# Monitoring Polyolefin Modification Along the Axis of a Twin Screw Extruder. I. Effect of Peroxide Concentration

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**ABSTRACT:** The evolution of the structure of polyolefins with different ethene/propene ratios in the absence or in presence of peroxide was monitored along a twin screw extruder. Small samples were quickly collected from the melt at specific barrel locations and characterized by rheological measurements. The rheological properties of the polyolefins are hardly affected when processing is carried out in the absence of peroxide. In the presence of peroxide both branching/crosslinking and degradation occur along the extruder, until the peroxide is fully converted. The degree of branching/crosslinking and/or degradation depends on the ethene/propene ratio, on the original molecular weight of the polymer and on the amount of peroxide added. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 58–68, 2001

**Key words:** processing; degradation; crosslinking; branching and rheology

## INTRODUCTION

Polymer melt processing has been associated with the development of physical phenomena created by thermal energy and mechanical stresses. However, it is also known that the input of mechanical and thermal energy to polymers may result in chemical or mechanochemical effects.[1–4] Processing of polyolefins yields products with properties that can be related to the chemical reactions induced by the operating conditions, the high temperatures, and the presence of oxygen.[1] If these reactions are uncontrolled, processed polymers with inferior properties may be obtained. These reactions are often referred to as "degradation." However, mechanochemical effects can also be used advantageously. For example, shear-in-

duced polymer reactions with fillers can enhance filler dispersion and, consequently, improve the properties of the compounds. Crosslinking of polyethene (PE), controlled degradation of polypropene (PP), and hydrolysis of polycondensate polymers are used to produce materials with improved properties. Frequently, chemicals are added during melt processing in order to enhance these mechanochemical effects. For example, branching or crosslinking of PE using peroxides or silanes produces materials with improved heat and chemical resistance and lower stress cracking and shrinkage.[3–17] The degradation of PP initiated by peroxides yields grades with lower molecular weight and/or a narrower molecular weight distribution.[2–6,18–23] These types of reactions only modify the physical structure of the polymers. In order to change the chemical structure of the polymer, other types of reactions by adding extra chemicals, such as grafting, transesterification, and imidization, or by adding other polymers (i.e., reactive blending), may be performed.[1–4] In short,

**Table I   Polyolefins, Characteristics, and Amounts of Peroxide Used**

| Polyolefin | Manufacturer/Grade | Propene Content (wt %) | Molecular Weight, $\bar{M}_w$ (kg/mol) | Amount of Peroxide (phr) |
|---|---|---|---|---|
| PE1 | HDPE–DSM Stamylan HD 2H280 | 0 | 60 | 0; 0.1; 1 |
| PE2 | HDPE–DSM Stamylex 7359 | 0 | 30 | 0 |
| PE3 | LDPE–DSM Stamylan LD 2100TN00 | 0 | 360 | 0; 0.1 |
| EPM1 | Exxon PE 805 | 22 | 120 | 0; 0.1 |
| EPM2 | Exxon EPM X1-703F2 | 27 | 80 | 0; 0.1 |
| EPM3 | Exxon VA 404 | 55 | — | 0; 0.1 |
| PP | DSM Stamylan P 13E10 | 100 | 500 | 0; 0.1; 1 |

HDPE, high density polyethylene; LDPE, low density polyethylene.

it may be useful to have reactions during processing for a wide range of applications.

It has been demonstrated that extruders are effective reactors in which the chemical modification of polymers can be achieved economically.[1–4] However, extruders have largely been used as black boxes, where the process and the product quality are improved by changing the operating conditions without having an actual insight into the chemical reactions developing along the screw axis. In order to change this situation material sampling techniques have been developed.[24,25] For example, sampling devices have been used to study the evolution of chemical conversion and morphology development in PA-6/EPM/EPM-g-MA (polyamide 6/ethylene propylene rubber/ethylene propylene rubber modified with maliec anhydride) blends along the screw.[26] These devices can be located along the barrel and samples can be collected, in a few seconds, for subsequent characterization. In the present work these devices are used to study the evolution of polyolefin structure upon processing in a twin-screw extruder in the absence or in the presence of peroxide. Various polyolefins with various ethene/propene ratios, such as PEs (0 wt %), EPMs (22–55 wt %), and PPs (100 wt %), were studied.

## EXPERIMENTAL

### Materials

A series of polyolefins with varying ethene/propene ratio, supplied by DSM and Exxon, were selected. Their characteristics together with the

amount of peroxide used in each experiment are presented in Table I. The peroxide, 2,5-bis(tert-butylperoxy)-2,5-dimethylhexane (Trigonox 101: DHBP), used as the initiator for crosslinking or degradation reactions, was supplied by Akzo Nobel, the Netherlands. The half-life time of the peroxide at 200°C is 6.1 s.

### Processing

The polyolefins were tumble mixed with different concentrations of peroxide and processed in a laboratory modular Leistritz LSM 30.34 intermeshing corotating twin-screw extruder (Fig. 1). No special precautions against the presence of oxygen were taken. For all experiments, the barrel set temperature was 200°C, the screw speed 75 rpm and the flow rate 5 kg/h. Samples for subsequent off-line characterization were quickly collected along the extruder axis using a series of sampling devices (see Ref. 24 for details) and were immediately quenched in liquid nitrogen in order to avoid further reaction. The location of these devices is also shown in Figure 1. Generally, locations where significant stresses develop were chosen for this purpose. The screw contains a series of transport elements separated by three mixing zones, consisting of staggered kneading disks and a left-hand element, respectively. They produce intensive mixing, together with the development of local pressure gradients. Melting of the solid polymer is caused by the mechanical stresses developed by the mixing block upstream.

The melt temperature was also measured at the sampling points. A needle type thermocouple with a small time constant (1 s) was used. Imme-
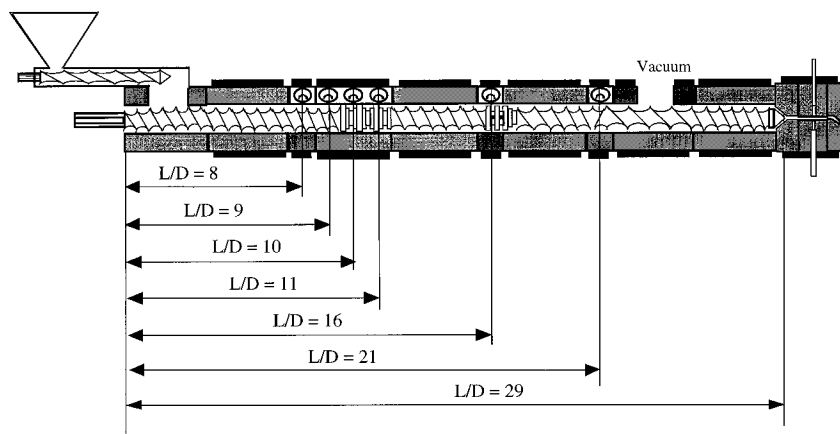
**Figure 1**   Extruder layout and sampling locations.

diately after rotating the sampling device in order to collect polymer material, the preheated needle was stuck into the molten volume and a measurement was made. The error associated with this simple procedure is estimated to be of only a few degrees Celsius, as shown in a separate work.[27]

### Residence Time Distribution

Residence time parameters at various locations along the extruder and upon exiting the die were determined using a simple procedure. After reaching steady state upon processing, a small amount of silicon dioxide tracer (with a specific surface of 175 m$^2$/g) was incorporated into the feed stream at time $t = 0$. Samples of polymer plus tracer were then collected from a specific sampling point at known time intervals. The technique was repeated for each sampling location. The relative amount of silica present in each sample was determined by ashing the sample and is a straightforward measure of concentration at a specific time. From this data it was possible to compute conventional residence time parameters, such as the cumulative residence time distribution $F(\theta)$ and the mean residence time, $\bar{t}$.[28]

### Materials Characterization

The materials were characterized in terms of their rheological behavior and gel content. Samples for rotational oscillatory rheometry were compression molded as disks of 40 mm in diameter and 2 mm in thickness for 10 min at 200°C, under a pressure of 30 tons. Isothermal frequency sweeps from 0.004 to 40 Hz were performed at 200°C in a TA Instruments Weissenberg rotational rheometer using parallel-plate geometry.

The gap and diameter of the plates was 1.8 and 40 mm, respectively. In order to maintain the material behavior within the linear viscoelastic domain, the applied strain was 0.01.

The possibility of error affecting the rheological data due to unwanted changes in chemistry during sample preparation must be considered. Thus, samples collected from the extruder were dissolved/precipitated, compressed, and analyzed under the same conditions. The results obtained were very similar to those without dissolution/precipitation.

For gel content weighted samples (about 1.5 g) were placed in 120 mesh stainless-steel cages and immersed in boiling toluene. The extractions were carried out under reflux for 24 h with solvent change after 12 h. After removal from the boiling solvent, the samples were dried in a vacuum oven during 5 h at 80°C in a nitrogen atmosphere. Then they were weighted and the gel contents were calculated.

## RESULTS AND DISCUSSION

Since various polyolefins with different structure (ethene/propene ratio) were studied, the results obtained in each case will be presented and discussed separately. Then, a general correlation between branching/crosslinking and/or degradation reactions and peroxide decomposition will be established.

A simple observation of the polymer samples removed from the extruder with the sampling devices showed that, under the processing conditions selected, melting was not complete at *L/D* = 8 (Fig. 1). However, only one *L/D* downstream a more or less homogeneous melt had already developed. There-
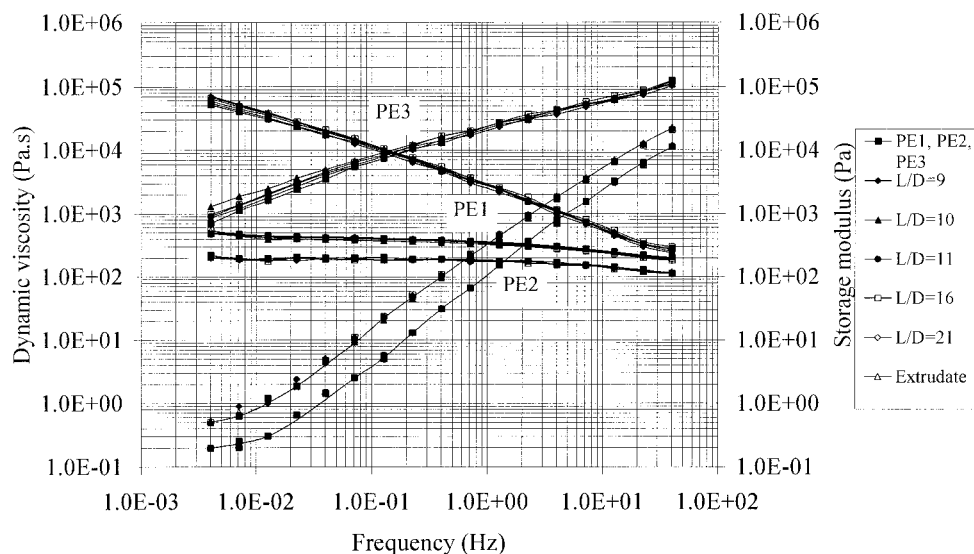
**Figure 2**  Dynamic viscosity and storage modulus of PE1, PE2, and PE3 along the extruder.

fore, data on samples from location $L/D = 8$ will not be included in the following discussion.

**Polyethene**

Figure 2 shows the rheological behavior (dynamic viscosity and storage modulus vs oscillation frequency) of PE1, PE2, and PE3 along the extruder. The linear PE1 and PE2 (both HDPEs) exhibit a Newtonian plateau at the low frequency range while the long chain branched PE3 shows a sig-

nificant decrease of viscosity with increasing frequency, and a relatively high elasticity. When these polymers are processed in the absence of peroxide, there is no evidence of mechanochemical effects taking place, i.e., the PEs are relatively stable under the operating conditions selected.

When 0.1 phr of DHBP is added to PE1, both the viscosity and the storage modulus increase significantly upon melting as a result of branching/crosslinking. This is demonstrated in Figure
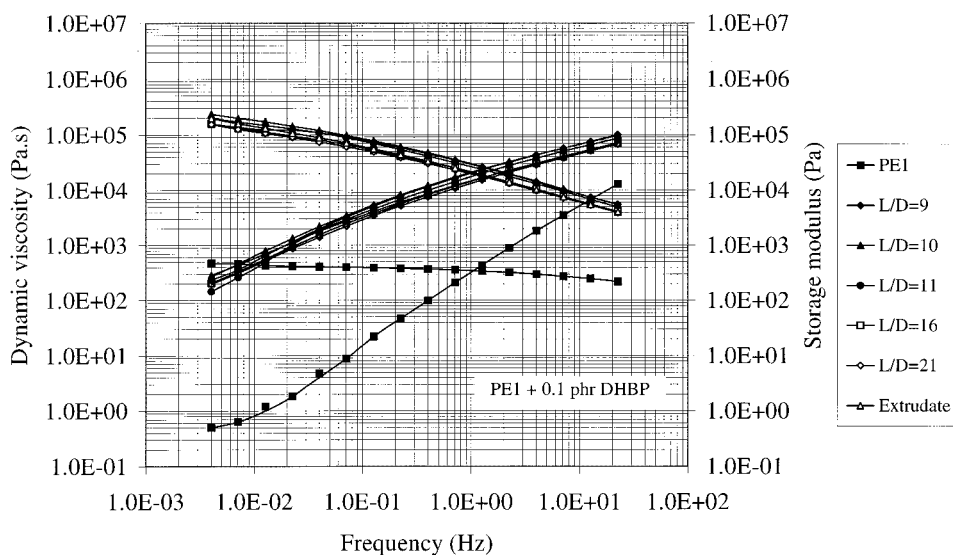


**Figure 3**  Dynamic viscosity and storage modulus of PE1 along the extruder with 0.1 phr DHBP.
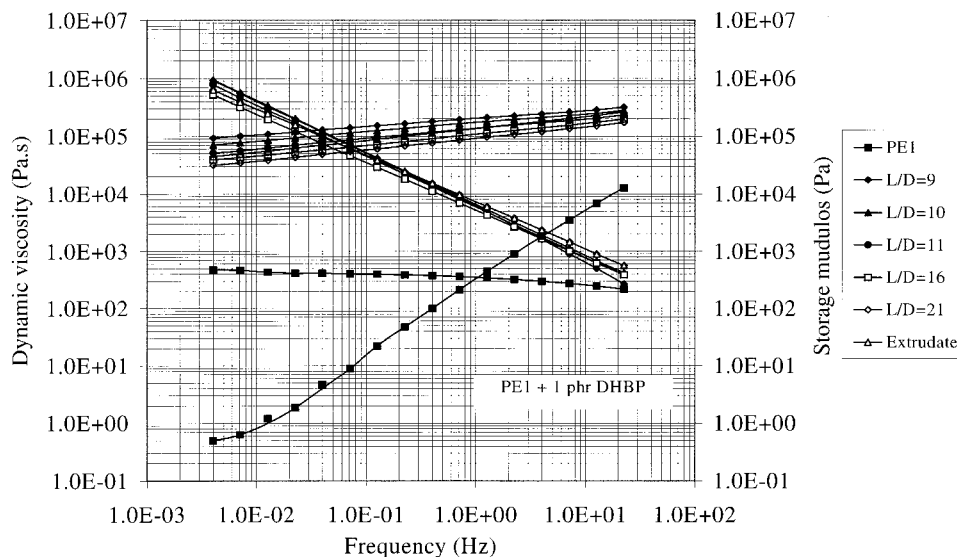
**Figure 4**  Dynamic viscosity and storage modulus of PE1 along the extruder with 1 phr DHBP.

3, which compares the response of the original PE with that measured along the extruder and at the die exit. After melting little changes are perceived downstream. When using 1 phr DHBP, the viscosity and elasticity increase is even larger (at 7 $\times$ 10$^{-3}$ Hz: $\eta'$, $4 \times 10^2 \rightarrow \sim 6 \times 10^5$ Pa s; $G'$, $6 \times 10^{-1} \rightarrow 1 \times 10^5$ Pa), as depicted in Figure 4. This increase is significant up to $L/D = 11$, then the values decrease slightly along the extruder.

The variation of the gel content can eventually confirm the above results on the evolution of the branching/crosslinking reactions along the ex-

truder. As shown in Figure 5, the gel content along the extruder remains low when 0.1 phr DHBP is used, no differences being perceived from $L/D = 9$ onward. When 1 phr of peroxide is used, the gel content increases along the extruder until it reaches a plateau (55%) at $L/D = 16$. These measurements show that branching/crosslinking reactions are not complete in the first part of the extruder, but they probably continue until all peroxide is decomposed, as it will be discussed later.

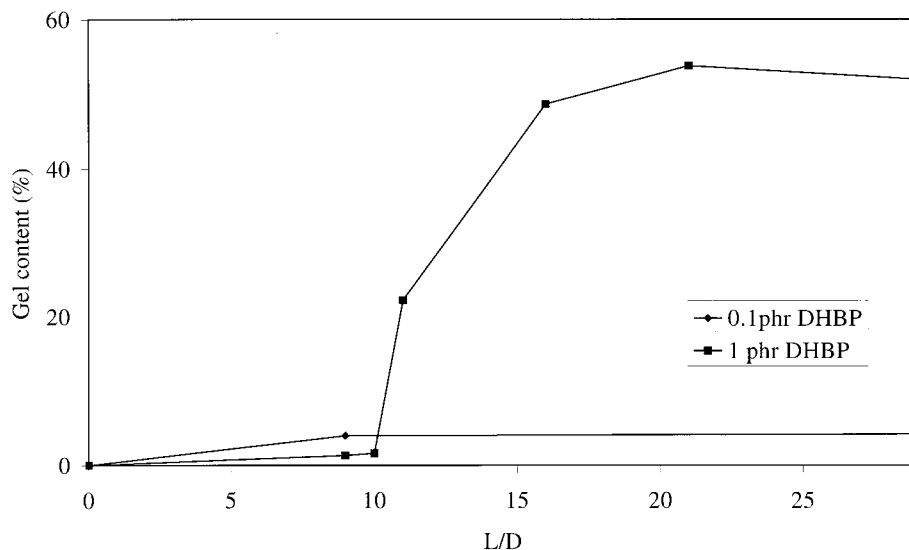When 0.1 phr peroxide is added to PE3, an increase in viscosity and storage modulus, partic-



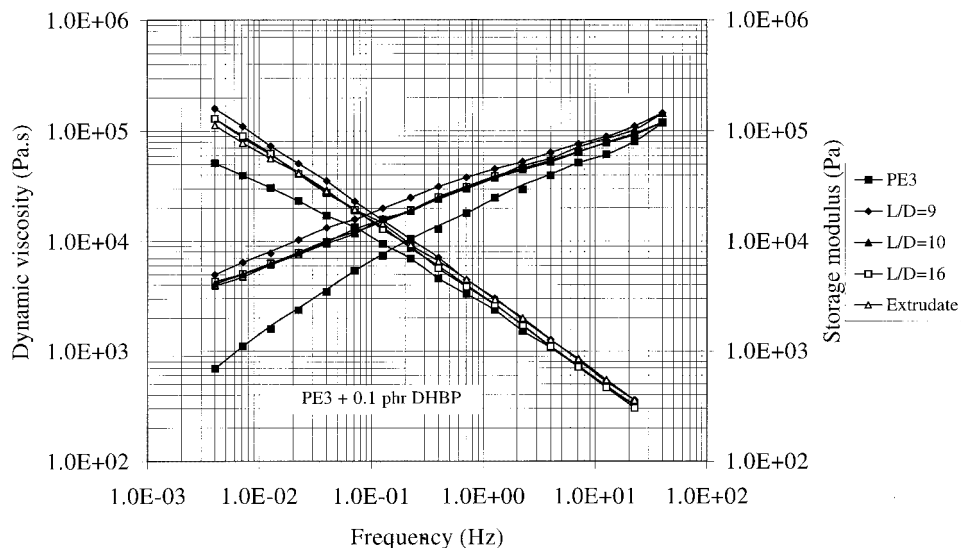**Figure 5**  Gel content of PE1 along the screw axis, with 0.1 and 1 phr DHBP.

**Figure 6**  Dynamic viscosity and storage modulus of PE3 along the extruder with 0.1 phr DHBP.

ularly at the lower frequency range, is observed (Fig. 6), again as a consequence of branching/crosslinking in the melting zone. Further downstream a small decrease in viscosity and storage modulus seems to take place, which is probably due to the degradation of the network formed earlier. The changes observed with PE3 when processed in the presence of peroxide are small when compared with those of PE1, which can be attributed to the differences in the initial molecular weight. An increased molecular weight facil-

itates the formation of a network, but on the other hand degradation effects are more likely to occur.

## Polypropene

Figure 7 shows the evolution of viscosity and storage modulus of PP samples taken along the extruder during processing with 0, 0.1, and 1 phr, respectively, at constant frequency ($7 \times 10^{-3}$ Hz). In the absence of peroxide those parameters decreased slightly along the screw, i.e., some degra-
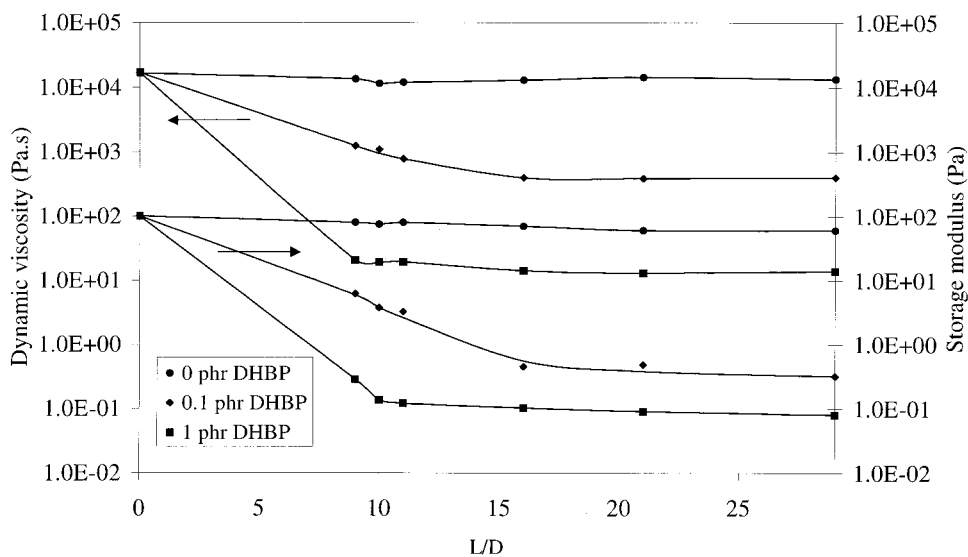


**Figure 7**  Dynamic viscosity and storage modulus at $7 \times 10^{-3}$ Hz of PP along the extruder with 0, 0.1, and 1 phr DHBP.
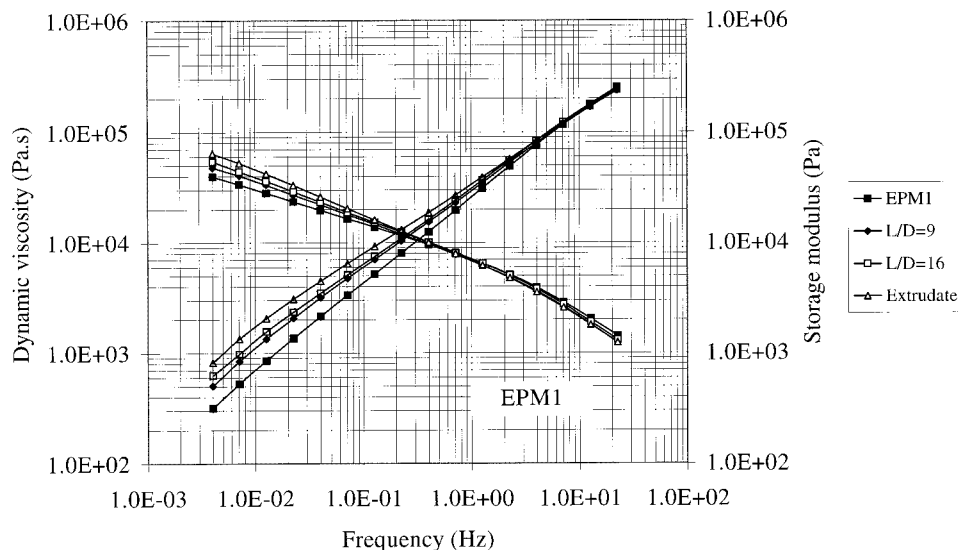
**Figure 8**   Dynamic viscosity and storage modulus of EPM1 along the extruder.

dation occurred under these processing conditions. However, this decrease is much more important particularly in the melting zone when adding 0.1 phr DBHP is added (Fig. 7). In the presence of 1 phr of peroxide a dramatic degradation occurs already at $L/D = 9$ (the viscosity decreases from $1.8 \times 10^4$ to 20 Pa s at $7 \times 10^{-3}$ Hz) and the process continues along the extruder. The degraded PP has very low viscosity and elasticity, indicating a relatively small average chain length and low entanglement density.

### Ethene/Propene Copolymers

The rheological measurements of the various EPM copolymers (Table I) are depicted in Figures

8–10. At low frequencies, both the viscosity and elasticity of EPM1 increase along the extruder (Fig. 8). In the presence of 0.1 phr peroxide (Fig. 11) the dynamic viscosity and storage modulus increase significantly upon melting, but remain constant thereafter. Thus, branching/crosslinking occurs with this material. EPM2 processed by itself shows a small gradual increase in viscosity and storage modulus along the screw axis (Fig. 9). In the presence of 0.1 phr peroxide, the values of the rheological parameters increase up to $L/D = 11$ and then they decrease (Fig. 11). Clearly, branching/crosslinking takes place, followed by degradation. EPM3 evidences a small decrease in viscosity along the extruder upon processing
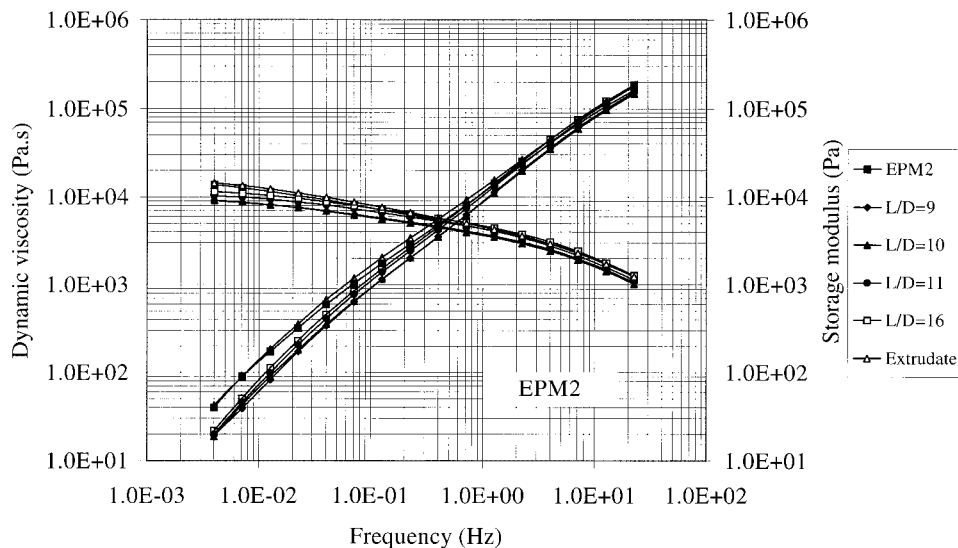


**Figure 9**   Dynamic viscosity and storage modulus of EPM2 along the extruder.
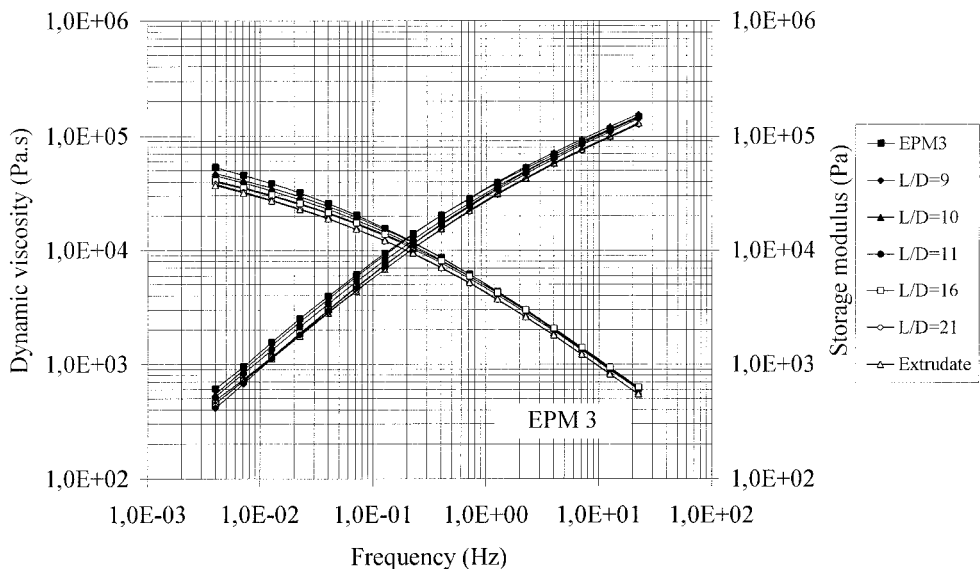
**Figure 10**   Dynamic viscosity and storage modulus of EPM3 along the extruder.

without peroxide (Fig. 10). This decrease becomes much more important in the presence of 0.1 phr peroxide (Fig. 11). The reported differences in behavior are related to the ethene/propene ratio of each copolymer. EPM1 has the lower propene content (22%); therefore, only branching/crosslinking occurs. As the propene content increases, both branching/crosslinking and degradation take place, degradation becoming the main reaction for a propene-rich copolymer such as EPM3 (55 wt % propene). Differences in the mo-

lecular weight of EPM1 and EPM2 should also be relevant. Since EPM1 has a higher molecular weight more branching/crosslinking should occur than for EPM2.

## Correlation Between Crosslinking/Degradation and Peroxide Decomposition

Figure 12 summarizes most of the previous results by depicting the relationship between the ratio of the dynamic viscosities of the modified
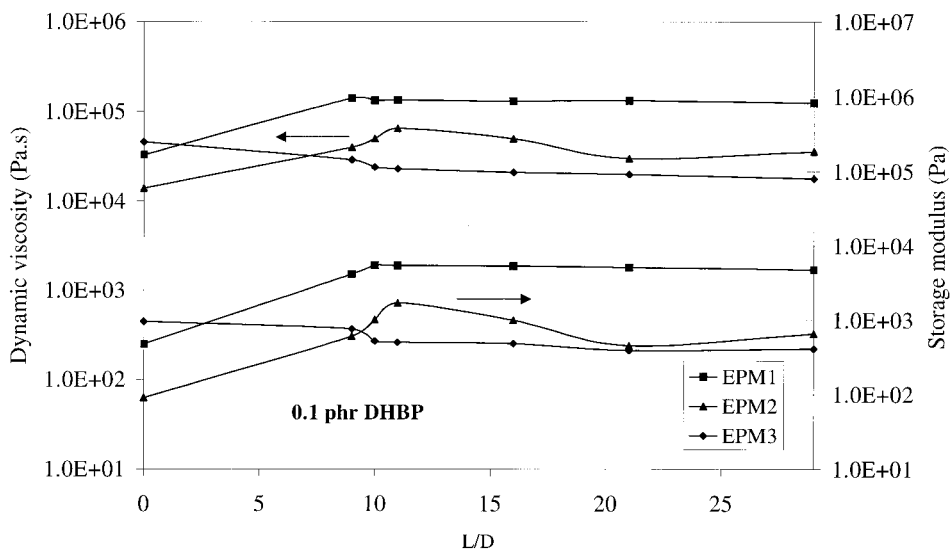


**Figure 11**   Rheological properties of EPM1, EPM2, and EPM3 along the extruder with 0.1 phr DHBP (dynamic viscosity and storage modulus at $7 \times 10^{-3}$ Hz).
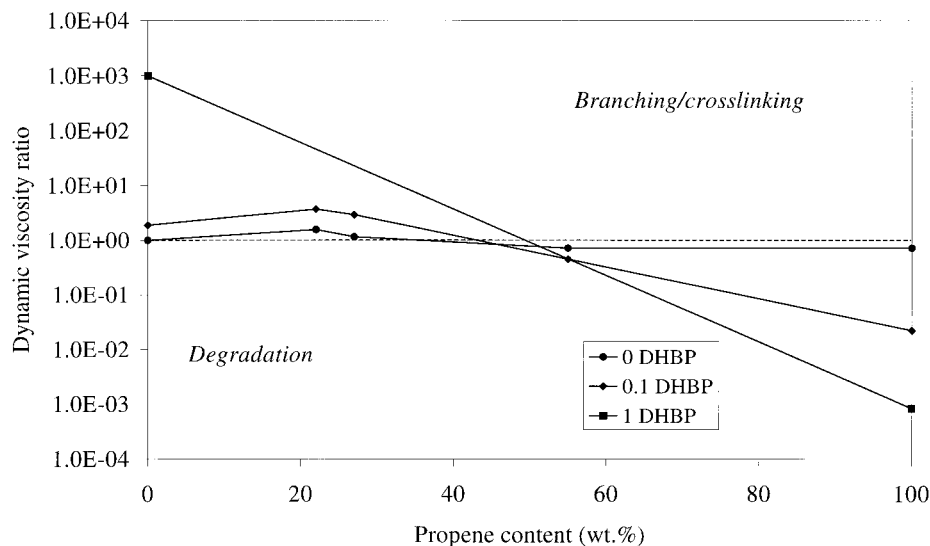
**Figure 12** Viscosity ratio of dynamic at $7 \times 10^{-3}$ Hz of the modified (0, 0.1 and 1 phr DHBP) and original polyolefins as a function of the propene content at $L/D = 29$.

(0.1 and 1 phr DHBP) and original polyolefins, at the die outlet, and their chemical composition (propene content). As expected, the viscosity ratio of the various materials decreases with increasing propene content from a value larger than unity for PE to a value far below 1 for PP. Figure 13 represents a simplified scheme of the reactions occurring during melt processing of polyolefins in the presence of peroxide.[2–9,19–23] The decomposition of the peroxide yields free radicals, which abstract H atoms from the polyolefin backbone. The subsequent reactions of the polyolefin radical depend on the chemical structure of the polyolefin. For example, since PE forms long chain branches when PE radicals terminate by bimolecular combination, a branched material with increased molecular weight, i.e., a material with higher viscosity and elasticity, is obtained.[2–4,10–17] In the case of PP, chain scission of the PP radicals occurs; thus, a material with a lower viscosity and elasticity is obtained.[2–4,16] In the case of an ethene/propene copolymer, the above reactions can take place simultaneously and the resulting structure will depend on the particular ethene/propene ratio and also on the original copolymer molecular weight.

In the preceding discussion the rheological response of processed polyolefins in the absence and in the presence of peroxide has been discussed qualitatively (i.e., in terms of crosslinking vs degradation development). Finally, a more quantitatively correlation between the degree of crosslinking/degradation and the peroxide decomposition

along the extruder will now be determined. The peroxide decomposition was calculated as the integral of a first order kinetics equation, using an Arrhenius law, peroxide decomposition data provided by Azko Nobel ($k_0 = 1.68 \times 10^{16}$ s$^{-1}$ and $E_A = 155.49 \times 10^3$ J/mole) and the melt temperature and residence time measured at each location (Table II). The temperature profiles denoted as lower and higher correspond to the lowest and highest temperatures measured at each location, considering all the materials. Figure 14
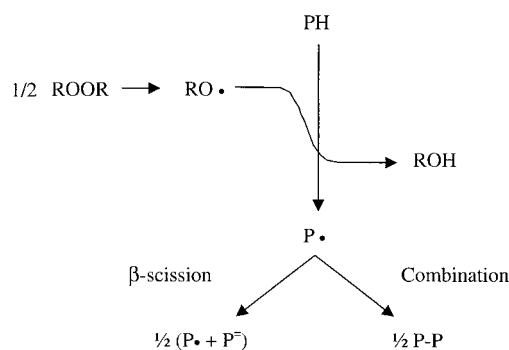


PE: combination → branching/crosslinking → viscosity and elasticity increase

PP: β-scission → degradation → viscosity and elasticity decrease

EPM: combination/β-scission → branching + degradation → viscosity similar to that

of original material

**Figure 13** Simplified scheme of the reactions during melt processing of polyolefins in the presence of peroxide.

**Table II   Experimental Mean Residence Times and Temperatures Profiles**

| Sampling Location (L/D) | Mean Residence Time, $\bar{t}$ (s) | Temperature Along the Axis (°C) | |
|---|---|---|---|
| | | Highest | Lowest |
| 9 | 25 | 153 | 160 |
| 10 | 30 | 166 | 199 |
| 11 | 32 | 185 | 206 |
| 16 | 50 | 187 | 211 |
| 21 | 67 | 191 | 207 |
| Extrudate | 110 | 192 | 203 |

shows the calculated evolution of the peroxide decomposition along the extruder using the two temperature profiles. According to the calculations, DHBP starts to decompose at $L/D = 9$, and not before, simply because the temperature is too low. Then, decomposition becomes very fast because the melt temperature jumps to 190–200°C. Complete DHBP decomposition is achieved up to end of the extruder. Hence, according to the calculations, branching or degradation reactions are completed from $L/D = 21$ to the end of the extruder, depending on the set temperature. Figure 15, which depicts the evolution of the PE1 gel content (1 phr peroxide) and the calculated peroxide decomposition along the extruder, confirms the validity of this prediction. The shapes of the

curves are similar, demonstrating that there is a close correlation between the peroxide decomposition and crosslinking/branching.

## CONCLUSIONS

The evolution of the rheological response of PE, EPM, and PP processed in a twin screw extruder was monitored along the barrel.

Significant differences in viscosity were observed depending on the structure of the polyolefin being tested. In the absence of peroxide the rheological properties of the polyolefins were only moderately affected by the thermal/mechanical stresses inherent to processing. However, in the presence of peroxide branching/crosslinking and/or degradation occur along the extruder, until the peroxide is fully converted. The degree of branching/crosslinking and/or degradation depends essentially on the ethene/propene ratio, on the original molecular weight of the polymer and on the amount of peroxide added. In a quantitative approach, the change in rheological behavior could be correlated with the peroxide decomposition.
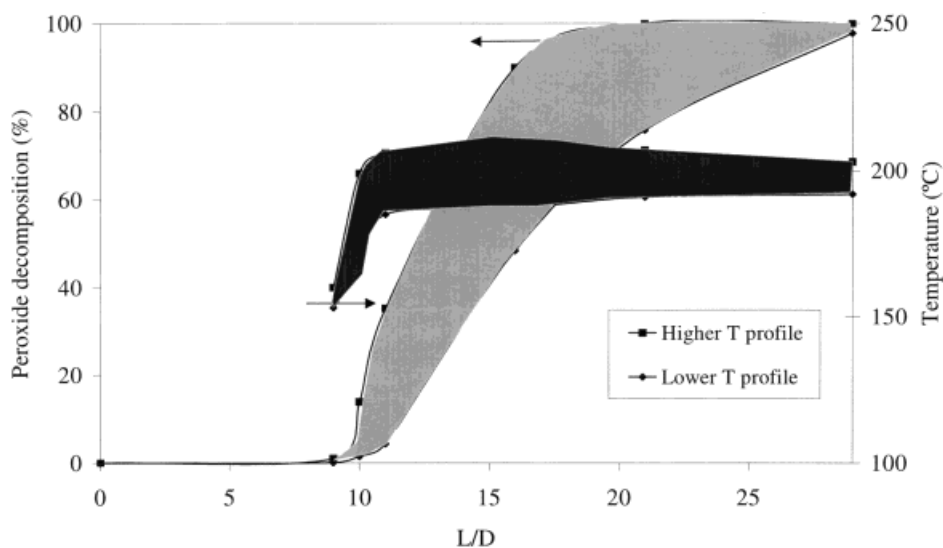
**Figure 14**   Melt temperature and calculated peroxide decomposition along the screw axis.
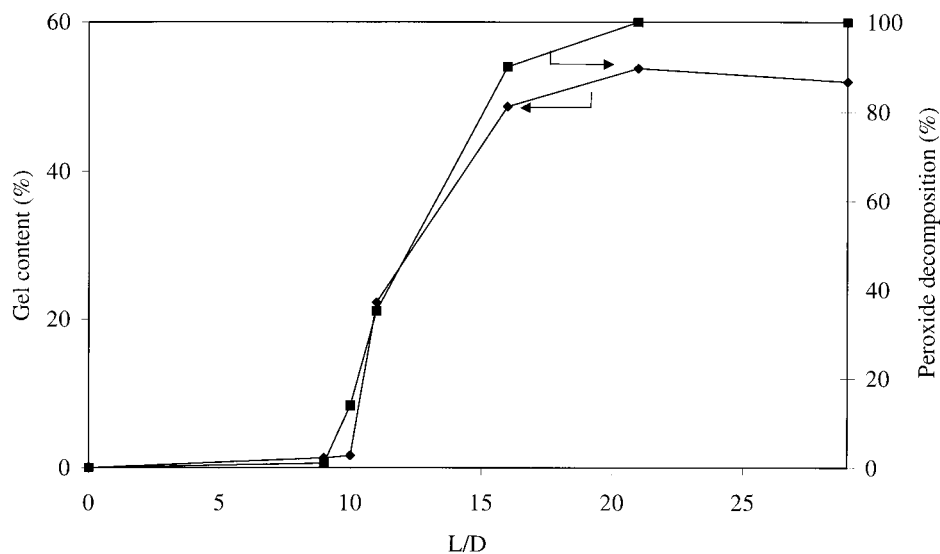
**Figure 15**   Evolution of gel content (PE 1 with 1 phr DHBP) and calculated peroxide decomposition along the extruder.

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