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Processing stability of high density polyethylene: effect of adsorbed and dissolved oxygen

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Abstract

The amount of oxygen adsorbed on the surface of a Phillips type HDPE polymer was determined by polarography. Oxygen content was decreased by degassing the samples several times, while it was increased by introducing oxygen into the hopper of the extruder. Polymer samples containing various amounts of oxygen were extruded without stabilizer and in the presence of a hindered phenolic antioxidant. The MFI and the color of the processed samples were measured by standard methods, while their chemical structure was characterized by FTIR spectroscopy. The amount of oxygen adsorbed on the samples is in the range of 20–25 ppm proving that processing takes place in an oxygen poor environment. The polymer powder adsorbs more oxygen than the granules due to its larger specific surface area and porous structure. Permeability measurements indicate that about the same amount or more oxygen is dissolved in the polymer than is adsorbed on the surface. Its estimated amount is around 40–70 ppm. In the oxygen poor environment of processing, the viscosity of the polymer decreases, while its color increases with the increasing oxygen content. The discoloration of stabilized samples is especially strong. Stability also decreases considerably with the increasing oxygen content. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Processing stability; Adsorbed and dissolved oxygen; HDPE

1. Introduction

Oxygen plays an important role during the processing and application of polyethylene [1–3]. Chemical reactions take place in both stages with different kinetics leading to changes in the chain structure of the polymer, thus considerably modifying its properties [4,5]. Chain scission and chain extension reactions always occur simultaneously during the degradation of polyethylene [2,6–10]. The direction of the degradation process depends very much on the amount of oxygen present [2,7,11–13]. Numerous models have been proposed in the past to describe these processes, which are always based upon the radical chain oxidation of polyethylene [4,7,12–25]. Such oxidation schemes might be valid during the application of the polymer when unlimited amounts of oxygen are available, but fail in the oxygen poor environment of processing [4,9,13,26,27].

A series of papers discuss the possible effects of oxygen on the processing stability of polyethylene. Basically all of them agree that oxygen is present during extrusion [2,4–6,23,28–30] and it participates in the reactions taking place in the melt [1,2,6,28]. Oxygen initiates degradation in various ways [2,4,5,23,30–32] such as the formation of hydroperoxides and increases the rate of degradation [3,9,23,28,29,31,33]. It was clearly shown that the amount of oxygen influences the properties of the final product [9]. Most characteristics deteriorate, particularly discoloration increases strongly with the increasing oxygen concentration [9,12,33]. Oxygen enters into the processing machine in two ways: a certain quantity is adsorbed on the surface of the polymer powder or granules, while another quantity is dissolved in the amorphous phase [4]. Not much is known about the relative magnitude of the sources. In fact very limited quantitative data are available in the literature about the amount of oxygen being present in the polymer melt during any of the processing operations [28,30,33].

In this study an attempt was made to determine, or at least estimate, the concentration of adsorbed and dissolved oxygen, which enters into an extruder during the processing of polyethylene. Polymer powder samples containing

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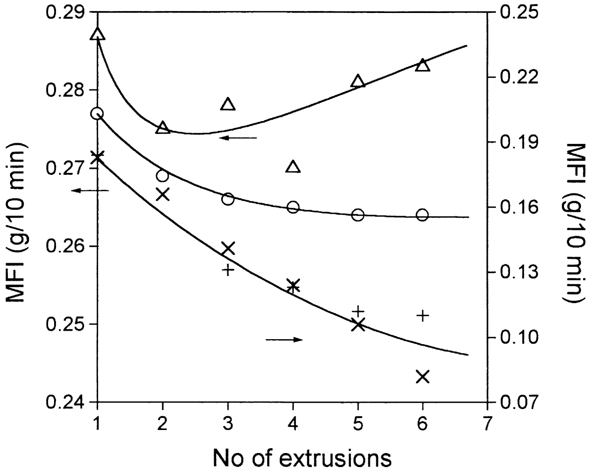

Fig. 1. Changes in the MFI of neat and stabilized (0.25 wt% I1010) HDPE samples, repeatedly extruded in different atmospheres; neat: (×) air, (+) argon; stabilized: (△) air, (○) argon.

various amounts of oxygen were prepared and extruded in a single screw extruder. The relative importance of the two oxygen sources was compared and their effect on the structure and properties of the extruded polymer was determined.

2. Experimental

The polyethylene used in the study was the Phillips type Tipelin FA 381 grade, produced by 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/cm^3 and nominal 1-hexene content of 3–5%. Powder samples with various amounts of oxygen were prepared and extruded in the presence and absence of a stabilizer. The PE powder and the antioxidant (0.25 wt% Irganox 1010, Ciba Specialty Chemicals Inc., Switzerland) were homogenized in a Baker Perkins high speed fluid mixer for 3 min. The polymer was extruded at 260°C on a Rheomex 3/4″ extruder attached to a HAAKE Rheocord EU 10 V driving unit.

The amount of oxygen adsorbed by powder samples and granules was determined by polarography. Dripping mercury electrodes were used for the measurement. Calibration was carried out with oxygen free and saturated water; the oxygen concentration of the latter is around 8.0 mg/dm^3 (the measured value was 8.28 ± 0.27 mg/dm^3). The amount of adsorbed oxygen was controlled by degassing the powder or granule samples in a vacuum oven and replacing the atmosphere by an inert gas, argon. Increased oxygen content was achieved by introducing oxygen gas into the hopper of the extruder; oxygen content was determined on samples taken directly from the hopper.

The amount of dissolved oxygen was estimated by two methods. Oxygen permeation was determined on compression molded plates by using an Ox-Tran 2/20 (Mocon, USA) apparatus. The instrument contains a Coulox oxygen sensor, which generates voltage when oxygen induces reactions on the graphite cathode and cadmium anode. The polyethylene plate used divides the measurement cell into two parts. Nitrogen flows on one side, while air on the other with a flow rate of 10 cm^3/min. Oxygen diffuses through the plate, it is detected by the sensor on the other side, and permeation is determined from the measured voltage. The solubility of oxygen was calculated from permeation by using a diffusion coefficient taken from the literature. The other technique assumed that dissolved oxygen can be removed from the polymer at a much slower rate than the adsorbed gas. Accordingly, instead of degassing the sample for a few minutes as described above, the powder was kept under vacuum for increasing periods of time up to 380 h. The oxygen content and properties of the samples were determined as a function of time by the techniques described below.

The MFI of the samples produced by extrusion was determined according to ASTM D 1238-79 at 190°C with a 2.16 kg load on a Göttfert MPS-D MFI tester. The thermoxidative stability of selected samples containing the stabilizer was characterized by the oxygen induction time (OIT) measured in a Perkin Elmer DSC 2 cell at 200°C. Color was determined on granules always in three parallel measurements by using a Hunterlab Colourquest 45/0 apparatus. Melting and crystallization characteristics of the polymer were determined on a Perkin–Elmer DSC 7 apparatus with 10°C/min heating and cooling rate, respectively.

The molecular structure of both the powder and the granules was characterized by Fourier transform infrared spectroscopy (FTIR). The spectra of the processed samples were recorded on ~120 μm thick films on a Mattson Galaxy 3020 apparatus. The concentration of methyl ($-CH_3$), vinyl ($-CH=CH_2$), *t*-vinylene ($-CH=CH-$) and vinylidene ($>C=CH_2$) groups were determined at 1376, 908, 965 and 890 cm^{-1} wave numbers, respectively. Diffuse reflectance Fourier transform infrared spectroscopy (DRIFT) was used to measure the functional group content of the PE powder.

3. Results and discussion

Before launching this study preliminary experiments were carried out to check the effect of oxygen on the properties of extruded HDPE. In these experiments extrusion was carried out in an argon atmosphere and air, but the oxygen content was not measured. The results of these preliminary experiments are reported first, followed by the discussion of the effect of changing oxygen concentration on the properties of the polymer.

3.1. Preliminary experiments

Similar to several other attempts reported in the literature [2,4,9,28,34], the effect of oxygen was determined in this study by processing the polymer under an inert atmosphere. The polymer powder was degassed, air was replaced by

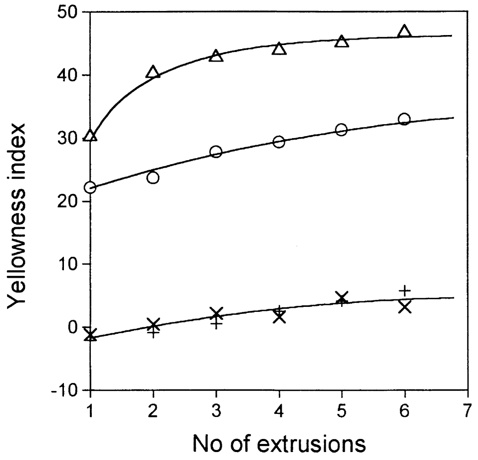

Fig. 2. Effect of atmosphere and processing history on the color of neat and stabilized HDPE samples; symbols are the same as in Fig. 1.

argon and the samples were subjected to multiple extrusion. Argon was used instead of nitrogen, due to its higher specific gravity compared to air and to its better ability to reduce oxygen diffusion during the transportation and processing of the polymer. Argon was also continuously introduced into the hopper during extrusion.

The effect of atmosphere on the MFI of the polymer is presented in Fig. 1. The MFI of the neat polymer decreases drastically with increasing processing history, but the presence of oxygen has only a very slight effect on it. The switch from air to argon has a much clearer influence on the viscosity of the stabilized polymer. Rather surprisingly, larger MFI, i.e. lower viscosity, was measured in air than in argon. The unambiguous explanation of these results is difficult. Since oxygen concentration was not measured either in the powder or in the extruder in these preliminary experiments, it might not have differed considerably in the two series. This assumption is obviously contradicted by the difference in the MFI of the stabilized samples extruded in air and argon, respectively. According to the literature information initiation reactions are similar in the absence and presence of oxygen [2]. The changes in MFI may be determined by these reactions, which offers an explanation for the slight effect of changing atmosphere. The stabilizer may react with oxygen directly [14,15,28,35] or hinder initiation, as well as subsequent reactions [7,14–16,22,24,25,28,36–38]. The results of Fig. 1 indicate that stabilizer efficiency is better in the presence of oxygen than in its absence. Oxygen takes part in the initiation of degradation, i.e. hydrogen abstraction, which is decreased by the use of the stabilizer, thus leading to an increased MFI. Moreover, it is also possible that the stabilizer interferes specifically with reactions leading to cross-linking, and chain extension in general, with the same result. Although some of these tentative explanations might be true, contradictions exist which obviously cannot be resolved without a better knowledge about the amount of oxygen being present in the extruder.

A clear difference exists in the color of the samples extruded under the various conditions. Discoloration of the neat polymer is weak and the atmosphere does not affect it much (Fig. 2). The slight discoloration is usually assigned to the formation of the oxygen containing chromophore groups [12]. Much stronger color develops in the presence of the stabilizer indicating that discoloration is caused mainly by the chinoidal transformation products of the phenolic antioxidant [28,37–39]. Yellowness is weaker under inert atmosphere indicating that oxygen plays a crucial role in the degradation and stabilization reactions taking place during the melt processing of PE, indeed. Color may develop in the direct reactions of oxygen and the stabilizer, but also in the secondary reactions between alkyl and alkoxy radicals and the antioxidant. The results presented in Fig. 2 are in complete agreement with the literature data claiming stronger discoloration with the increasing oxygen content.

The changes in the vinyl group content of the polymer are presented in Fig. 3 as a function of the number of extrusion steps. The increased oxygen content leads to a larger number of vinyl groups. The interpretation of the results is difficult, since the individual reactions leading to the changes in the vinyl group content of the polymer are not known. Moreover, these reactions differ definitely in the presence and absence of stabilizers shown also by the dissimilar dependence of vinyl content on processing history. However, similar to the two previous figures, Fig. 3 conveys an important message, i.e. the difference in the structure and properties of the polymer after the first processing step prevails in all subsequent extrusions. The oxygen content obviously influences the chemical and physical changes in this first step thus determining the properties of the product. It is clear, though, that without the quantitative determination of oxygen content further conclusions cannot be drawn from the results.

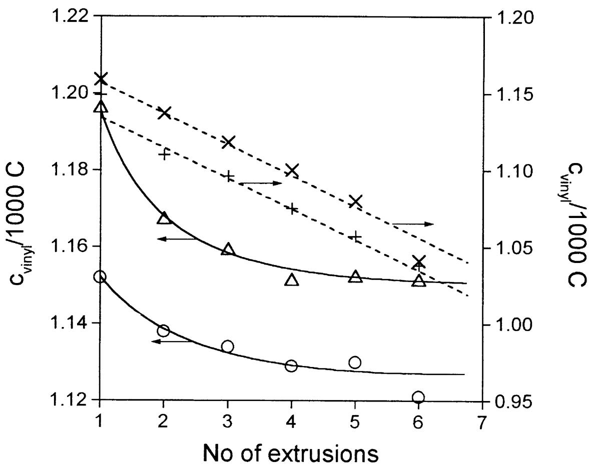

Fig. 3. Dependence of the vinyl group content of neat and stabilized HDPE extruded in air and inert atmosphere on the number of extrusion steps; symbols are the same as in Fig. 1.

Table 1
Oxygen content of various HDPE powder and granule samples

Sample		Oxygen content		
No.	Form	Mean	Deviation	
		(ppm)	(ppm)	(%)
1	Powder	24.0	3.9	16.3
2	Powder	23.7	1.3	5.5
3	Powder	28.1	3.1	11.0
4	Powder	23.7	1.3	5.3
5	Granule	18.4	0.3	1.6

3.2. Oxygen content

The reliability of the method used for the determination of oxygen content had to be checked first, thus the amount of adsorbed oxygen on various powders and granules was determined several times. The results obtained on selected samples are given in Table 1. The oxygen content of powder samples is between 24 and 28 ppm. The standard deviation of the measurement is between 5 and 15%. Considering all the technical difficulties of the determination, this accuracy is acceptable. The oxygen content of granules was always lower than that of the powder samples shown also by the example presented in Table 1.

As indicated before, very few quantitative data exist in the literature for the oxygen content of a polymer processed in an extruder [7,28,33]. Some results are presented in Table 2, most of them are considerably larger than the values of the present study. Unfortunately the method of determination is usually not specified. In the few cases when oxygen content is mentioned it is often not measured, but derived from assumptions and/or model calculations [7]. Existing information does not make the proper evaluation of the data presented in Table 2 or the selection of the best method for the determination of the amount of adsorbed oxygen possible. We can only hope that the experimental technique used by us makes the determination of the effect of the changing oxygen content possible at least on a relative scale.

In order to achieve this goal oxygen content must be changed in a sufficiently wide range. We assumed that the increasing number of degassing cycles and the exchange of atmosphere would lead to a decrease of the oxygen content. The results of a series of experiments are presented in Fig. 4. As expected the amount of adsorbed oxygen decreases with increasing number of cycles. These results are in accordance with the data of Table 1 indicating that the granules always adsorb less oxygen than the powder samples, by all probability due to their smaller specific surface area. They clearly proved that the amount of adsorbed oxygen can be controlled by the number of degassing cycles or by introducing oxygen into the hopper of the extruder. We must emphasize here, though, that these experiments were based on the assumption that the oxygen dissolved in the amorphous phase of the polymer is removed at a much slower rate than the adsorbed gas.

Table 2
Literature data on oxygen content of PE during processing

Sample	Processing technology	Atmosphere	Oxygen content (ppm)	References
PP	Extrusion	Air	259[a]	[28]
PP	Extrusion	Nitrogen	46[a]	[28]
PE	Extrusion		256[b]	[7]
PE	Extrusion		160[b]	[7]
PE	Extrusion		16[b]	[7]
PE	Film	Nitrogen	3000	[33]

[a] Calculated from specific surface area.

[b] Used in calculations as basic assumption.

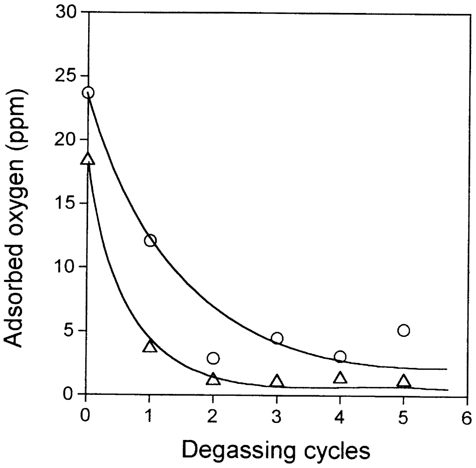

Fig. 4. Changes in the amount of adsorbed oxygen as a function of the number of degassing cycles; (○) powder, (△) granules.

3.3. The effect of adsorbed oxygen

Powder samples with changing oxygen content were prepared with the technique presented above and extruded with and without stabilizer. The MFI of the processed polymer is plotted against the amount of adsorbed oxygen in Fig. 5. In spite of the considerable scatter of the measured values, a few conclusions can be clearly drawn from the results. In accordance with everyday experience, the MFI of stabilized samples is higher, i.e. their viscosity is lower, than that of the neat polymer. This result demonstrates the reliability of our measurements and the validity of the derived results. It is also clear that MFI decreases with the increasing oxygen content. This observation contradicts the results presented in Fig. 1, where the MFI was higher for the samples processed in air than under an argon atmosphere. The contradiction might be caused by several factors. The differences as well as the changes are very small in Fig. 1; in the present series a similar variation can be observed among samples having approximately the same oxygen content (Fig. 5). We also know that the inherent properties

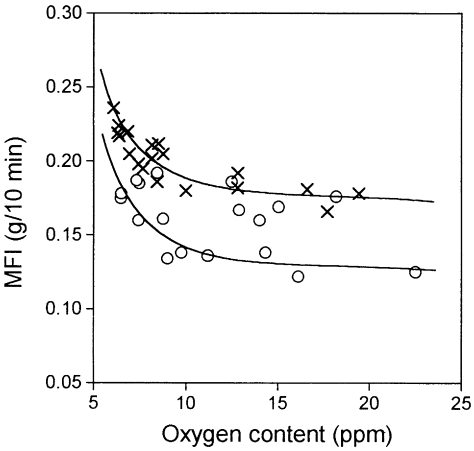

Fig. 5. Effect of adsorbed oxygen on the MFI of neat and stabilized HDPE; (○) neat, (×) stabilized with 0.25 wt% I1010.

of the polymer produced at various dates may change considerably [40], which might also influence the obtained values.

The decrease in MFI may be rationalized by assuming that the number of radicals forming in the melt increases with the increasing oxygen content. As a consequence, the number of chain extension reactions also becomes larger in the oxygen poor environment of processing. Moreover, the two correlations in Fig. 5 seem to run basically parallel to each other showing that oxygen acts similarly in the presence and absence of a stabilizer. This result indicates that oxygen plays an important role in the initiation of degradation and the stabilizer interferes at a later stage. Moreover, if we accept this conclusion it also means that the direct reaction of oxygen with the stabilizer is less important than the trapping of alkyl and alkoxy radicals.

Although the effect of oxygen on the MFI of stabilized samples is unambiguous, it is less clear in the case of the neat polymer. The scatter of the points is considerable and the MFI of several samples is relatively high. We must emphasize here the difficulties in the determination of the oxygen content and the large standard deviation of the measurement. Moreover, the determination of MFI is also complicated; viscosity changes considerably during the measurement itself as shown by Fig. 6. The MFI of all samples decreases as a function of the total residence time in the MFI testing device, but the time dependence is relatively weak for the stabilized samples. A strong MFI decrease is observed for neat polymer samples with a considerable variation in the slope of the correlations. Obviously, the MFI value derived from the measurements depends very much on the way of its determination (average, extrapolation, given residence time—averages were used by us) as well, which can completely alter the position of individual points in Fig. 5.

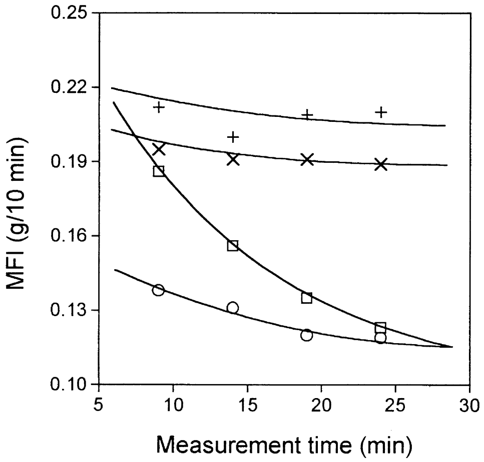

Fig. 6. Change of viscosity of various HDPE samples during MFI measurement; neat: (○) sample 3, (□) sample 8; stabilized: (×) sample 6, (+) sample 8.

Color is plotted against the amount of adsorbed oxygen in Fig. 7. The correlations are very clear and unambiguous both for the neat and the stabilized samples. Discoloration of the neat polymer is weak, but continuously increases with the increasing oxygen content. The much stronger color of the stabilized samples is caused by the chinoidal transformation products of the phenolic antioxidant. The results are in complete agreement with those presented in Fig. 2. They also indicate that the difference in the oxygen content of the two series, i.e. samples extruded in air or argon, respectively, was minor, leading to the contradictory results discussed earlier. Moreover, the stronger discoloration observed at high oxygen content is in agreement with the literature information [12] and practical observations.

According to Fig. 7 the intersection at zero oxygen content is not the same for the neat and the stabilized samples. The difference is small; it corresponds to 2–4 yellowness index unit. We assume that this color difference results from the oxygen dissolved in the polymer, which initiates reactions leading to the discoloration. As a consequence, its amount can be calculated from the rate of discoloration of the stabilized samples. According to these speculations, the amount of oxygen dissolved in the polymer is very small, in the order of 3–5 ppm.

Besides the rheological properties and color, one of the most important characteristics of a processed polymer is its stability. It might be important in long-term applications, but it is related also to the chemical reactions taking place during the processing of the polymer. The OIT of selected samples was measured and the results are plotted against their oxygen content in Fig. 8. Although the scatter of the points is considerable, the correlation is unambiguous; the thermoxidative stability clearly and definitively decreases with the increasing oxygen concentration.

3.4. Dissolved oxygen

The concentration of oxygen dissolved in a polymer is usually determined by the permeability measurements, the saturation experiments carried out at high vacuum [41–43],

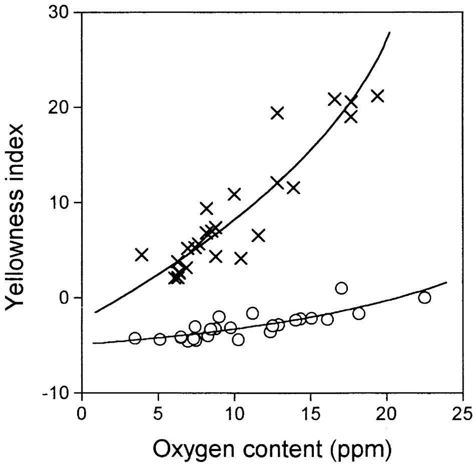

Fig. 7. Effect of adsorbed oxygen on the color of processed neat and stabilized HDPE samples; (○) neat, (×) stabilized with 0.25 wt% I1010.

or by the theoretical calculations. Similar to others, we measured the permeability of oxygen through our polymer to estimate this quantity. The amount of gas passing through a polymer film or plate is determined by the chemical and physical structure of the material, pressure difference, thickness, the size of the sample and the time of the measurement [41]. Transmission rate (Q) was determined on PE plaques as a function of thickness always at the same pressure difference. The correlation of transmission rate and specimen thickness is presented in Fig. 9. Permeability (P) is related to transmission rate (Q) according to Eq. (1)

$$P = \frac{Ql}{\Delta p} \tag{1}$$

where l is the thickness of the specimen and Δp the pressure difference. If Δp is known, permeability can be calculated from the slope of the straight line.

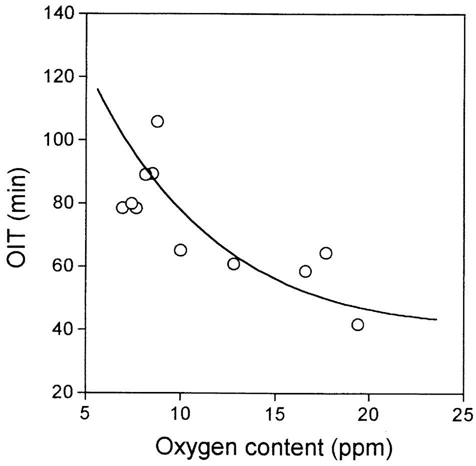

Fig. 8. Dependence of the oxidative stability of HDPE samples containing 0.25 wt% I1010 on the amount of adsorbed oxygen.

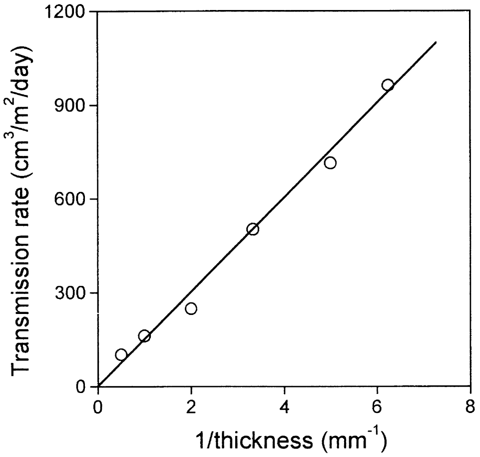

Fig. 9. Transmission rate of oxygen through HDPE plates plotted as a function of reciprocal specimen thickness.

Permeability is determined by the coefficient of diffusion (D) and solubility (S)

$$P = DS \tag{2}$$

The determination of diffusion coefficient is tedious and complicated, but the data are available in the literature [41,44–47]. In most studies the values published in Ref. [47] are used, which are listed in Table 3. As the table shows, the rate of diffusion depends strongly on crystallinity [46,48]; the dependence can be expressed by the following correlation [41]

$$D = D_a(1 - x_c) \tag{3}$$

where D and D_a are the diffusion coefficients of crystalline and amorphous polymers, respectively, while x_c represents the crystallinity. Further, a linear relationship exists between crystallinity and density. As a consequence, the diffusion coefficient can be derived from density (ρ) by

$$D = -B\rho + A \tag{4}$$

The diffusion coefficient calculated for our polymer in this way is also listed in Table 3 (0.32×10^{-6} cm^2/s). Using this value and the permeability derived from Fig. 9, the solubility was calculated resulting in an amount of 72 ppm oxygen, which is dissolved in the given polymer. This amount is considerably higher than that adsorbed on the surface of PE powder or granules and exceeds by an order of magnitude the value estimated from discoloration (see Fig. 7).

Table 3
Diffusion coefficients of various polyethylenes

Polymer	Density (g/cm^3)	Diffusion coefficient $\times 10^{-6}$ (cm^2/s)	References
LDPE	0.914	0.46	[41,44,45,47]
FA 381	0.938	**0.32**^{a}	
HDPE	0.964	0.17	[41,44,45,47]
LDPE	0.894	12.00	[47]
LDPE	0.900	4.20	[28]

^{a} Calculated from Eq. (4).

Table 4
Solubility of oxygen in polyethylene at 23°C

PE type	Density (g/cm^3)	Solubility ($cm^3/(cm^3$ bar))	Solubility (ppm)	References
LDPE	0.914	0.0478	68	[44,47]
HDPE	0.964	0.0182	25	[44,47]
LDPE		0.0650		[41]
HDPE		0.0470		[41]
Amorphous	0.855	0.0144	22	[49]
Amorphous	0.855	0.0769	117	[43]
LDPE	0.894	0.0717	105	[47]
FA 381	0.938	**0.0246**	**34**[a]	

[a] Calculated from the data of Refs. [43,44,47]

In order to check the validity of the estimate, the published solubility data for PE are listed in Table 4. The information is not always complete (e.g. missing density), it is occasionally contradictory (e.g. $S = 0.0470$ $cm^3/(cm^3$ bar) for HDPE [41], while 0.0144 for an amorphous PE [49]), and covers a very wide range.

The amount of dissolved oxygen can also be estimated from the crystallinity of the polymer by using the published solubility data. If in accordance with Michaels and Bixler [43,47] we assume that the solubility is a linear function of crystallinity and use their values in the calculations, an oxygen solubility of 34 ppm can be determined for our polymer. Although this value is much lower than the 72 ppm calculated above, it shows that the amount of dissolved oxygen reaches or most probably exceeds the quantity adsorbed on the surface of the polymer. Obviously dissolved oxygen plays an important role in the chemical and physical changes occurring in the polymer during its processing.

Further factors which may change the amount of dissolved oxygen are the form, morphology and previous thermal history of the samples. Our attention was called to the possibility that the powder samples taken from the reactor might have higher crystallinity than the granules cooled quickly in a water bath. The melting temperature and the heat of melting of several powders and the corresponding granules are given in Table 5. According to the results the crystallinity of the two kinds of samples is very similar, thus the form and origin of the polymer do not influence considerably the amount of dissolved oxygen.

Table 5
Comparison of the melting characteristics of HDPE powder and granules

Sample			Melting characteristics	
No.	Form	Stabilizer (wt%)	Melting temperature (°C)	Heat of melting (J/g)
P1	Powder	–	126.2	135.1
P2	Powder	–	125.9	131.7
P3	Powder	–	125.2	124.1
G01	Granule	0	127.5	131.4
G02	Granule	0	127.0	127.8
G03	Granule	0	126.4	128.3
GS1	Granule	0.25	127.2	133.4
GS2	Granule	0.25	126.2	130.4
GS3	Granule	0.25	127.0	130.7

Another series of experiments was designed on the basis of our assumption that the dissolved oxygen cannot be removed easily from the polymer; thus longer time is needed for the gas to diffuse from inside of a sample to the surface. Since solubility of oxygen is lower [41,50] and its diffusion rate faster [41] at higher temperatures, the polymer powder samples were stored in a vacuum oven for a long time at elevated temperatures (50 and 80°C) expecting that the amount of dissolved oxygen will decrease with time. Samples taken at various intervals were extruded and characterized by the usual techniques.

Yellowness index is presented as a function of degassing time in Fig. 10. We have seen earlier that the discoloration indicated degradation reactions very sensitively and the color was related to the amount of oxygen being present. The color decreases as a function of the degassing time at both temperatures used. The only unexpected phenomenon is the increase of color at longer storage times at 80°C. We assume that the degradation reactions take place already at this temperature and lead to the color development. This explanation is supported also by the fact that the increase of color begins earlier for the neat polymer than for the stabilized material. Moreover, the storage at 50°C does not result in discoloration; the yellowness index decreases during the entire period of the experiment.

Also the amount of oxygen which was not removed during degassing can be estimated from the observed color change by using the results of the previous section (see Fig. 7). The calculations yield about 2 ppm dissolved oxygen at 50°C and 4 ppm at 80°C. The obtained quantity is obviously much lower than the value calculated from permeability and diffusion data. However, it is in the same range as that obtained from the extrapolated color difference of the two correlations in Fig. 7. These results indicate that our assumption of the slow removal of dissolved oxygen was erroneous, and only a small amount, 1–5 ppm, oxygen remains in the polymer after a limited degassing time.

4. Conclusions

Our experiments confirmed previous information about the importance of oxygen in the degradation reactions taking place during the melt processing of polyethylene. Contrary to literature data, direct measurement of the amount of adsorbed oxygen showed it to be in the range of 20–25 ppm proving that the processing takes place under an oxygen poor environment. The polymer powders adsorb more oxygen than the granules due to their larger surface and porous structure. Permeability measurements indicate that about the same amount or even more oxygen is

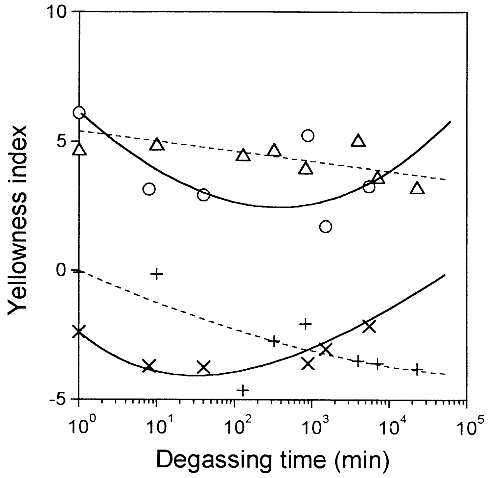

Fig. 10. Effect of degassing time on the color of HDPE processed with and without a stabilizer; neat: (×) ageing at 80°C, (+) 50°C; stabilized (○) 80°C, (△) 50°C.

dissolved in the polymer than is adsorbed on the polymer. Its estimated concentration is in the order of 40–70 ppm. In spite of the difficulties in the determination of adsorbed oxygen and the preparation of samples with controlled oxygen content, clear correlations were determined between oxygen content and polymer properties. In the oxygen poor environment of processing, the viscosity of the polymer decreases, while its color increases with the increasing oxygen content. The discoloration of stabilized samples is particularly strong. As expected the stability of the latter also decreases considerably with the increasing oxygen concentration. As a consequence, oxygen must be excluded from all processing operations to the highest possible extent, especially since even proper stabilization cannot eliminate completely the detrimental effect of oxygen.

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References

[1] Sadrmohaghegh C, Scott G. Eur Polym J 1990;16:1037.
[2] Rideal GR, Padget JC. J Polym Sci, Symp 1976;57:1.
[3] Shlyapnikov YuA, Serenkova A. Polym Degrad Stab 1992;35:67.
[4] Moss S, Zweifel H. Polym Degrad Stab 1989;25:217.
[5] Foster GN, Wasserman SH, Yocka DJ. Angew Makromol Chem 1997;252:11.
[6] Zamorsky Z, Tomis F. Acta Polym 1984;35:463.
[7] El'darov EG, Mamedov FV, Gol'dberg VM, Zaikov GE. Polym Degrad Stab 1996;51:271.
[8] Pauquet JR. Plast Rubber Compos Process Appl 1998;27:19.
[9] Holmström A, Sörvik EM. J Appl Polym Sci: Symp 1976;57:33.
[10] Thurmer A, Malík J, Dongiovanni EK, Stoll H. Polym Polym Comp 1999;7:99.
[11] Chakraborty KB, Scott G. Eur Polym J 1977;13:731.
[12] Holmström A, Sörvik EMJ. Appl Polym Sci 1974;18:779.
[13] Drake WO, Pauquet JR, Todesco RV, Zweifel H. Angew Makromol Chem 1990;176/177:215.
[14] Shlyapnikov YuA, Tyuleneva NK. Oxid Commun 1997;20:434.
[15] Shlyapnikov YuA, Tyuleneva NK. Polym Degrad Stab 1997;56:311.
[16] Barr-Kumarakulasinghe SA. Polymer 1994;35:995.
[17] Gijsman P, Hennekens J, Vincent J. Polym Degrad Stab 1993;42:95.
[18] Hlouskova Z, Luston J, Szocs F. J Appl Polym Sci 1993;48:1843.
[19] Gillen KT, Celina M, Clough RL, Wise J. Trends Polym Sci 1997;5:250.
[20] Gugumus F. Polym Degrad Stab 1996;52:145.
[21] Wise J, Gillen KT, Clough RL. Polymer 1997;38:1929.
[22] Kharitonov VV, Psikna BL, Zaikov GE. J Chem Biochem Kinetics 1997;3:201.
[23] Gol'dberg VM, Zaikov GE. Int J Polym Mater 1996;31:1.
[24] Mason LR, Doyle TE, Reynolds AB. J Appl Polym Sci 1993;50:1493.
[25] Pospisil J, Nespurek S. Polym Degrad Stab 1995;49:99.
[26] Yongcheng Y. Polym Degrad Stab 1993;39:193.
[27] Scheirs J, Bigger SW, Delatycki O. Polymer 1989;30:2080.
[28] Henman TJ. In: Scott G, editor. Development in polymer stabilization-1, London: Applied Science Publishers, 1979. p. 39.
[29] Harlin A. Polym Degrad Stab 1993;42:89.
[30] Hinsken H, Moss S, Pauquet JR, Zweifel H. Polym Degrad Stab 1991;34:279.
[31] Zolotova NV, Denisov ET. J Polym Sci 1971;9(A-1):3311.
[32] Igarashi S, Yamamoto O, Kambe H. Kolloid-Zeitschr Zeitschr Polym 1964;199:97.
[33] Quackenbos HH. Polym Engng Sci 1966;6:117.
[34] Sen AK, Mukherjee B, Bhattacharyya AS, De PP, Bhowmich AK. Polym Degrad Stab 1992;36:281.
[35] Kolesnikova NN, Tyuleneva NK, Shlyapnikov YuA. Polym Degrad Stab 1993;39:305.
[36] Scott G, Yusoff MF. Polym Degrad Stab 1981;3:13.
[37] Kovarova-Lerchova J, Pospisil J. Eur Polym J 1977;13:975.
[38] Pospisil J. Adv Polym Sci 1980;36:69.
[39] Scheirs J, Pospisil J, O'Connor MJ, Bigger SW. In: Clough RL, Billingham NC, Gillen KT, editors. Polymer durability, Adv Chem Ser 249, Washington, DC: ACS, 1996. p. 359.
[40] Epacher E, Kröhnke C, Pukánszky B. Polym Engng Sci (accepted).
[41] Van Krevelen DW. Properties of polymers. Amsterdam: Elsevier, 1976 (chap. 18, p. 403).
[42] Kulkarni SS, Stern SA. J Polym Sci, Phys 1983;21:441.
[43] Michaels AS, Bixler HJ. J Polym Sci 1961;50:393.
[44] Pauly S. In: Brandrup JE, Immergut H, editors. Polymer handbook, New York: Wiley, 1989. p. 435 (chap. 6).
[45] Aggarwal SL. In: Brandrup J, Immergut EH, editors. Polymer handbook, New York: Wiley, 1966. p. 41 (chap. 6).
[46] Takeuchi H. J Chem Phys 1990;93(6):4490.
[47] Michaels AS, Bixler HJ. J Polym Sci 1961;50:413.
[48] Peterlin A, McCrackin FL. J Polym Sci, Polym Phys 1981;19:1003.
[49] Budzien JL, McCoy JD, Weinhauf DH, LaVidette RA, Peterson ES. Macromolecules 1998;31:3368.
[50] Pace RJ, Datyner A. J Polym Sci: Polym Phys 1980;18:1103.