change this quantity. Despite this reasoning, the extrapolated hypothetical color was different for all recipes and changed between -7.8 and -3.5 units of the yellowness index. At that time, we could not give an unambiguous explanation for the observed differences.

Discoloration of the polymer measured in the present series of experiments is plotted against the number of extrusions in Figure 1 for the various additive contents. Equation (1) describes color change well; the fit was extremely good, with determination coefficients describing the quality of the fit around 0.99 in all cases. In Figure 1, the solid lines represent color calculated by eq. (1) using the YI_0 and k_1 parameters obtained in the fit.

Besides the suitability of the overall first-order kinetics to describe color development during multiple extrusion, the figure calls attention to

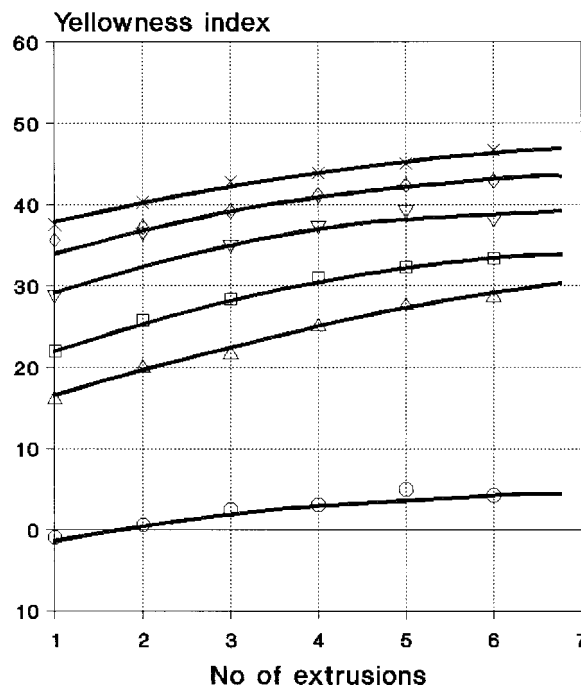


Figure 1 Color development in HDPE containing various amounts of Irganox 1010 stabilizer plotted as a function of processing history. Stabilizer concentration: (○) 0, (△) 0.025, (□) 0.05, (▽) 0.10, (◇) 0.15, and (×) 0.25 wt %.

some other important facts as well. In complete agreement with the assumption of the model, the color depends very strongly on the amount of stabilizer present. The color of the neat polymer and the sample containing the lowest amount of stabilizer differ significantly from each other, indicating that in the second case, discoloration is caused by the stabilizer. Although color development during multiple extrusion depends on the amount of stabilizer present, it does not change linearly with it.

Even more important is the fact that a very large increase occurs in yellowness index in the first extrusion step. At 0.25 wt % stabilizer content, this increase is about 40 units compared to the virgin polymer. The total change is less than 10 units during the following degradative extrusions. As a consequence also, the hypothetical initial color of the polymer depends strongly on the amount of stabilizer added, as is shown in Figure 2. The two figures call attention also to the different behavior of the virgin and the stabilized polymer; the mechanism of color development is different in the two cases. Chemical modification of the polymer leads to some weak color develop-

ment in the first case,²² while discoloration is caused mainly by the stabilizer in the second.^{14-17,23-26}

The above observations raise questions about the chemical processes taking place in the first processing step and in the subsequent extrusions. On the one hand, the reactions might be the same in the first step and in the subsequent extrusions, but their specific rates differ. On the other hand, completely different processes could take place in the two stages. Although a clear answer cannot be given for this question at the moment, some indication is supplied by the comparison of the chemical structure of the initial polymer powder and the films prepared from the granules after the first and sixth extrusions. The data are presented in Table I. They show that the change in the functional group content is completely different in the first extrusion, when the powder is first processed to granules than in the subsequent five processing steps. A relatively large change of the vinylidene and especially that of the methyl content takes place; vinyl and methyl content increase, while vinylidene and vinylene decrease in the first extrusion. Further processing, on the other hand, leads to much smaller changes in the functional group content of the polymer. Although it is not obvious from the table, vinylidene and

Table I Changes in the Chemical Structure of the Polymer Resulting from Various Processing Histories at 0.025 wt % Irganox 1010 Content

Functional Group	Functional Group Content/1000 C for Samples		
	Powder	Film after Extrusion	
		1st	6th
—CH=CH ₂	0.956	1.044	1.039
>C=CH ₂	0.233	0.151	0.147
—CH=CH—	0.069	0.040	0.046
—CH ₃	2.016	3.752	3.863

methyl content usually remain nearly constant during the degradative extrusions (second through sixth steps). On the other hand, the amount of the other two functional groups change in the opposite direction as in the first step; that is, vinyl content decreases, while the number of vinylene groups increases.

It appears to be evident that different reactions take place in the two stages; however, the reason of this dissimilarity is not clear at all. Up to now, such a mechanism has not been reported at all. Although existing mechanisms of polyolefin degradation differ slightly from each other, they are all based upon the radical chain mechanism of oxidation.^{3,4,27-36} This scheme cannot be applied here and does not explain the differences observed between the first and subsequent processing steps. The amount of oxygen present in the two stages is definitely different; the powder adsorbs much more oxygen than the granules. Being well known that the amount of oxygen plays a crucial role in the degradation of polyolefins, it also may change the direction of the reactions. The presence of irregular structural units, seen as weak sites, may also result in a different behavior. The reactivity of such sites must be higher than that of the regular —CH₂— units; thus, they may completely be consumed in the first extrusion step, or at least their concentration may decrease considerably. Additional study is needed to further elucidate these questions.

Finally, the rate constant of discoloration, k'_1 is presented in Figure 3 as a function of stabilizer content. The rate of color development of the virgin polymer differs considerably from that of the stabilized samples showing again the dissimilarity in the chemical reactions taking place in the

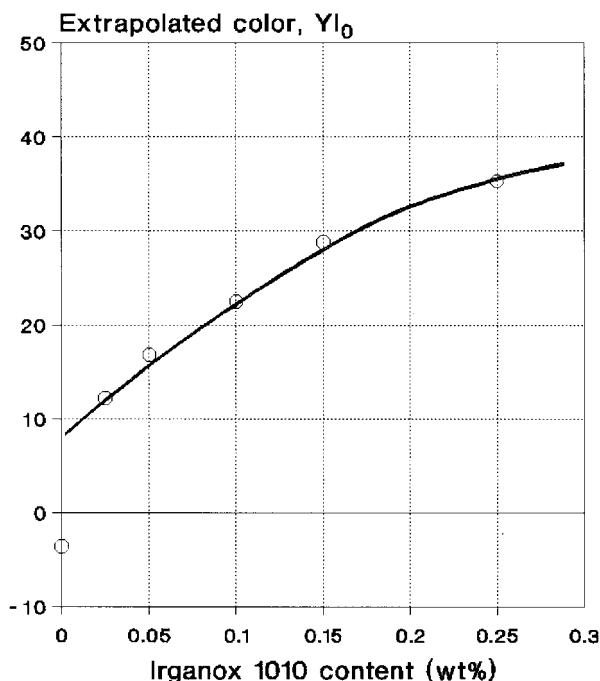


Figure 2 Dependence of hypothetical initial color of the polymer on stabilizer content.

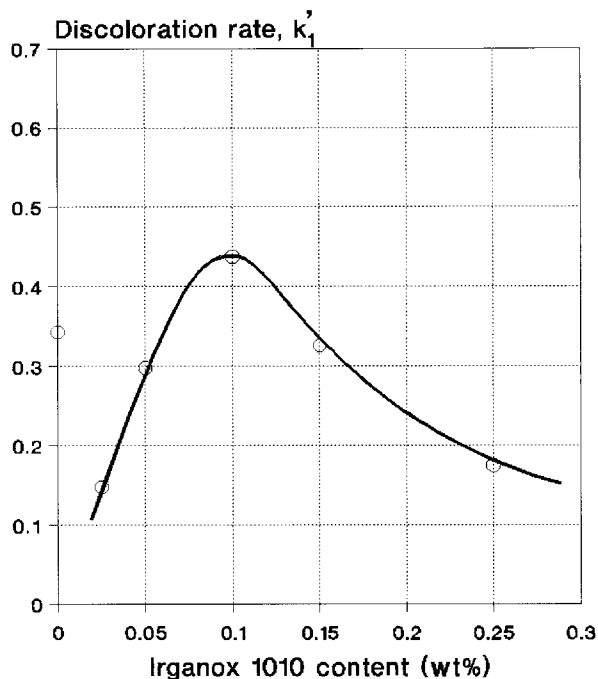


Figure 3 Effect of stabilizer content on the rate of discoloration during multiple extrusion.

presence and absence of the stabilizer. The rate of discoloration shows a maximum as a function of I1010 content; it increases up to 0.10 wt %, then decreases again. This calls attention to the limitations of the kinetic treatment used. When a large amount of stabilizer is present, the stabilizer, the radicals formed, and the reaction products enter into secondary reactions with each other, which lead to a decrease in the rate of discoloration. Stabilizer molecules or their transformation products may react with each other.^{14,17,26} Some of these products are more efficient stabilizers^{14,15,17} than the original compound, but they can be completely colorless. The first-order overall reaction kinetics used is a formal description of color development, but it can be useful for practical purposes, for example, in recipe development.

Stability

The approach presented above, which describes color development successfully, could be related also to the stability of the polymer containing different amounts of stabilizers and subjected to various processing conditions. We assumed that while color depends on the concentration of transformation products of already consumed stabi-

lizer, the actual stability of the polymer is determined by its residual concentration, that is, by the unchanged and still efficient antioxidant. This stability can be measured and is reflected in the results of test methods, such as OIT,³⁷⁻⁴⁰ although several limitations of this approach have been pointed out in the literature. The final expression describing the dependence of stability change on processing history was

$$\text{OIT} = \text{OIT}_0 + Bc_0 \exp(-k'_2n) \quad (2)$$

where k'_2 is the overall rate constant of stability change, and B is a proportionality constant. By assuming $k'_1 = k'_2$ a good correlation was found between the quantity calculated from eq. (2), that is, $c_0 \exp(-k'_1n)$, and the measured OIT values.¹ It was shown¹ that $\text{OIT}_0 = 0$, showing that the neat polymer has a much lower stability than the stabilized samples.

By using the rate constant determined from the dependence of color on processing history (see Fig. 1) and expressing c_0 in moles of phenolic —OH groups, the exponential was calculated for the present series of experiments and is presented in Figure 4 as a function of the number of extrusions. According to the expectations, the cor-

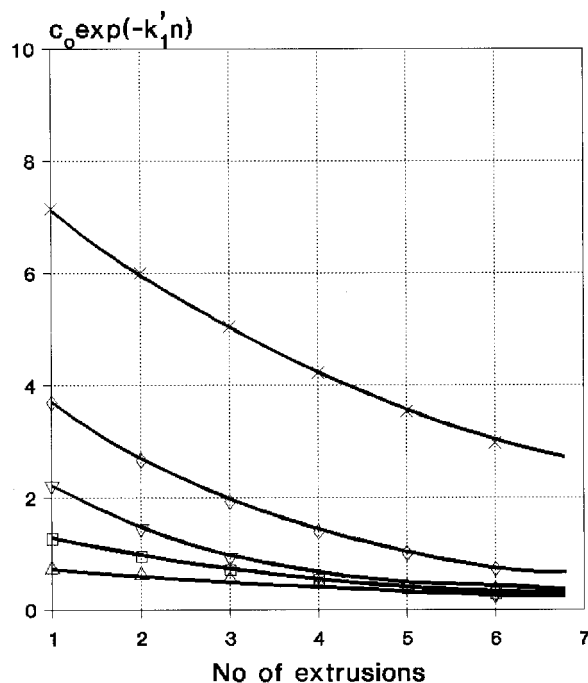


Figure 4 Dependence of predicted stability of HDPE on the number of extrusions and stabilizer content. Symbols are the same as in Figure 1.

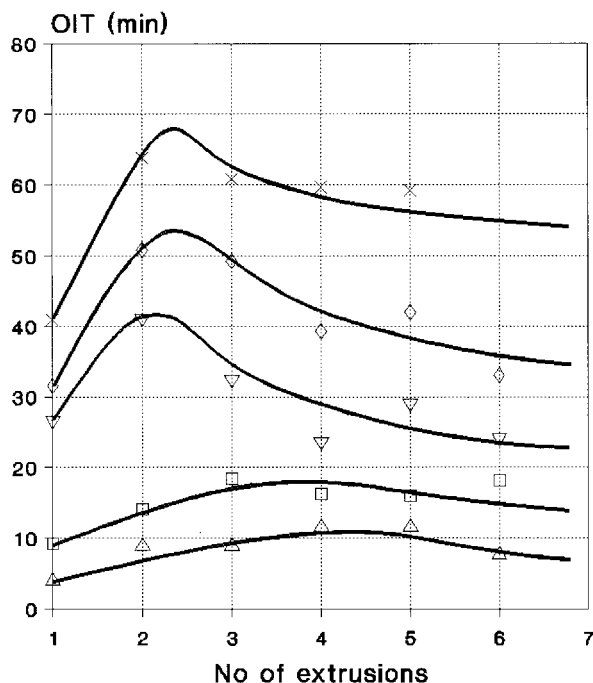


Figure 5 Effect of processing history on the stability (OIT) of the polymer at stabilizer concentration of (Δ) 0.025, (\square) 0.05, (∇) 0.10, (\diamond) 0.15, and (\times) 0.25 wt %.

relations show that stability should increase with stabilizer content and decrease with increasing processing history.

The actual measured stability (OIT) values are plotted against the number of extrusions in Figure 5. The dependence of stability on processing history differs considerably from the prediction of Figure 4, a maximum appears in OIT at a certain number of extrusions. The position of this maximum is defined by the amount of stabilizer added. It shifts to lower values as the stabilizer content of the polymer increases. One can only speculate about the reason for the appearance of this maximum, or more precisely, for the low values measured after the first few extrusions. The maximum might have chemical reasons, as follows: it might be related to the presence of the weak sites mentioned above, or it can be caused by some reaction products formed in the melt during extrusion. Insufficient distribution and diffusion of the stabilizer may also influence the actual stability of the polymer. Only further studies may give an answer to these questions.

In Figure 6, measured OIT data are plotted against the value of the exponential term calculated from eq. (2). No correlation can be detected between the two quantities, or a very unusual,

unexpected correlation exists between them due to the maximum observed in Figure 5. A closer scrutiny of the functions of Figure 5, however, reveals that beyond the maximum, the dependence of OIT on processing history strongly resembles the prediction of Figure 4. If only the OIT values measured after the maximum are considered against the prediction, a completely different picture is obtained (Fig. 7). In this representation, a very strong correlation exists between the predicted and measured values. At higher stabilizer content, the correlation is not linear, showing again the limits of the simple first-order approach used for the overall reaction kinetics. However, at low concentrations, in the range used in the previous study (up to 1.2 mmol $-\text{OH}/\text{kg}$ polymer), the correlation is completely valid. Moreover, the data measured in the previous study (indicated by asterisks in Fig. 7) agree well with the results of the new series, in spite of using a different batch of the polymer and a completely different additive package. The results have some practical relevance as well. Residual stability can be estimated from color measurements in this case. Furthermore, they show also the benefit of using a phosphonite costabilizer and call attention to the well-

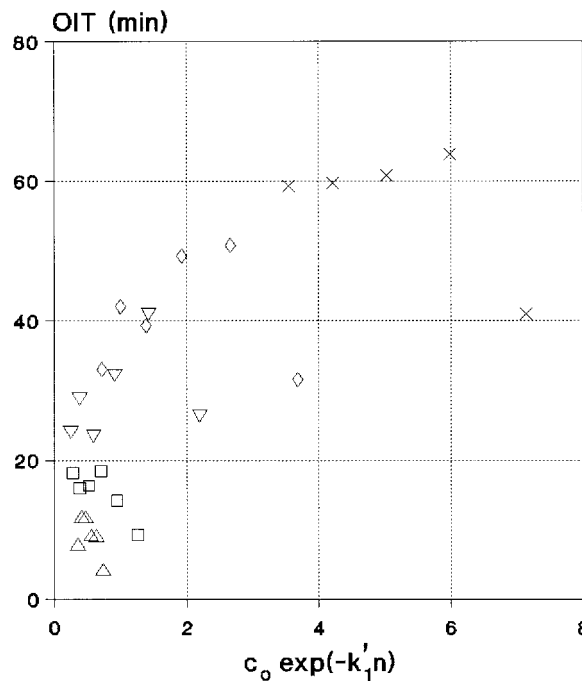


Figure 6 Lack of correlation between the measured and predicted stability of HDPE containing various amounts of Irganox 1010 stabilizer. Symbols are the same as in Figure 5.

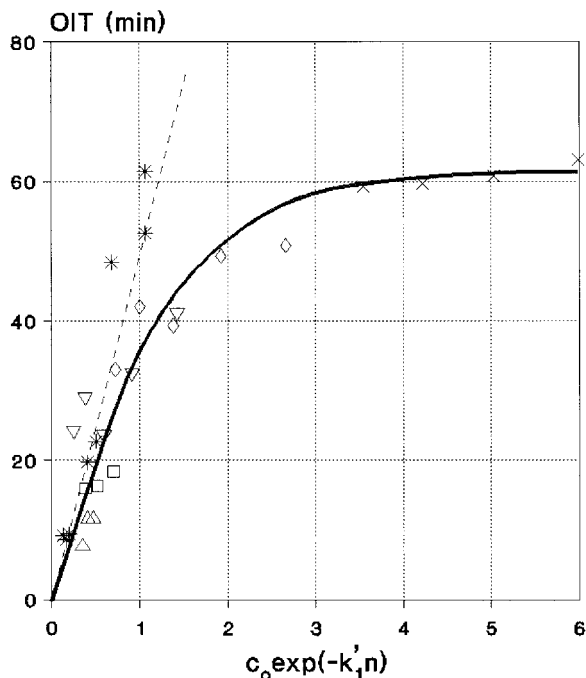


Figure 7 Correlation of the measured stability and the quantity calculated from Eq. (2) [$c_0 \exp(-k_1'n)$] for the decreasing part of the correlations in Figure 5. Symbols are the same as in Figure 5; asterisks indicate data measured in the previous series.¹

known fact that stabilizer content has an optimum; further increase of its amount does not lead to an improvement in stability.

Correlation of Properties

In our previous study, most properties could be related to each other; color was related to the rheological properties of the polymer, while the correlation of the latter with the mechanical characteristics of the films was even closer. The validity of the observed correlations is checked in this section.

The dependence of MFI on processing history is presented in Figure 8. Processing stability strongly improves with increasing stabilizer content. Although their concentration dependence is different, the correlations show exactly the same features as those presented in Figure 1 for color. Compared with unstabilized HDPE, a large increase in MFI occurs upon the addition of even the smallest amount (0.025 wt %) of the stabilizer Irganox 1010. The differences in the melt stability of the polymer become significant, especially during the subsequent, repeated extrusions. How-

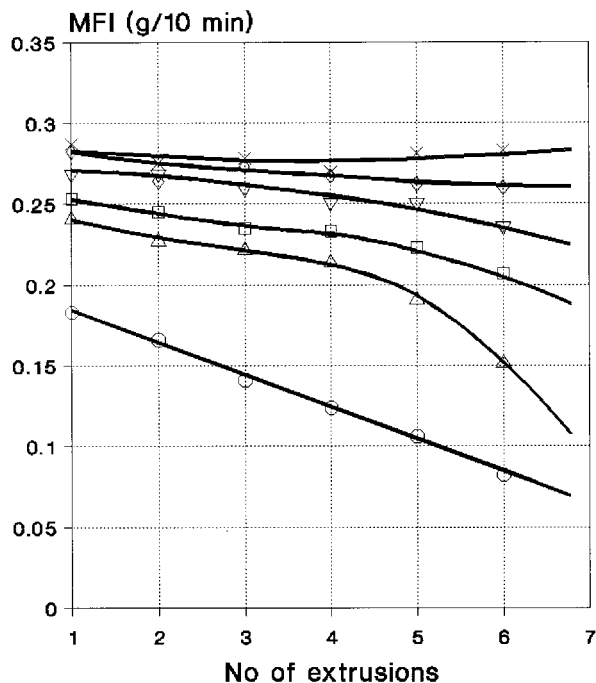


Figure 8 Effect of processing history and stabilizer content on the MFI of HDPE. Irganox 1010 concentration: (○) 0, (△) 0.025, (□) 0.05, (▽) 0.10, (◇) 0.15, and (×) 0.25 wt %.

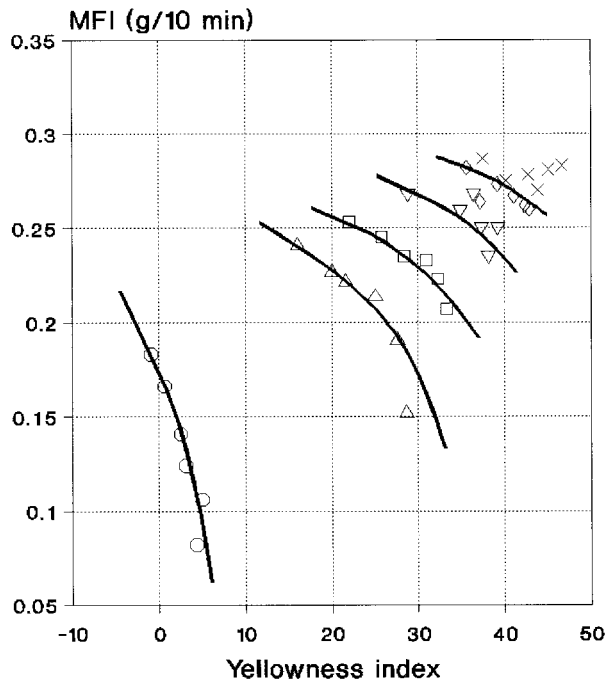


Figure 9 Correlation of MFI and color for a HDPE containing various amounts of stabilizer. Stabilizer concentration: (○) 0, (△) 0.025, (□) 0.05, (▽) 0.10, (◇) 0.15, and (×) 0.25 wt %.

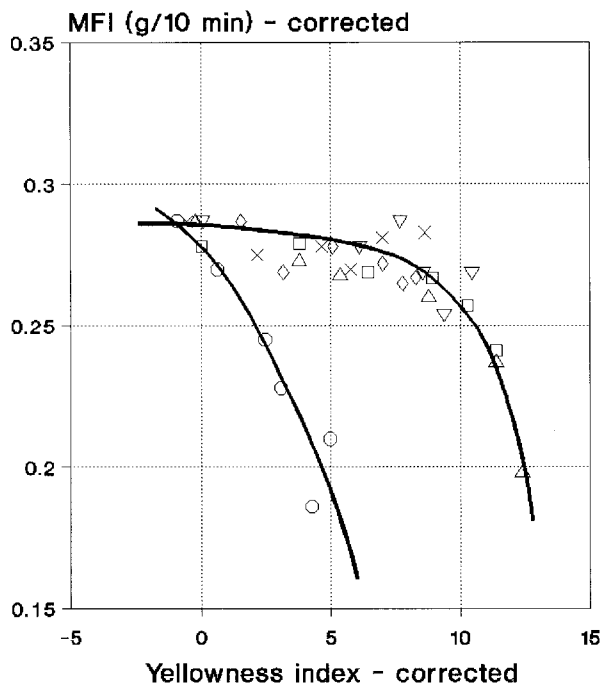


Figure 10 Correlation of the corrected values of color and MFI. Symbols are the same as in Figure 9.

ever, the improvement of processing stability depends nonlinearly on the concentration of the antioxidant used. The results suggest again the importance of the first processing step and the fact that all reactions are related to each other. Although color development was assigned to the reactions of the stabilizer, while the changes in the MFI are obviously related to the modification of the chain structure, the two are not independent from each other.

This statement is strongly supported by the results shown in Figure 9, where MFI is plotted against the yellowness index of the samples. Six independent correlations are obtained corresponding to the six different stabilizer concentrations from 0 to 0.25 wt %. Although the individual correlations are close, the existence of a generally valid one cannot be proven in this way. Attention was called previously to the two-step nature of polyolefin degradation during processing. If at each stabilizer content, we deduct the initial color from all others and also correct MFI by its initial change, the relationship of Figure 10 is obtained. The generally valid correlation leads to several conclusions. We can state that a strong correlation exists between discoloration of the polymer and the detected MFI change. Naturally, com-

pletely different correlations are valid for the neat polymer and for the one containing a phenolic antioxidant. The results indicate again that degradation proceeds in two steps during the processing of PE. As pointed out above, the changes occurring in the first step of processing have crucial impact on all properties of the polymer.

Similar considerations can be applied also to the mechanical properties of the films blown from the granules produced in the various extrusion steps. As an example, the correlation between color and tear resistance measured perpendicularly to the direction of extrusion is presented in Figure 11. Similarly to Figure 9, separate correlations are obtained at different stabilizer contents. Correction of color by the initial value leads to Figure 12, suggesting again the general validity of the correlations and the importance of the first processing step. Finally, the correlation of tear resistance and MFI is presented in Figure 13. The data were not corrected here, suggesting that the changes in the molecular structure of the polymer determine both properties. The deviation of a few points from the general correlation (all were measured after the first extrusion) indicates, though, that molecular structure (molecu-

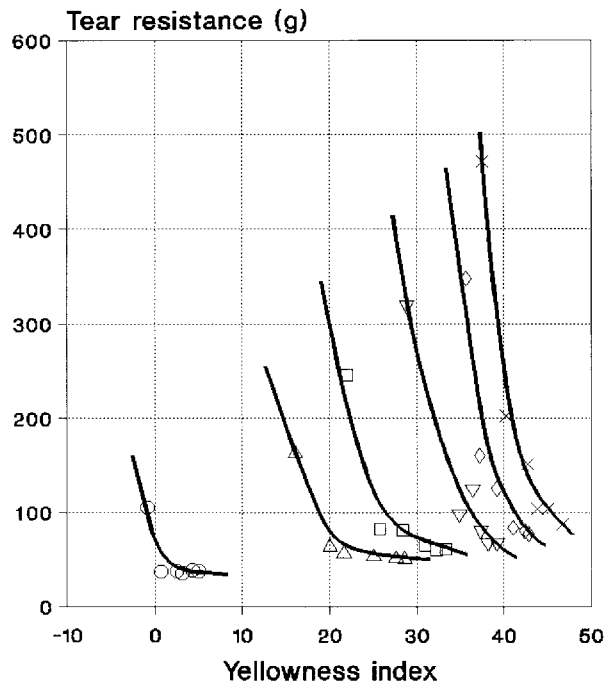


Figure 11 Tear resistance measured in the perpendicular direction plotted as a function of the color of the polymer. Stabilizer content: (○) 0, (△) 0.025, (□) 0.05, (▽) 0.10, (◇) 0.15, and (×) 0.25 wt %.

lar weight, molecular weight distribution, and long chain branching) influences MFI and mechanical properties somewhat differently. This observation agrees well with expectations and polymer processing experience.

CONCLUSIONS

Multiple extrusion experiments carried out with a chromium-type HDPE polymer containing various amounts of a sterically hindered phenolic antioxidant indicated that two different sets of degradation and stabilization reactions take place in the first processing step and during subsequent extrusions. These two steps were indicated by the different extent of changes taking place in the two stages and by the dissimilar modification of chemical structure of the polymer shown by FTIR analysis. Color development could be described well by the simple first-order overall reaction kinetics proposed earlier; discoloration could be related to the residual thermal stability of the polymer. A maximum was observed in stability as a function of processing history that could not be explained unambiguously. It might be related to chemical or to physical interactions with the matrix. The ex-

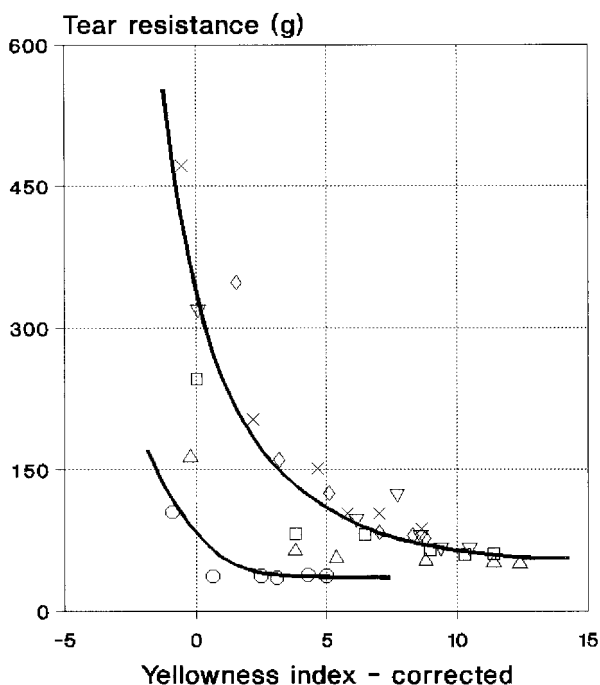


Figure 12 Correlation of tear resistance and color corrected for initial color change. Symbols are the same as in Figure 11.

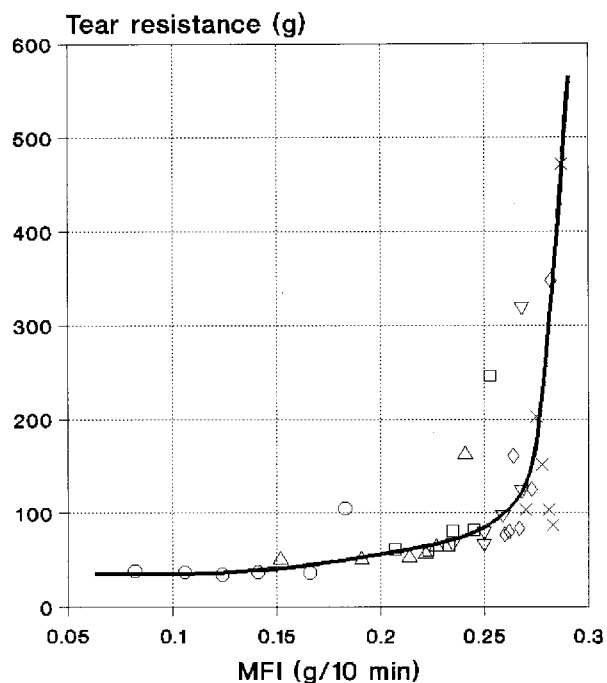


Figure 13 Correlation of mechanical (tear resistance) and rheological (MFI) characteristics of HDPE containing various amounts of stabilizers. Symbols: (○) 0, (△) 0.025, (□) 0.05, (▽) 0.10, (◇) 0.15, and (×) 0.25 wt % Irganox 1010 concentration.

istence of general correlations was observed among properties. Discoloration could be related to stability, but also to the changes of MFI and mechanical properties of the final product. Color develops mainly in the reactions of the stabilizer, while those of the polymer lead to a modification of its chain structure determining rheological and mechanical characteristics.

The authors are grateful for the valuable advice of colleagues and, specifically, to Dr. Lajos Ávár and Dr. Ján Malík at Clariant Huningue S. A. The financial help of the National Scientific Research Fund of Hungary (Grant No. F023065) and the support of the Varga József Fund of the Faculty of Chemical Engineering, TUB, are acknowledged for making the experiments possible. Also, the support of our colleagues at TVK, Dr. Gábor Nagy, István Domenik, and Ágnes Orbán-Mester, is greatly appreciated.

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