CHEMICAL REACTIONS DURING THE PROCESSING OF STABILIZED PE; STRUCTURE/PROPERTY CORRELATIONS

Edina EPACHER* **, Erika FEKETE* **, Markus GAHLEITNER*** and Béla PUKÁNSZKY* **

* Department of Plastics and Rubber Technology
Technical University of Budapest
H–1521 Budapest, P.O. Box 92, Hungary
** Central Research Institute for Chemistry
Hungarian Academy of Sciences
H–1525 Budapest, P.O. Box 17, Hungary
*** PCD Polymere GmbH
St.-Peter-Straße 25
A–4021 Linz, Austria

Abstract

Interesting correlations were observed in an optimization project directed towards the development of a recipe for blown film production. Analysis of the data and additional experiments indicated that some reactions take place during the processing of stabilized PE which also change the structure of the polymer. Modification of the rheological properties of the polymer and the mechanical characteristics of blown films can be related to these chemical processes. A close correlation was found among basically all rheological and mechanical properties. A tentative explanation was given which relates chemistry to the structure of the polymer and the properties of the product. According to the hypothesis long chain branches are formed during processing which decrease MFI, change the orientation of the film in the perpendicular direction and result in a considerable decrease in the strength of the blown films.

Keywords: thermal degradation, multiple extrusion, rheology, film properties, long chain branching, discolouration.

1. Introduction

As an effect of heat, shear and oxygen, chemical reactions take place during the processing of most polymers including polyethylene (PE). These reactions lead to modifications in their chain structure, which in turn change the properties. In order to avoid these, usually unfavourable, changes stabilizers are added to the polymer. The type and amount of stabilizers used depend on the type of the polymer, processing technology and application conditions of the product. The development of an appropriate stabilizer package is a complicated task and requires optimization of various properties and price [1]–[3]. The variation in properties taking place during processing and

application is smaller in the presence of stabilizers, but new reactions are initiated which lead, among others, to the discolouration of the polymer [4]–[9]. Nevertheless, the properties of stabilized PE are obviously not constant during processing or throughout the lifetime of the product.

A series of experiments was carried out in order to develop an optimum stabilizer package for the production of blown films. Analysis of the results indicated that several reactions take place during the processing of PE also in the presence of stabilizers. These reactions lead to stabilizer consumption [10] and result in changes in the chemical structure of the polymer chain. In a previous paper the possible reactions were discussed and it was shown that changes in some properties (colour, stability) during processing can be described quantitatively by first order overall reaction kinetics. A tentative explanation was given for the phenomenon, which assumed that hydrogen abstraction from the polymer chain is the initiating and rate determining step in these reactions.

Multiple extrusion of various recipes was carried out as usual in such optimization experiments. The melt flow index was routinely measured on all samples, while a detailed rheological characterization was also carried out on selected samples. The mechanical properties of films blown from granulates of various composition and processing histories were determined in a subsequent step. The goal of this paper is to discuss the changes in the rheological properties of PE during multiple processing and the consequent modification of the mechanical properties of the produced films. A general scheme is proposed which relates chemical reactions to the changes in the structure of the polymer and these latter to the properties of the product.

2. Experimental

The polymer used in the study was the Phillips type Tipelin FA 381 grade polyethylene of TVK, Hungary, with an 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%. 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 on films blown from the granulates obtained in the homogenization extrusion and from those produced in the 3rd and 5th degradative extrusions (4th and 6th extrusions). Altogether 8 samples were selected for further studies in a way to cover the complete range of MFI and mechanical property changes. 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.

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.

Rheological characterization of the samples was carried out on a Rheometrix RDS II apparatus in parallel plate configuration at 190 °C between frequencies of 10^{-2} and 4×10^2 rad/s with 5% strain. Storage (G') and loss (G'') moduli were determined from which the complex viscosity (η^*) was calculated; during the evaluation of the results characteristic quantities (G_c, ω_c, η_0) were deduced for further study.

Molecular weight and its distribution was 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.

Shrinkage of the blown films was determined according to the standard procedure of ASTM D 1204. 250×100 mm test specimens were cut from the films and put into an oven at 140 °C. Dimensional changes were measured after 1 hour both in parallel and perpendicular direction to that of the extrusion.

3. Results

The experimental results are presented in two sections. First the rheological properties and their interrelation are discussed. Mechanical properties of the films are shown in a subsequent section. General correlations of all measured properties are presented in a final section, where also a tentative explanation is given about the relationship of molecular structure and polymer as well as product properties.

3.1. Rheology

MFI is a simple technical quantity determined by a standard method. It is extensively used for the characterization of various polymers, but it can be used excellently for the monitoring of the melt stability of polyolefins in multiple extrusion experiments [11]–[14]. *Fig. 1* demonstrates this statement well. MFI of our polymer stabilized according to recipe 1 and 11 changes considerably with processing history and significant differences can be observed in the efficiency of the two stabilizer packages as well. In our previous paper these changes in MFI could be related to the modification of the chemical structure of the polymer chain. In accordance with literature data [11]–[13], a correlation was found between the vinyl group content of the polymer and its MFI. However, in spite of this correlation, the relationship between this quantity and molecular characteristics (molecular weight, molecular weight distribution, branching) [14]–[16] are not completely clear. MFI is determined in a relatively short (8 mm) and wide (2.095 mm) capillary, end effects are considerable [17], [18], melt elasticity influences the measured values. We hoped that rotational rheometry would supply more detailed and accurate information about the rheological characteristics of our samples.

Rotational rheometry was carried out on 8 selected samples. The results for two of these are compared in *Fig. 2*. All properties of the two samples differ considerably from each other, especially MFI and the strength of the films show significant deviations in the two cases. According to *Fig. 2* also the linear viscoelastic properties of the samples show characteristic differences. Moduli and complex viscosity of Sample 6/0 (recipe No/number of extrusions) are considerably lower than those of Sample 10/5 and in the case of the former sample the cross-over point ($G' = G''$, indicated by circles in the Figure) is situated at a higher frequency than for Sample 10/5. The evaluation of the results showed that rotational rheometry detected similar dependence of properties on processing history and on the composition of the stabilizer package as all other techniques.

Characteristic quantities were derived from the results of the rheological measurements. One of these was the zero shear viscosity (η_0) which was determined with extrapolation by fitting *Eq. (1)* to the experimental data

$$\log \eta = \frac{\log \eta_0}{(1 + k\omega)^n} , \tag{1}$$

where k and n are fitting constants. An acceptable fit was obtained with the correlation, in fact it was much better when *Eq. (1)* was used than with any of the existing rheological correlations containing η_0, i.e. Carreau [19], Ellis [20], etc., which fully justified the use of the proposed equation. Other parameters used in further analysis were the modulus measured at the crossover point (G_c) and the corresponding frequency (ω_c). These characteristic
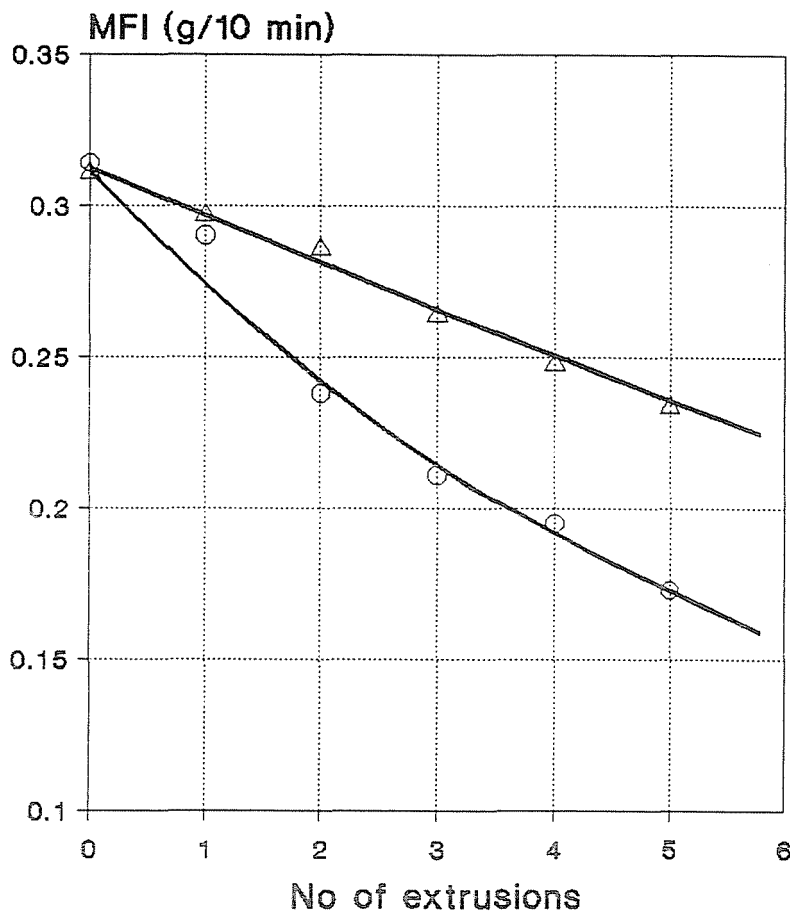
Fig. 1. Effect of processing history on the MFI of PE processed with two different stabilizer packages; (◯) Rp. 1, (△) Rp. 11

values are listed for the selected samples in *Table 1*.

The data of the table show considerable differences in all of these quantities from one sample to the other, in accordance with previous experience. An analysis of the results proved, indeed, that all linear viscoelastic characteristics are in very close correlation with each other, which is not too surprising at all. The correlations were non-linear for all combinations of the linear viscoelastic parameters. However, a very close correlation was observed between the linear viscoelastic properties and MFI as well. According to *Fig. 3* MFI depends linearly on G_c and a similar dependence of MFI was observed on ω_c as well. The correlation between MFI and zero shear viscosity is non-linear, but it is also very close (*Fig. 4*) [14], [18].
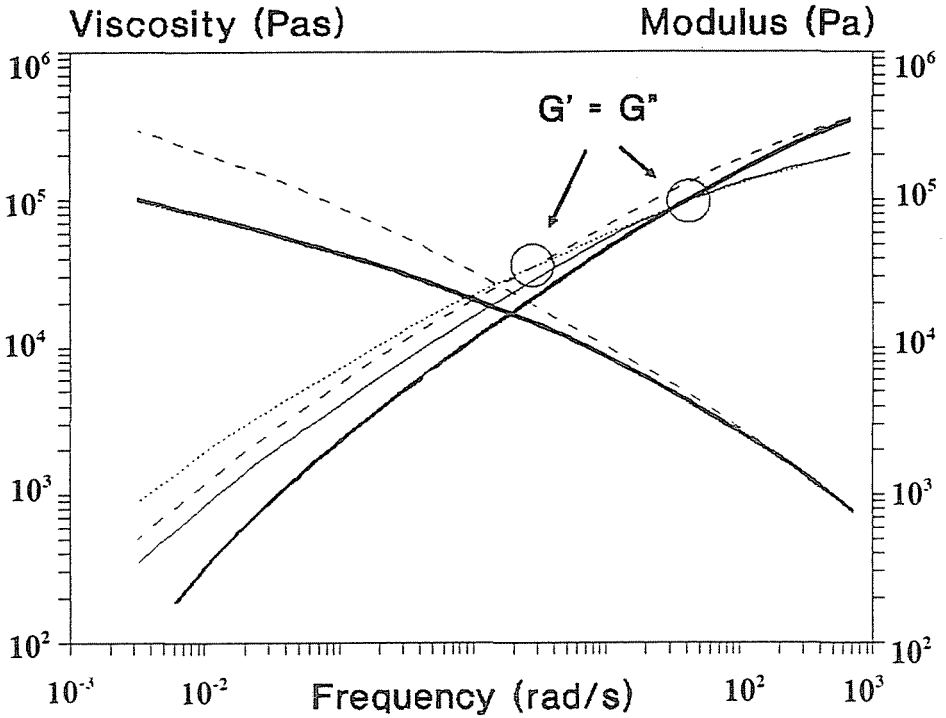
Viscosity (Pas)   Modulus (Pa)

$G' = G''$

Fig. 2. Linear viscoelastic characteristics of two samples subjected to different shear history and containing different stabilizer packages;
$-$, $-$ 6/0, $- - -$, $\cdots$ 10/5, $-$, $- - -$ G', η^*, $-$, $\cdots$ G''

These results clearly prove that all rheological properties are closely related to each other and change considerably during multiple extrusion of the PE grade used in the experiments. Beside processing history, also the composition of the additive package has a strong influence on the measured values. Since linear viscoelastic parameters are determined by the molecular structure of the polymer (molecular weight, molecular weight distribution, branching) [21]–[25] these should change during processing as a result of chemical reactions taking place in the melt. Moreover, since a very close correlation exists between linear viscoelastic parameters and MFI, this latter quantity must reflect the same changes in the molecular structure of the polymer as for example η_0.

Table 1. Linear viscoelastic characteristics of selected PE samples

Sample No	ω_c (rad/s)	G_c (kPa)	η_0 (MPas)
6/0	15.15	52.17	0.056
7/0	14.75	52.45	0.054
11/3	10.71	46.24	0.077
7/3	7.56	39.77	0.091
8/3	4.91	33.83	0.113
211/5	6.15	37.46	0.104
5/5	2.62	25.76	0.137
10/5	1.73	22.76	0.160

3.2. Mechanical Properties

Since a film grade polymer was used in the experiments and the recipe was developed accordingly, films were blown from the polymer after certain processing steps and their mechanical properties were measured. All three methods used were specifically developed for the characterization of films and the measurements yielded 4 quantities, since tear resistance was measured in two directions. Comparison of all data revealed that some characteristics change in a wide range, while others remain nearly constant. The correlation of tear resistance measured in the two directions and pendulum impact strength is shown in *Fig. 5*. A rather close correlation exists between tear strength measured perpendicularly to the extrusion direction and pendulum impact, while a complete lack of correlation is observed for the other direction. In fact parallel tear strength remains practically constant independently of processing history and composition in the complete range of parameters. Very similar correlations exist between the result of the dart test and tear strength measured in the two directions. These results clearly prove that the mechanical properties of the films are determined by the changes occurring in the transverse direction, but neither the character of these changes nor the reason for the constant tear strength in the parallel direction are clear at the moment.

Blown films are oriented during their production. In the process used in this project both the draw rate and blow ratio were the same in all cases. It is well known that the strength and stiffness of polymeric materials increase in the direction of orientation and decrease perpendicularly to it, i.e. mechanical properties are basically determined by the extent of orientation of the films. The orientation of the selected samples was determined in both directions by shrinkage measurements. Tear strength is plotted against shrinkage in *Fig. 6*. As it is expected orientation changes strongly in the perpendicular direction leading to correspondingly large changes in tear re-
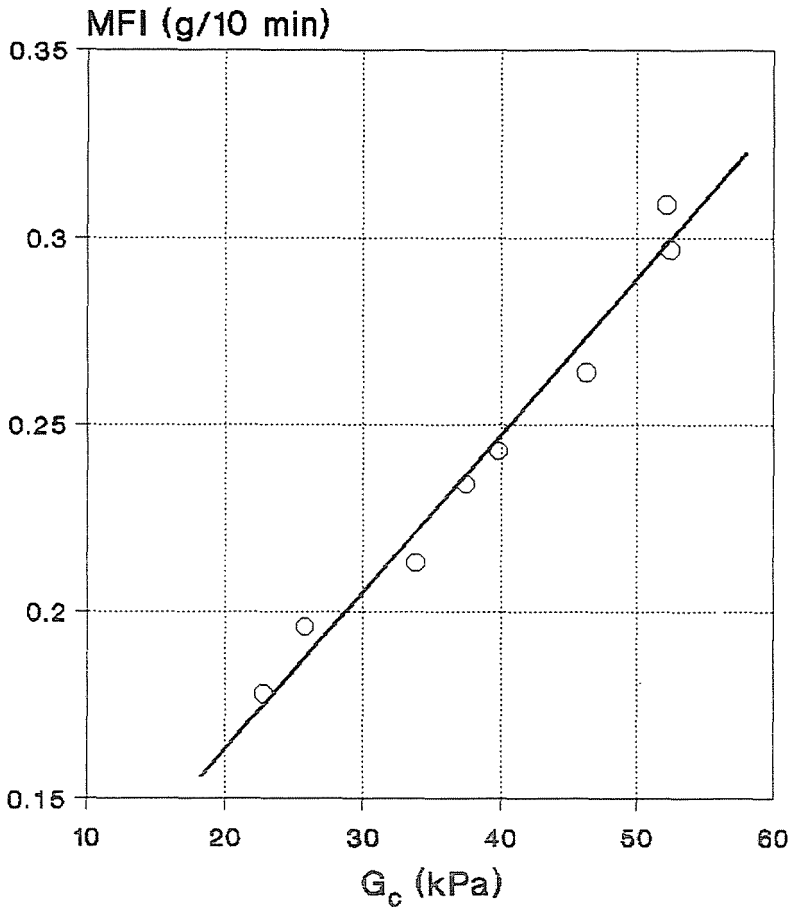
Fig. 3. Correlation of linear (G_c) and non-linear (MFI) viscoelastic characteristics
of the selected PE samples

sistance. Both shrinkage and tear strength remain constant in the other
direction and in spite of the somewhat higher shrinkage, tear resistance is
low in this direction.

It was shown in the previous section that all rheological properties
change considerably and these changes were assumed to be caused by modi-
fications in the chain structure of the polymer. Shrinkage is plotted against
MFI in *Fig. 7.* It is clear that parallel orientation is practically independent
of MFI. Only a slight increase can be observed with the decrease of melt
flow index occurring during multiple processing (see *Fig. 1*). Orientation
perpendicularly to the direction of extrusion, on the other hand, changes
significantly, it increases with increasing processing history. It is completely
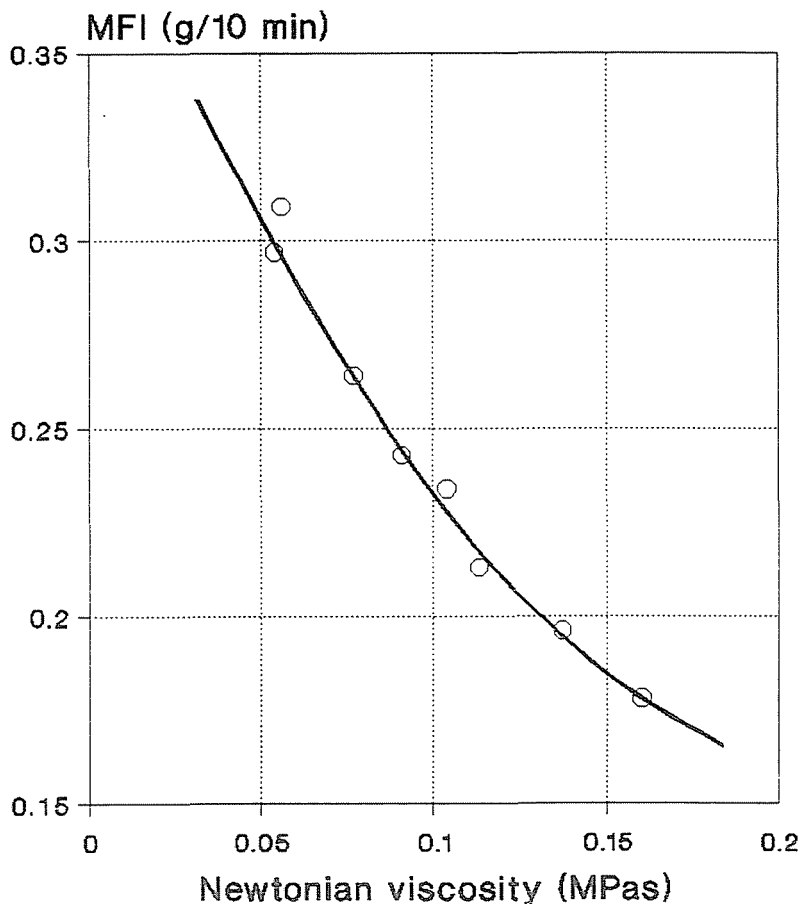
Fig. 4. Relationship of MFI and η_0 for the selected PE samples

clear from the results that the chemical reactions taking place during the extrusion of our PE result in some changes in the structure of the polymer, which in turn lead to increased orientation and decreased strength, but only in the perpendicular direction. The correlation of tear resistance and MFI proves again that a close correlation exists between structure and properties (*Fig. 8*). Although *Fig. 8* follows from *Figs. 6* and *7*, it also proves that the correlation is generally valid for the samples of our study and that the deviating points in the preceding figures result from the considerable standard deviation of the shrinkage and strength measurements. The explanation for the close correlation of properties and especially for their considerable dependence on direction needs further considerations; an attempt is made to explain some of the observed phenomena in the next section.
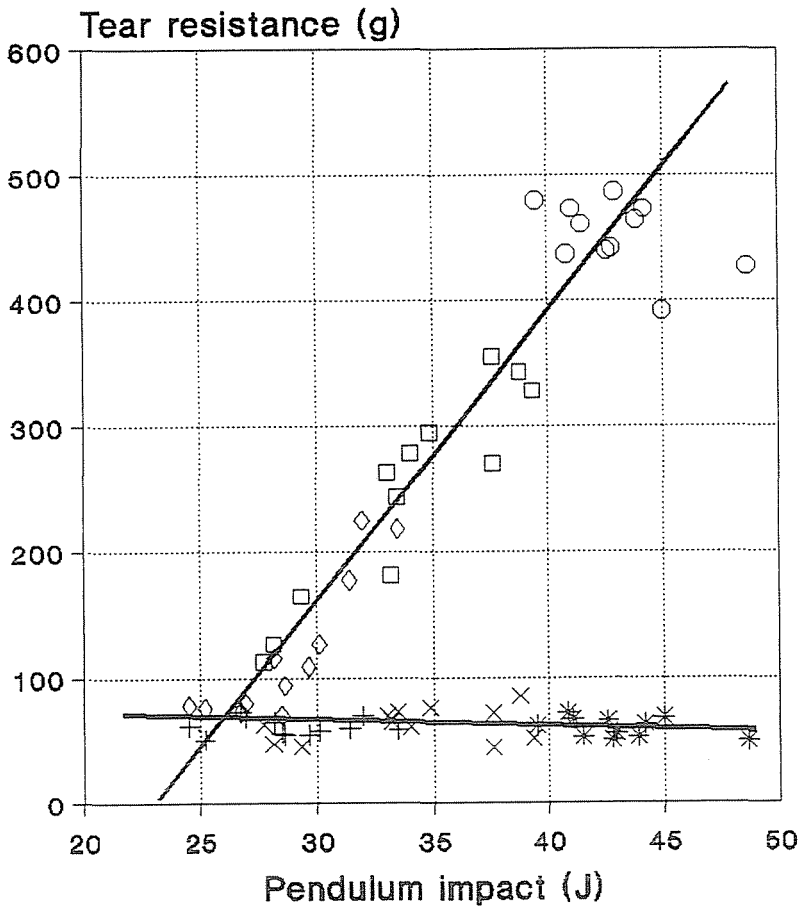
Fig. 5. Correlation between the tear strength and pendulum impact resistance of films blown from granules of different composition and processing histories (◯), □, ◇) perpendicular, (+, ×, ⋆) parallel; (◯), ⋆) 1st, (□, ×) 4th, (◇, +) 6th extrusion

4. Discussion

The results summarized in a previous paper [26] and those presented here clearly indicate that chemical reactions take place during the processing of polyethylene which result in a considerable modification of polymer properties. The scheme in *Fig. 9* attempts to show the correlation of chemistry, structure and properties. Oxygen introduced into the extruder with the polymer initiates radical reactions in which the polymer and the stabilizer take part. These reactions lead to stabilizer consumption (colour, decrease
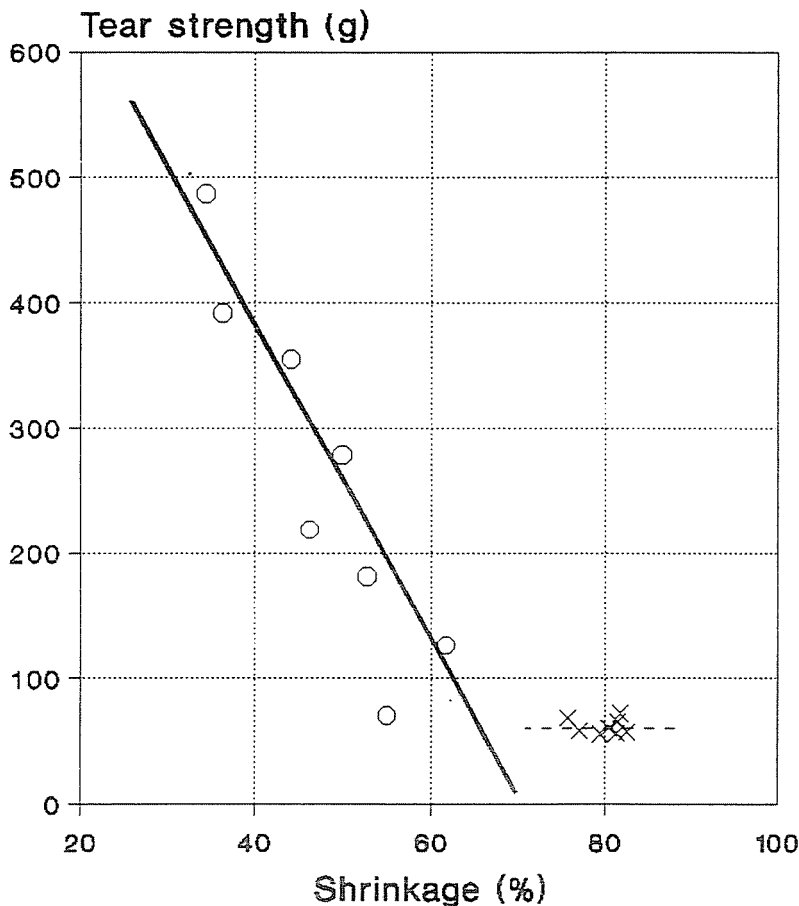
Tear strength (g)

Fig. 6. Dependence of tear resistance of blown films on their orientation; (○) perpendicular, (×) parallel

of stability), on the one hand, and to the modification of the polymer chain, on the other. Chemical modification of the polymer can proceed into two main directions: chain scission and cross-linking. The ratio of the two reactions depends on the amount of oxygen present, the types and amounts of stabilizers added, the structure of the polymer, processing conditions and other factors. In the absence of excessive oxygen polyethylene has a strong tendency for cross-linking, the dominating process in most cases is the increase in molecular weight. Cross-linking does not only change the size of the molecules, but also their structure (e.g. long chain branching) and might result in the development of a network structure, as well. Considerable gel formation is usually accompanied by decreasing molecular weight
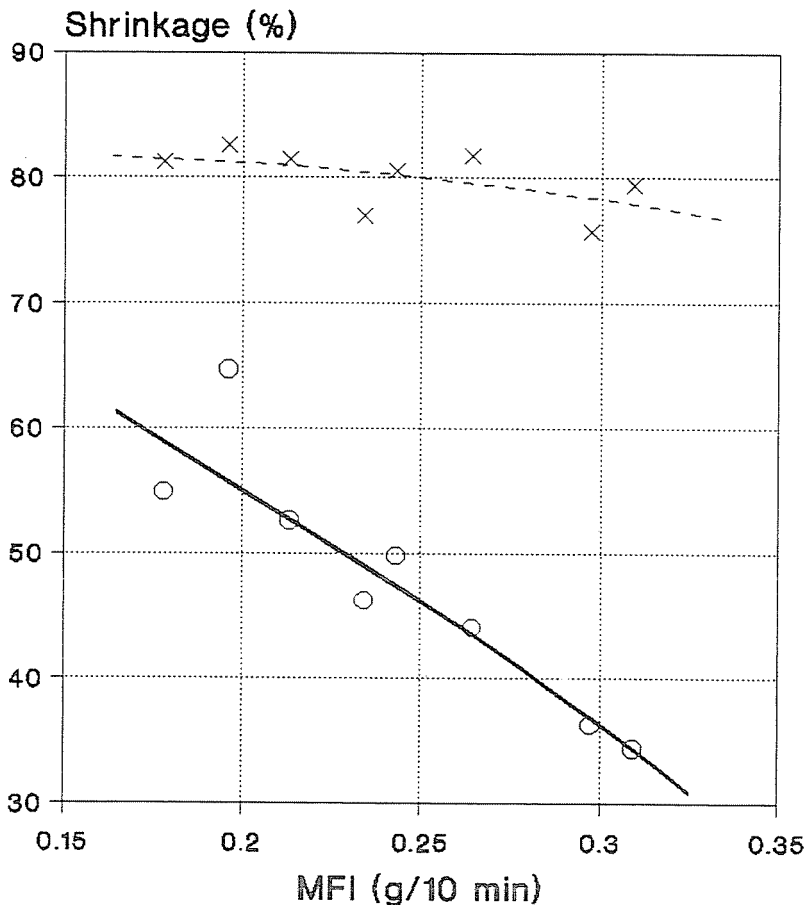
Fig. 7. Correlation of shrinkage and MFI of the selected samples; (○) perpendicular, (×) parallel

of the soluble fraction and the development of a heterogeneous structure. The relation of the chemical reactions and the resulting changes in polymer properties was proved by the correlation of the number of vinyl groups and MFI shown earlier [26].

The increase in MFI indicates considerable changes in the molecular structure, i.e. in molecular weight, molecular weight distribution and/or long chain branching. Zweifel and coworkers [11]–[13] explained the observed correlation between the vinyl functionality and MFI by the addition of alkyl radicals to the vinyl group. This reaction should lead to a considerable increase in molecular weight. GPC measurements and the determination of intrinsic viscosity, however, showed only minor changes both in molecular
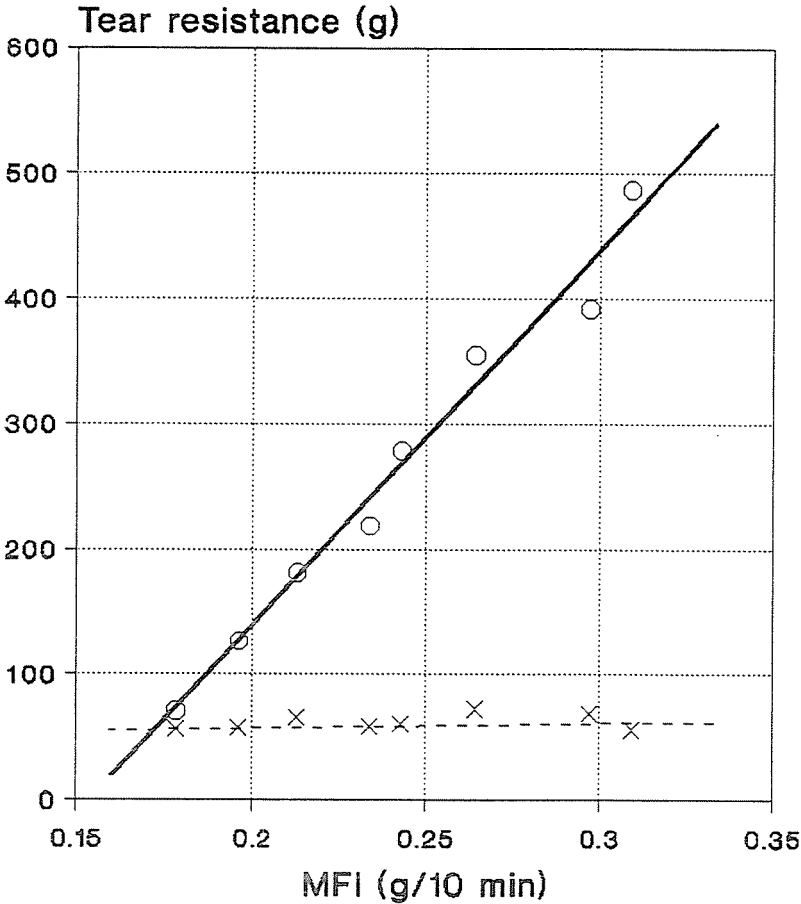
Fig. 8. Correlation of tear resistance and MFI for the selected samples: (○) perpendicular, (×) parallel

weight and molecular weight distribution (*Table 2*). Although a correlation was observed between molecular weight distribution and $1/G_c$ (polydispersity factor) [27], [28] (*Fig. 10*) as it is expected, the changes in the molecular weight distribution are extremely small, practically negligible.

Obviously molecular weight and molecular weight distribution do not change much during processing, although this could explain the increase in η_0 and the decrease in MFI with increasing processing history. It has been shown on many occasions that η_0 is proportional to some power – usually 3.4 – of molecular weight [29]–[38] and the number of entanglements increase accordingly [39]–[41]. However, entanglements can be created by long chain branching as well [40], in fact viscosity increases very steeply with increasing
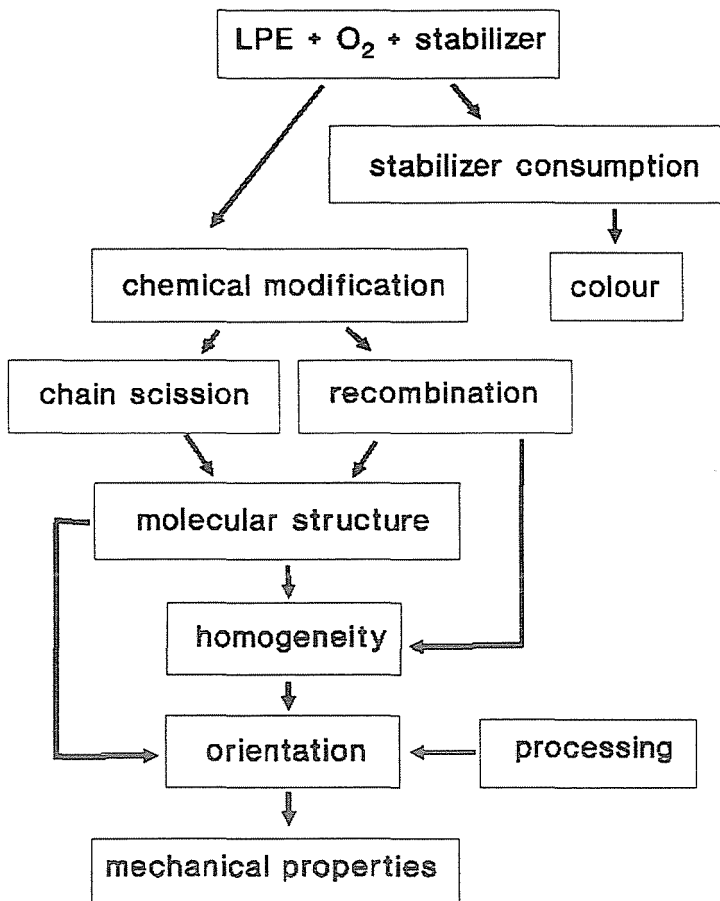
Fig. 9. Scheme showing the correlation of chemistry, structure and property changes during the processing of polyethylene

length of the branches [40], [43]. The scheme proposed by ZWEIFEL et al. [11]–[13] to describe property changes during processing may explain the formation of long chain branches as well. The addition of a radical to a double bond yields a new active species which can further react with another radical or a polymer chain. The formation of a few branches would not lead to considerable changes in the detected molecular characteristics (M_n, M_w, M_w/M_n, $[\eta]$) for several reasons. Gel permeation chromatography is not very sensitive to high molecular weight fractions, on the one hand, while both GPC and solution viscosity measure the hydrodynamic volume of the molecules, on the other. This quantity, however, decreases on branching [44], [45], thus the measured molecular characteristics change only slightly.

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

Sample No[a]	Molecular weight (g/mol)		$\frac{M_w}{M_n}$	$[\eta]$
	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$		
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

[a] recipe/extrusion number

Moreover, the number of reactions (branches) is very small, shown by the small changes in the vinyl group content of the polymer (max. 0.2/1000 carbon atoms).

Long chain branching explains not only the increase in MFI, but also the changes in the mechanical properties of the films [46], [47], as well as their dependence on direction. Orientation is fairly constant in the longitudinal direction leading to a constant, but rather low tear strength. This latter can be easily explained by the easy propagation of the crack along oriented structures. In samples with a low number of long branches – i.e. high stability, low number of extrusions – the tear strength is high in the perpendicular direction for the same reason. With increasing processing history and decreasing stability the number of branches increase, resulting in increased orientation (shrinkage) in the perpendicular direction and a consequent decrease of tear strength, because crack propagation becomes easier.

Although the above presented tentative explanation is in complete accordance with the experimental results and gives an answer to most questions, it needs further verification. Numerous techniques are known for the determination of long chain branching [45], [48]–[54], but these are usually complicated, tedious and not very reliable, thus verification of the hypothesis presented above may prove to be difficult.

5. Conclusion

The results presented here and in our previous paper unambiguously prove that chemical reactions take place during the processing of stabilized PE. All the changes resulting from these reactions are related to each other. Colour
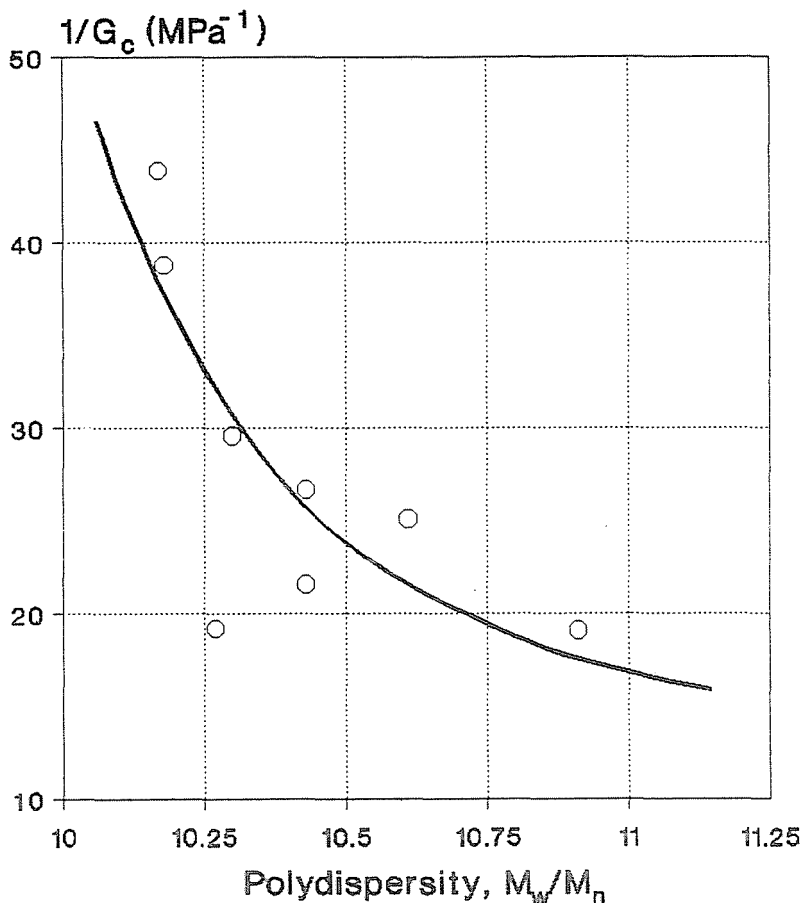
Fig. 10. Correlation of polydispersity factors determined by GPC (M_w/M_n) and rotational viscometry ($1/G_c$)

development and stabilizer consumption correlate well with the modifications in the structure of the polymer chain, which, on the other hand, determine the rheological properties of the polymer and the mechanical characteristics of the product. All rheological characteristics, including MFI show close correlation indicating that also MFI reflects changes in the polymer structure. Analysis of the data indicates that a few long chain branches are formed during processing which lead to a considerable modification of properties. The branches considerably modify the orientation of the molecules, thus changing the resistance of blown films against crack propagation. Attention must be called here to the fact that although the correlations presented seem to be unambiguous, the results were obtained in an optimiza-

tion project. Two phenolic antioxidants, a secondary stabilizer and other additives complicate the evaluation of the results and the establishment of general conclusions. Experiments with a well defined system are under way, hopefully they will verify the tentative explanations given here and clear up uncertainties.

Acknowledgements

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