

# CHEMICAL REACTIONS DURING THE PROCESSING OF STABILIZED PE; DISCOLOURATION AND STABILIZER CONSUMPTION

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Received: June 2, 1998

## Abstract

A series of experiments was carried out to develop an additive package for HDPE blown films. The evaluation of the results yielded interesting correlations relating the colour of the polymer to its chain structure and to the properties of the films. Additional experiments proved that all reactions are related to each other. The discolouration of the polymer could be described by simple first order reaction kinetics and a linear correlation was found between stability and a quantity calculated from the kinetic model. The reaction of the vinyl functionality of the polymer seems to be related to the changes in its rheological properties. In spite of the good general correlations found, some details remained unexplained and need further investigation.

*Keywords:* thermal degradation, phenolic antioxidants, discolouration, stability, functional groups, product properties.

## 1. Introduction

A large amount of polyethylene (PE) is applied in the packaging industry mostly as film. During the processing of the polymer chemical reactions take place under the effect of heat, shear and oxygen, which change the structure of the chains and the properties of the processed material. A small number of reactions leads to considerable changes in the properties of the polymer [1]-[5]. To avoid these changes and retain inherent properties, stabilizers are added before processing, which initiate new reactions resulting in the consumption of the stabilizer [6], development of colour [7]-[12], etc. Optimization of the composition of a stabilizer package is of great technical

and financial importance in industrial practice shown also by papers dealing with this aspect of stabilization [13]–[15].

During such an optimization project interesting correlations were observed which demonstrated the importance of chemical reactions taking place during the processing of stabilized polyethylene. The correlation presented in *Fig. 1* shows considerable changes in the melt flow index (*MFI*) of the polymer as a function of processing history and composition and the consequently large differences in the tear resistance of the films blown from the corresponding granulates. Similar correlations were observed between other properties of the processed material including colour, functional group content of the polymer, film shrinkage, etc. Although similar changes have been shown in the neat polymer before [1]–[3], [16], less information is available for stabilized materials.

The goal of our study was to investigate these correlations with the help of the available data and some additional experiments, as well as to obtain as much information as possible about the chemistry/structure/property correlations in a stabilized Phillips type 1-hexene copolymer of ethylene. The most important results related to chemistry and the changes in the molecular structure of the polymer are presented in this paper, while rheological and mechanical properties will be described in a subsequent publication.

## 2. Proposed Schemes of PE Degradation and Stabilization

Numerous studies have been published on the degradation of polyolefins [17]–[20]. Practically all are based on the chain reaction of hydrocarbon oxidation. This approach assumes that the degradation proceeds through initiation, propagation, chain branching and termination steps and oxygen, as well as peroxy and alkoxy radicals play an important role in the degradation. Such a scheme is presented in *Fig. 2* showing the interrelation of degradation reactions.

Although the initiation reaction is usually not defined, the irregularities of the chain seem to play an important role in degradation [11], [21]–[24]. ZWEIFEL and his co-workers [1]–[3] have shown that during the multiple extrusion of a neat HDPE the number of vinyl groups continuously decreases and they related this decrease to the change in the molecular weight and *MFI* of the polymer. Simultaneously with the decrease in vinyl concentration, the vinylene content of the polymer increases, while the number of vinylidene groups does not seem to change. The major problem of the scheme of *Fig. 2* and other similar approaches is that the extrusion of polyolefins takes place in oxygen poor environment [2], [11], [25], thus no sufficient amount of oxygen is available to carry on the oxidation chain, oxygen is consumed very early during processing. Nevertheless, all studies on polyolefin degradation prove that a large number of reactions take place during

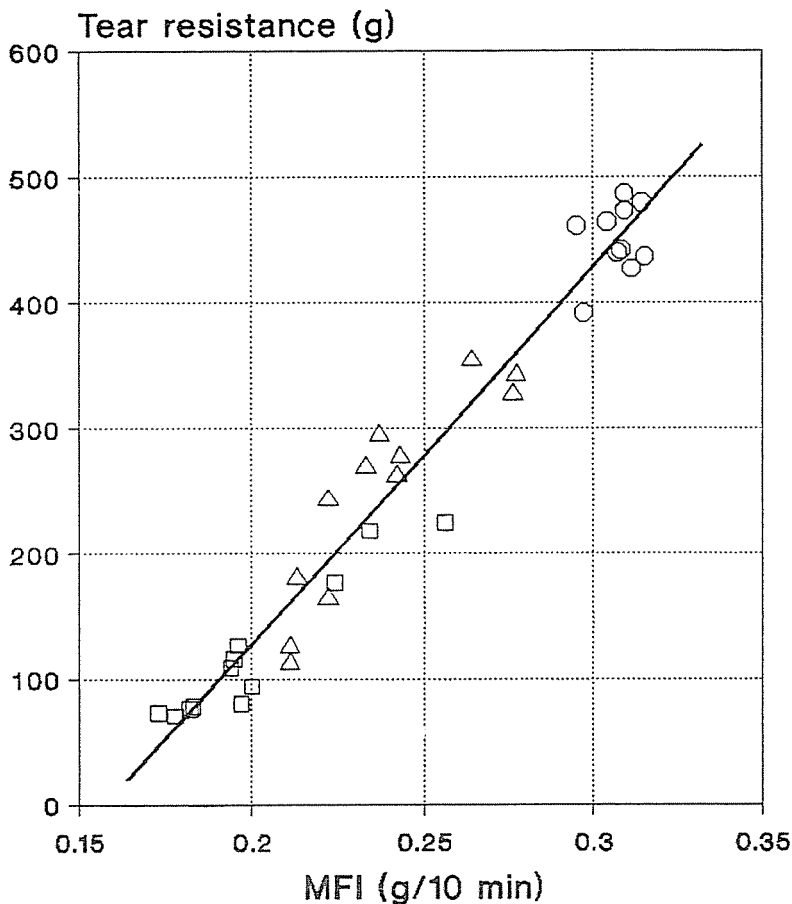


Fig. 1. Correlation between the *MFI* of granulates prepared in multiple extrusion and the mechanical property of films blown from them, (○) 1st, (△) 4th, (□) 6th extrusion

the processing of the polymer and small changes in the molecular structure result in considerable modification of properties.

The possible reactions of hindered phenolic antioxidants are also numerous and their interrelations complicated. Although the basic correlations are clear, i.e. hydrogen abstraction from the phenolic -OH group of the stabilizer and the formation of a stabilizer radical, further reactions may also take place [6]. The reactions of the stabilizer result in quinoidal structures which lead to colour development; both active and inactive reaction products are formed in the process [12]. The transformation products of the stabilizer may also react with each other and some of the reaction products

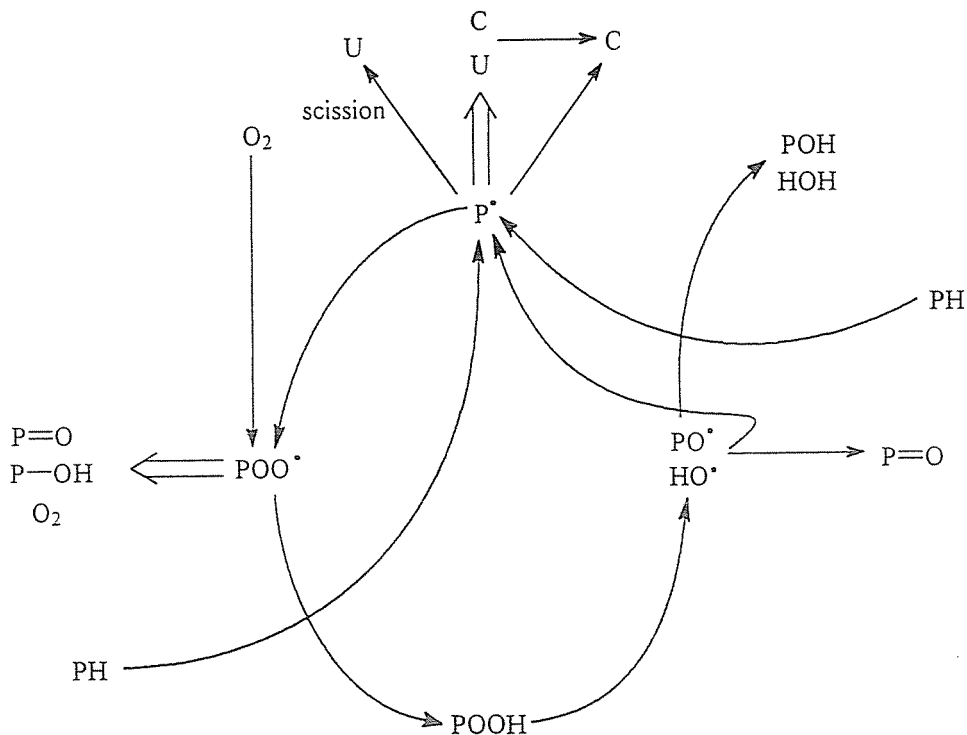


Fig. 2. Scheme for the oxidation chain reactions of polyolefins

are more efficient stabilizers than the original molecule [9], [10], [26], [27]. These reactions have been studied in detail for BHT [9], [10], but less knowledge is available about the reactions and metabolites of the most commonly used phenolic antioxidants like Irganox 1010 or Irganox 1076.

As a consequence of the numerous reactions and their complicated interrelations, the exact mechanism of polyolefin degradation and stabilization is not known yet. The structure of the polymer, processing conditions, the amount of oxygen, all determine the direction of the changes and decide whether mainly chain scission or cross-linking takes place [6], [25], [28], [29]. The large number of reactions make the kinetic treatment of the processes very difficult and the determination of simple correlations almost impossible. Even less knowledge is available on the relationship of the chemical reactions, the resulting changes in the molecular structure of the polymer and the properties of the processed product [1].

### 3. Experimental

The polymer used in the study was the Phillips type Tipelin FA 381 grade of TVK, Hungary, with an *MFI* of 0.28 g/10 min (190 °C, 2.16 kg), a density of 0.938 g/cm<sup>3</sup> and nominal 1-hexene content of 3–5%. 11 recipes were studied in which two phenolic antioxidants (Irganox 1010 and Irganox 1076, Ciba-Geigy, Switzerland) were combined with a phosphonite co-stabilizer (Sandostab PEPQ, Clariant Huningue, France) in various amounts. All recipes contained also 500 ppm zinc stearate.

The PE powder and the additives were homogenized in a Baker Perkins high speed fluid mixer for 3 minutes. Homogenization extrusion was carried out on a VS 40 type extruder of Tanabe Plastics Machinery Co. Ltd. at 155, 170, 190, 190 and 190 °C zone temperatures and 90 rpm. The homogenized material was subjected to 5 degradative extrusion steps, which was executed on a Rheomex 3/4" extruder attached to a HAAKE Rheocord EU 10 V driving unit. The temperature of all zones was set to 260 °C during multiple extrusion. Films for mechanical testing were blown on a Tanabe VS 30 extruder having a 24 L/D screw of 30 mm diameter. The films were prepared with a blow ratio of 1:4 at 40 rpm and 175, 190, 190 and 190 °C set temperatures.

*MFI* and colour were determined routinely on all 66 samples. Mechanical properties were measured after the 1st, 3rd and 5th degradative extrusions, while all other measurements were carried out on selected samples. Altogether 8 samples were selected for further studies in a way to cover the complete range of property changes in *Fig. 1*. 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 colour of the granulates was measured on a Hunter Lab LS 5100 apparatus. Yellowness index (YI) according to ASTM D 1925-79 and Phillips Colour Number (CNp) were determined, the former will be used in further evaluation.

Three 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.

Thermoxidative stability was characterized by the oxidation induction time (OIT) measured in the DSC 30 cell of a Mettler TA 3000 equipment at 200 °C. The melting and crystallization characteristics of the extruded polymer were measured in the same apparatus on 10 mg samples at 10 °C/min heating and cooling rates in two runs. The functional group content of the polymer was determined by FTIR spectroscopy on a Mattson Galaxy 3020 spectrometer. The methyl content was deduced from the absorption at 1378, while vinyl at 908 cm<sup>-1</sup> wave number. The molecular weight and

its distribution were determined on a Waters 150C GPC apparatus in 1,2,4-trichlorobenzene at 135 °C. Intrinsic viscosity was measured with an Ubbelohde viscometer at 135 °C in decalin.

## 4. Results and Discussion

For the sake of simplicity the phenomena related to the reactions of the stabilizer and the polymer, respectively, are discussed in separate sections. In a third section an attempt is made to find correlations between the two groups of observations.

### 4.1. Property Changes Related to the Reactions of the Stabilizer

As it was discussed before, hindered phenols are hydrogen donating antioxidants which inhibit oxidation by competing with the polymeric substrate for peroxy radicals [6], [20], [30]. Stabilizer molecules can take part in various transformation reactions the products of which are conjugated dienones in many cases [10], [12]. The formations of these compounds lead to the discolouration of the polymer which is regarded as an undesired fact, but rarely discussed in detail. However, the study of colour development might give some insight into the processes taking place during the processing of the polymer and might even give an indication about the properties of the product.

Discolouration of two of the recipes during multiple extrusion is shown in *Fig. 3*. The shape of the correlation was the same in all cases and a similar correlation was observed basically in all cases when phenolic antioxidants were used for the stabilization of the polymer, even for polymers stabilized with an additive package completely different from the one used in the present study.

Literature data and experimental observations indicate that in the majority of cases colour is caused by the transformation reactions of the phenolic antioxidants, or more exactly their coloured reaction products [9], [10]. As a consequence, we must assume that discolouration is proportional to the amount of stabilizer which reacts during the processing of the polymer. Because of the large number of reactions taking place and the complicated interrelations between the various reactions and products, the kinetics cannot be described exactly. Nevertheless, the above presented assumption can be expressed in quantitative terms even without the exact knowledge of the individual reactions in the following way

$$YI = YI_0 + A(c_0 - c), \quad (1)$$

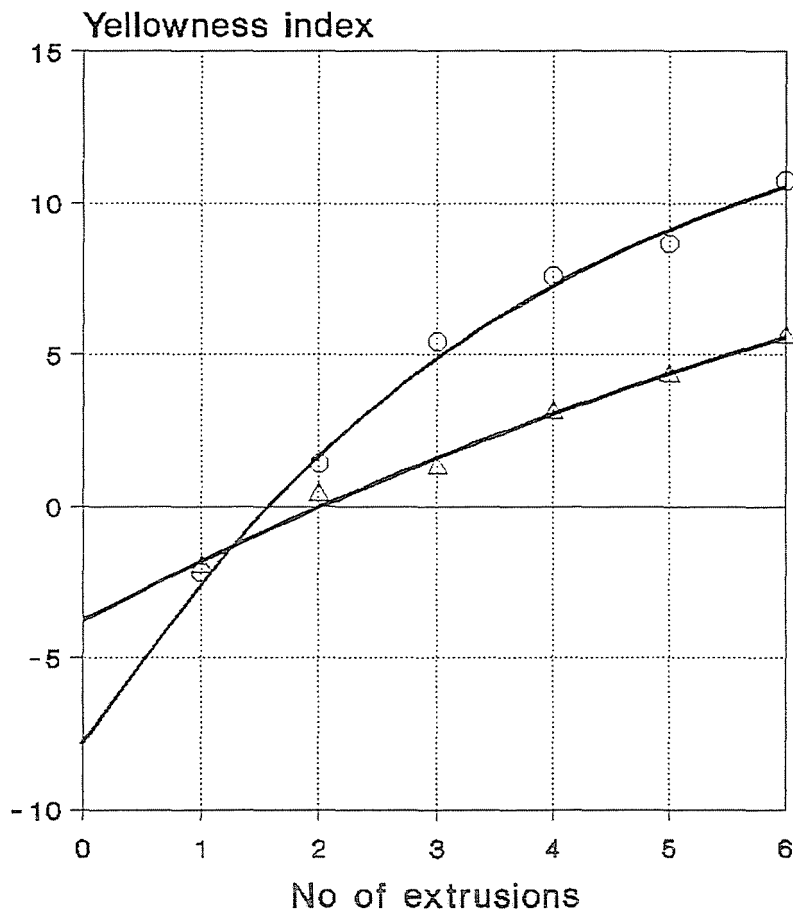


Fig. 3. Colour development in two recipes during multiple extrusion; measured values: (○) Rp. 2, (△) Rp. 10, — calculated from Eq. (4)

where  $YI$  is the actual colour of the sample,  $YI_0$  is a hypothetical colour before any processing,  $(c_0 - c)$  is the amount of stabilizer reacted during processing and  $A$  is a proportionality constant converting stabilizer concentration to colour. Assuming that the concentration of macro radicals is constant, stabilizer consumption

$$\frac{dc}{dt} = -k_1c, \quad (2)$$

where  $t$  is time and  $k_1$  is the overall rate constant of the reaction. It must be emphasized here that we discuss overall processes which include all reactions leading to stabilizer consumption and discolouration of the polymer. Car-

rying out the necessary operations and introducing the results into *Eq. (1)* we obtain for the time dependence of colour

$$YI = YI_0 + Ac_0[1 - \exp(-k_1t)]. \quad (3)$$

Since we study the discolouration of the polymer as a function of processing history, the independent variable must be replaced by the number of processing steps ( $n$ ) which leads to

$$YI = YI_0 + Ac_0[1 - \exp(-k'_1n)]. \quad (4)$$

The validity of the explanation given above, which includes several assumptions and neglects all the details of the actual chemical processes, may be checked by fitting *Eq. (4)* to the experimental data. This has been done and excellent fit was obtained in all cases as it is shown by the solid lines plotted in *Fig. 3*. The good fit indicates that all reactions are of first order, which is hardly probable, or a rate determining process exists which has the same order. The selection of this rate determining first order process seems to be almost impossible if we consider the scheme in *Fig. 2* and the large number of possible reactions. Nevertheless, it is obvious to assume that hydrogen abstraction from the polymer chain is the initiating and rate determining step of these reactions. Free radicals are created in this reaction and the rate of all radical reactions are extremely high. Naturally, this tentative explanation must be proven experimentally, but the verification seems to be rather difficult at the moment.

The results of the curve fitting procedure are collected in *Table 1* together with the composition of the studied recipes expressed as total antioxidant and phosphonite content in moles. The extremely good fit shown by the high value of the correlation coefficient ( $R^2$ ) is clearly seen from the table. Although the fit is apparently good, the data of the table show also the drawbacks of the procedure applied. The initial, hypothetical colour of the polymer is different in each case. The deviations might result from the standard deviation of the colour measurement or from some other effect. It is obvious to assume, though, that the initial colour of the PE powder was the same, since the addition of low amounts of stabilizers, which are white anyway, probably does not change the initial colour. It is even more difficult to explain the fact that no correlation whatsoever was found between any of the calculated quantities ( $YI_0$ ,  $k'_1$ ,  $Ac_0$ ) and the composition of the stabilizer package. Further study is needed in order to explain these phenomena.

We might expect some correlation between discolouration and the stability of the samples, since both are related to the stabilizer content of the polymer. However, according to *Fig. 4*, no correlation exists between the two quantities. This might be surprising at first, but a more thorough consideration reveals that while colour must depend on the amount of stabilizer consumed during processing, stability is determined by the amount still present at the time of the *OIT* measurement.



Table 1. Composition of the recipes and kinetic parameters of discolouration calculated from Eq. (4)

Recipe No	Composition (mmol/kg)		$Y I_0$	$A c_0$	$k'_1$	$R^2$
	$\Sigma A O^a$	$PEPQ$				
1	1.59	0.29	-5.51	22.0	0.212	0.9749
2	2.95	0.29	-7.82	22.6	0.280	0.9937
3	2.35	0.29	-6.12	18.8	0.265	0.9948
4	1.59	0.68	-6.17	13.0	0.349	0.9857
5	0.68	0.58	-5.67	18.0	0.189	0.9964
6	0.57	0.58	-4.09	17.8	0.140	0.9948
7	1.36	0.39	-6.56	16.7	0.258	0.9956
8	0.94	0.39	-6.17	13.9	0.388	0.9973
9	1.70	0.48	-6.40	19.4	0.199	0.9978
10	0.94	0.48	-3.75	20.4	0.102	0.9924
11	2.64	0.48	-6.21	18.3	0.233	0.9972

<sup>a</sup> mmol -OH/kg

Using the same simple line of thought and formalism presented above, the amount of unreacted stabilizer can be calculated and the value of  $OIT$  expressed quantitatively again. We assume that stability is a linear function of the number of functional groups present, i.e.

$$OIT = OIT_0 + Bc, \quad (5)$$

where  $OIT$  is the stability of the sample at zero antioxidant content and  $B$  is a proportionality constant. By combining Eq. (5) with Eq. (2) and carrying out the necessary operations we obtain

$$OIT = OIT_0 + Bc_0 \exp(-k_2 t), \quad (6)$$

where  $k_2$  is the overall rate constant and  $t$  is time which can be replaced by the number of extrusions, i.e.

$$OIT = OIT_0 + Bc_0 \exp(-k'_2 t). \quad (7)$$

The validity of the treatment can be checked by comparing the measured  $OIT$  values to a quantity calculated according to the approach presented above, that is to  $c_0 \exp(-k'_2 n)$ . Since the same expression was used for the description of colour and  $OIT$  change, the two rate constants must be equal to each other, i.e.  $k'_1 = k'_2 \cdot c_0$  is the total moles of phenolic -OH groups. The use of this quantity is strongly supported by the observation

of GUGUMUS [31].  $OIT$  is plotted against the calculated quantity in *Fig. 5*; the correlation is surprisingly good, especially if we consider the simplicity of the treatment and the fact that the amount of co-stabilizer does not appear in the correlations at all. Nevertheless, the results are good and their validity is further supported by the fact that  $OIT_0$  is zero in accordance with experimental observations.

Although the results need more theoretical support and explanation, especially the lack of correlation between the quantities calculated from discolouration kinetics and composition, their practical relevance is clear. The long term stability of any recipe can be predicted approximately on the basis of relatively simple colour measurements. Moreover, the data suggest that a rate determining reaction exists in the stabilization which determines colour development and the consumption of the stabilizer during processing.

#### 4.2. Changes in the Structure of the Polymer

ZWEIFEL and co-workers [3] studied the changes in the structure and properties of neat and stabilized PP and PE during multiple extrusion. They found drastic changes in the molecular weight and  $MFI$  of neat PP, but in the case of virgin HDPE the changes and correlations were much less unambiguous. Even smaller modifications of these properties are expected in the presence of an efficient stabilizer package. *Table 2* supports this assumption, indeed, the molecular weights and intrinsic viscosities of the selected 8 samples are practically the same, no tendency can be observed at all. The results of *Table 2* are, however, very difficult to understand since they completely contradict the results presented in *Fig. 1* where considerable changes were observed both in  $MFI$  and tear resistance.

*Table 2.* Molecular weight and intrinsic viscosity of selected HDPE samples

Sample No <sup>a</sup>	Molecular weight (g/mol)		$\frac{m_w}{M_n}$	$[\eta]$ (cm <sup>3</sup> /g)
	$M_n \times 10^{-4}$	$M_w \times 10^{-4}$		
6/1	22	226	10.27	1.954
7/1	22	240	10.91	1.932
11/4	23	240	10.43	1.967
7/4	23	244	10.61	1.930
8/4	23	237	10.30	2.005
11/6	23	240	10.43	2.057
5/6	22	224	10.18	2.051
10/6	24	244	10.17	2.044

<sup>a</sup> recipe/extrusion number

Nevertheless, the melting and crystallization characteristics of the samples show a similar independence of the variables in *Table 3*. Changing molecular characteristics usually affect the kinetics of crystallization, while branching decreases the regularity of the chains. Both should result in some change of the characteristic temperatures ( $T_m$ ,  $T_c$ ) and the heat of melting or crystallization ( $\Delta H_m$ ,  $\Delta H_c$ ). None of the characteristics change, which indicates either unaltered molecular structure – but see *Fig. 1* – or the extent of modification is so small that the DSC technique cannot detect it.

*Table 3.* Melting and crystallization characteristics of selected samples measured in the 2nd heating or cooling run, respectively

Sample No	Heating		Cooling	
	$T_m$ (°C)	$\Delta H_m$ (J/g)	$T_c$ (°C)	$\Delta H_c$ (J/g)
6/1	126.8	161.3	116.8	162.1
7/1	126.2	166.5	116.6	168.2
11/4	127.0	163.6	116.0	162.2
7/4	126.2	163.0	115.9	159.7
8/4	126.3	157.4	115.8	157.4
11/6	126.5	158.1	116.5	165.3
5/6	126.3	158.8	116.7	160.3
10/6	126.3	156.9	116.7	161.3

A clear proof of the change in the structure of the polymer chains is supplied by FTIR measurements. Both measured quantities, i.e. methyl and vinyl content of the polymer depend on the number of extrusions and on composition; both decrease with increasing processing history and decreasing stabilizer content (*Fig. 6*). The changes in the vinyl content may be explained by the hypothesis of ZWEIFEL et al [1]–[3]. They claim that the addition of alkyl radicals to the vinyl group results in a decrease of this functionality and in the increase of *MFI*. The correlation of *Fig. 7* further corroborates this statement showing a very close correlation between the vinyl content of the polymer and its *MFI*.

It is much more difficult to give an acceptable explanation for the decrease in the methyl content. According to the results, the number of methyl groups decreases with increasing processing history similarly to the vinyl content. The disappearance of this functionality might be explained by the scission of short branches or recombination of long chains. The latter is not probable, though, since the molecular weight remains constant, as *Table 2* shows. The results must be thoroughly checked and further experiments carried out to find an explanation for this phenomenon.

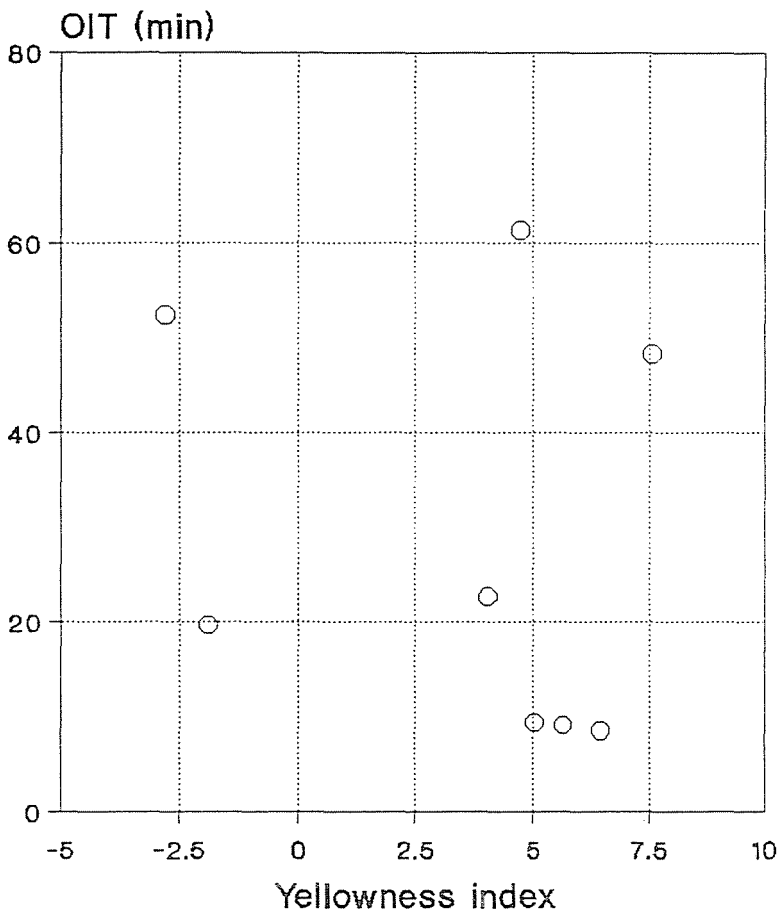


Fig. 4. Complete lack of correlation between the colour and stability of the selected PE samples

## 5. Discussion

Although some of the above presented observations need further experimentation and a more detailed explanation, it is obvious that during the processing of polyethylene chemical reactions take place in which both the polymer and the stabilizer take part. All of these reactions seem to be in relation with each other resulting in stabilizer consumption and changes in the molecular structure of the polymer. The modification of the chain structure results in a drastic change of rheological and mechanical properties. Our results strongly support the observation of ZWEIFEL et al [1]–[3] about the strong correlation between the vinyl functionality of the polymer and its

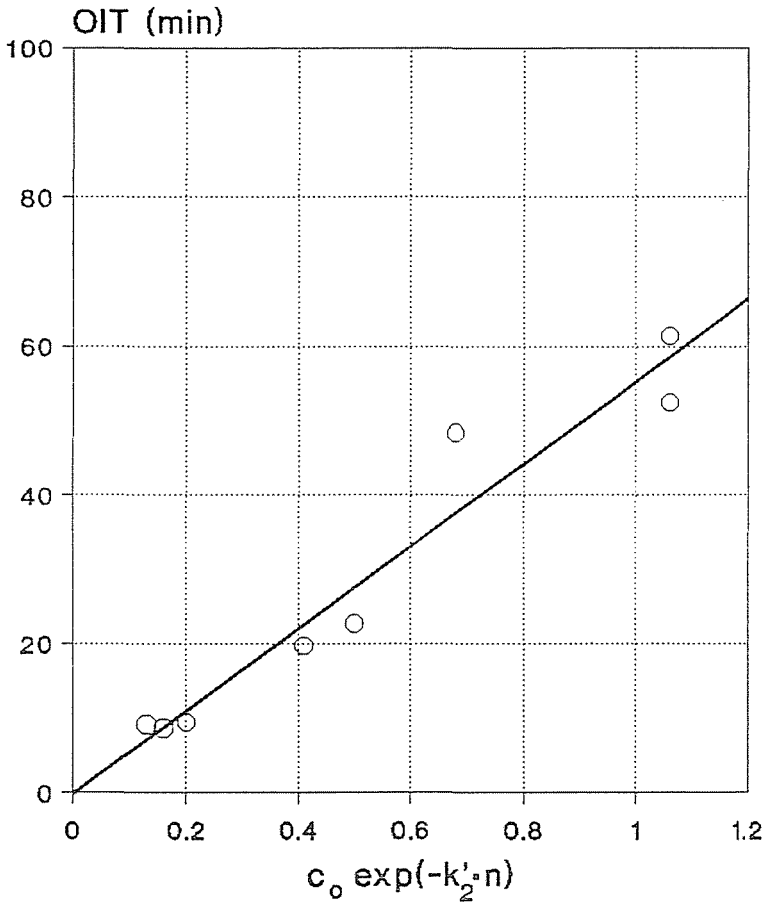


Fig. 5. Correlation of measured and predicted stability of the selected samples

### *MFI.*

Other correlations must exist which can give further support to the interrelation of all reactions taking place in the polymer melt. Stabilizer consumption leads to colour development, but it was shown that stabilization hinders the changes in the vinyl content of the polymer which seems to be responsible for the increase in viscosity (decrease in *MFI*). As a consequence, discolouration and *MFI* should be inversely correlated to each other. The two quantities are plotted against each other in Fig. 8. The Figure strongly supports our assumption and proves that an increase in the number of reactions leading to a coloured product decreases the number of coupling reactions of the polymer which result in an undesirable decrease in *MFI*. More generally, the correlation of Fig. 8 proves the interrelation of all reactions during processing.

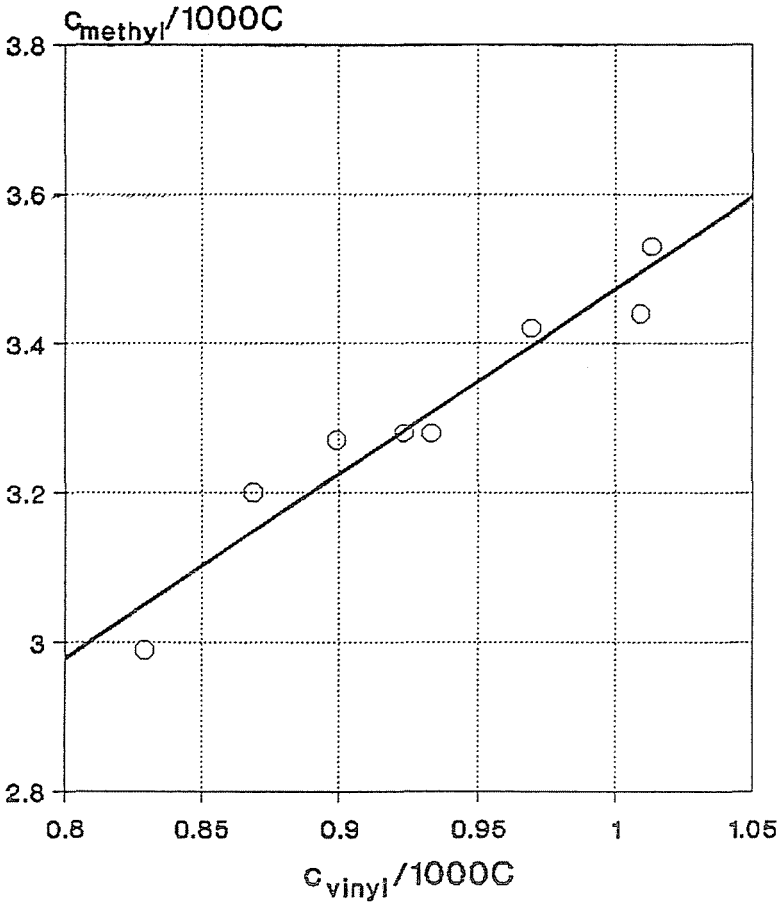


Fig. 6. Changes in the functional group content of the polymer

## 6. Conclusion

The experiments carried out as part of an optimization project and some additional measurements proved that several reactions take place during the melt processing of polyethylene. All these reactions seem to be related to each other. The success of the simple first order overall kinetics used for the quantitative analysis of the results indicates that a single reaction exists which determines the overall rate of changes. In spite of the numerous reactions which possibly take place in the melt, all changes including discoloration, stabilizer consumption, change of rheological and mechanical properties seem to be proportional to each other. The exact correlations between the molecular structure of the polymer and its properties could not be established, but the observed contradictions indicate that a very small

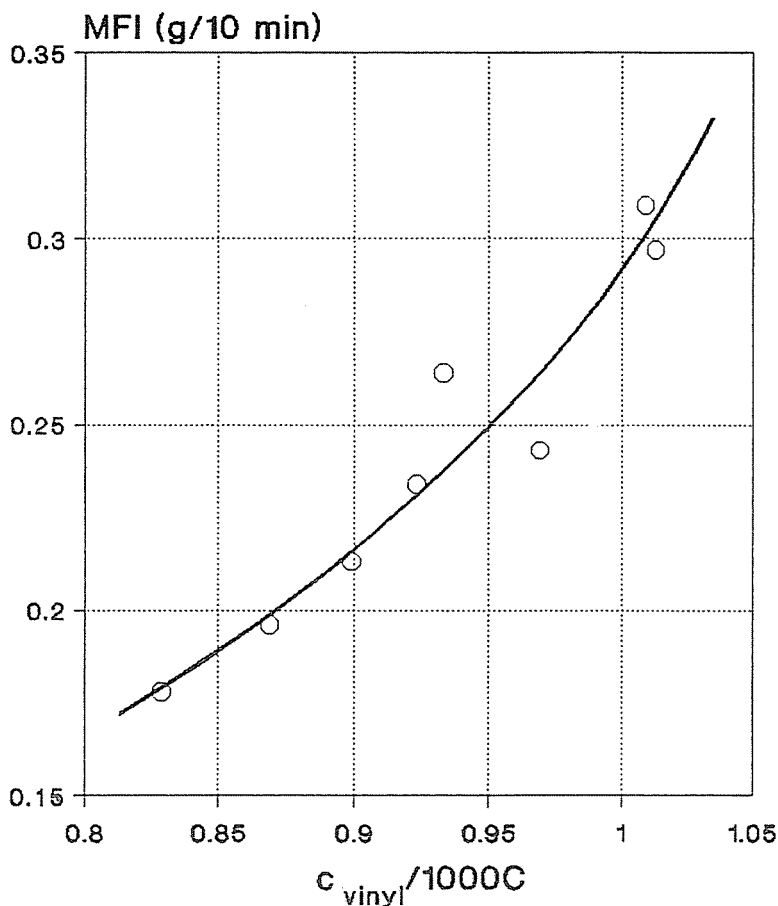


Fig. 7. Dependence of *MFI* on the number of vinyl groups in the polymer chain for the selected samples

number of reactions lead to drastic changes in properties. A subsequent paper discusses these structure/property correlations in more detail.

### Acknowledgements

The authors are grateful for the financial support of Clariant Huningue S.A., and specifically to Dr. L. Ávár, K. Stoll and R. Wolf, for the optimization study which initiated this research. The financial help of the National Scientific Research Fund of Hungary (Grant No. F 023065) is acknowledged for making possible the additional experiments. Also the help of our colleagues

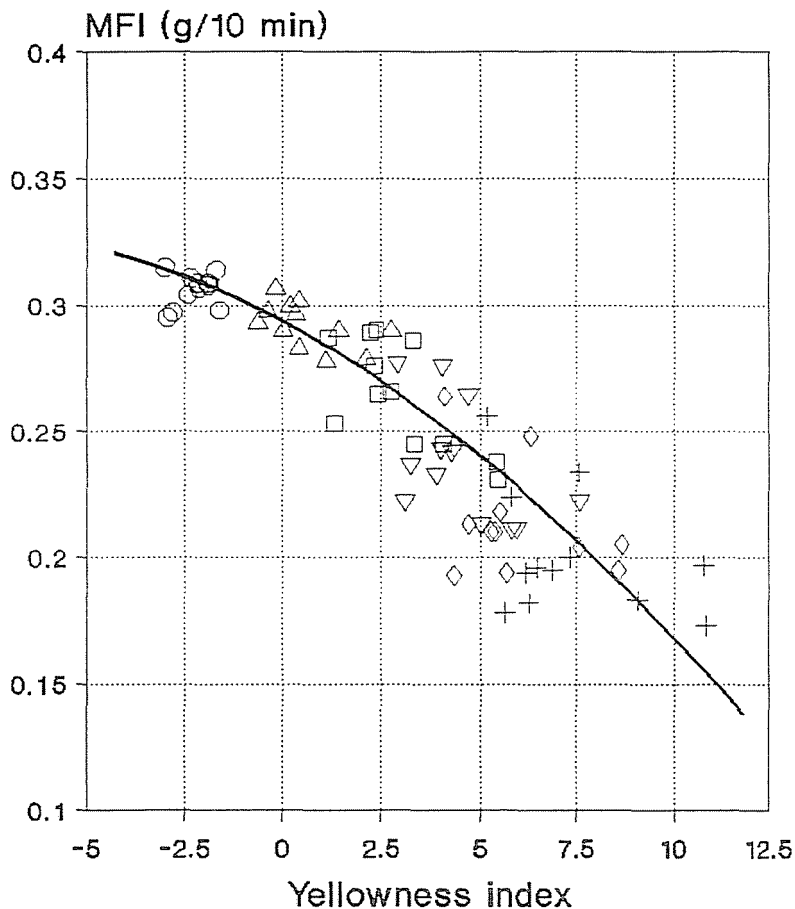


Fig. 8. Correlation of colour and *MFI* of PE subjected to multiple extrusion, (○) 1st, (△) 2nd, (□) 3rd, (▽) 4th, (◇) 5th, (+) 6th extrusion

at TVK, I. Domenik, Á. Orbán-Mester and S. Zirig, is greatly appreciated.

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