

Evolution of Peroxide-Induced Thermomechanical Degradation of Polypropylene Along the Extruder

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ABSTRACT: An experimental study of the peroxide-induced degradation of polypropylene in a corotating twin-screw extruder, operating under various conditions, was reported. Runs were performed without and with peroxide in different concentrations. The evolution of the chemical reactions along the extruder was characterized by on-line rheological measurements and by determination of the molecular weight of samples collected at the same locations. The results evidenced the relationships between peroxide concentration and processing conditions with rheological properties and molecular structure of the modified materi-

als. The concept of chain-scission distribution function elucidated the mechanisms involved in the thermomechanical degradation of PP, which is by chain scission and is dependent on the level of stress imposed by the screw elements, temperature, and concentration of hydrogen-abstracting agents. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 2711–2720, 2004

Key words: processing; degradation; molecular weight distribution; polypropylene (PP); rheology

INTRODUCTION

Polypropylene (PP) is produced commercially with heterogeneous Ziegler–Natta catalysts. The synthesized polymers have a very broad molecular weight distribution with a high molecular weight tail, which accounts for their high melt elasticity levels.^{1–3} It is generally accepted that degradation of PP follows a series of free-radical reactions: peroxide decomposition, hydrogen abstraction, chain scission, and termination^{4–9} (Fig. 1).

Degradation by free-radical reactions in the melt is also typical of PP. This type of reaction can be induced by mechanochemical effects, as a result of high temperature and shear stress and the presence of oxygen.¹ However, in some cases high reactivity is desired, for which peroxides are then usually chosen.^{2–4} The free radicals generated by peroxide decomposition abstract hydrogen atoms from the tertiary carbon sites, leading to β -scission. A reduction in molecular weight is obtained, which corresponds to lower melt viscosity and tailored processability for specific applications.^{2,3} In fact, nowadays controlled chain degradation is an important industrial technique for the production of PP with a prescribed rheological behavior.^{4–9}

It has been demonstrated that extruders are efficient reactors in which the successful chemical modification of polymers can be achieved economically.^{1–3} Several authors have studied polypropylene degradation during extrusion,^{4–9} to create a kinetic model able to predict the relationship between initiator concentration and viscosity/molecular weight of the degraded polypropylene extrudates. Berzin et al.¹⁰ developed a theoretical model that predicts the molecular weight evolution along the extruder under different processing conditions. However, confrontation of the predictions with experimental data on molecular weight evolution was not carried out because the latter was not available.

In a previous work,¹¹ the authors monitored the evolution of the structure of polyolefins with different ethene/propene ratios either in the absence or in the presence of peroxide along a twin-screw extruder. This was possible because of the development of a technique for quickly collecting relevant samples from specific locations of the extruder.¹² It was observed that the rheological properties of the polyolefins are hardly affected when processing is carried out in the absence of peroxide. However, in the presence of peroxide both branching/crosslinking and degradation occur along the extruder, until the peroxide is fully decomposed. 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.

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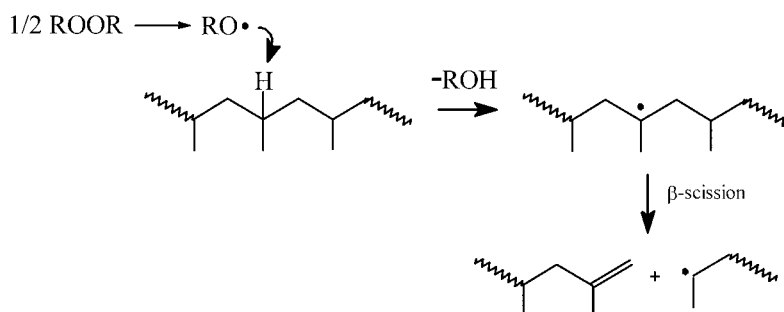


Figure 1 Mechanism of peroxide-induced degradation of PP.

The present article aims to provide greater experimental insight into polypropylene degradation upon processing in a twin-screw extruder, in the absence or in the presence of peroxide, under varied processing conditions, by using on-line capillary rheometry and off-line molecular weight determination. Correlations between peroxide concentration and processing conditions with rheological properties and molecular weight of the modified materials will be investigated.

EXPERIMENTAL

Materials

Polypropylene (PP; Stamylen P 12E62 from DSM (The Netherlands) with a melt flow index of 0.8 g/10 min at 230°C/21.6 N), and 2,5-bis(*tert*-butylperoxy)-2,5-dimethylhexane (DHBP; Trigonox 101 from Akzo Nobel, Belgium), used as initiator for the degradation reac-

tions, were selected for this work. From the data provided by the manufacturer, the calculated half-life time of the peroxide at 200 and 220°C is 6.1 and 1.2 s, respectively.

Processing

Polypropylene was tumble mixed with different concentrations of peroxide and processed in a laboratory modular Leistritz LSM 30.34 intermeshing corotating twin-screw extruder (Fig. 2) using the processing conditions shown in Table I, at a constant flow rate of 2.3 kg/h (which was set by a K-TRON gravimetric feeder). This procedure was adopted because of its simplicity: the powder is well distributed in the PP pellets and absorption occurs immediately upon melting of the latter. Previous work on grafting of maleic anhydride onto polyethylene showed that this proce-

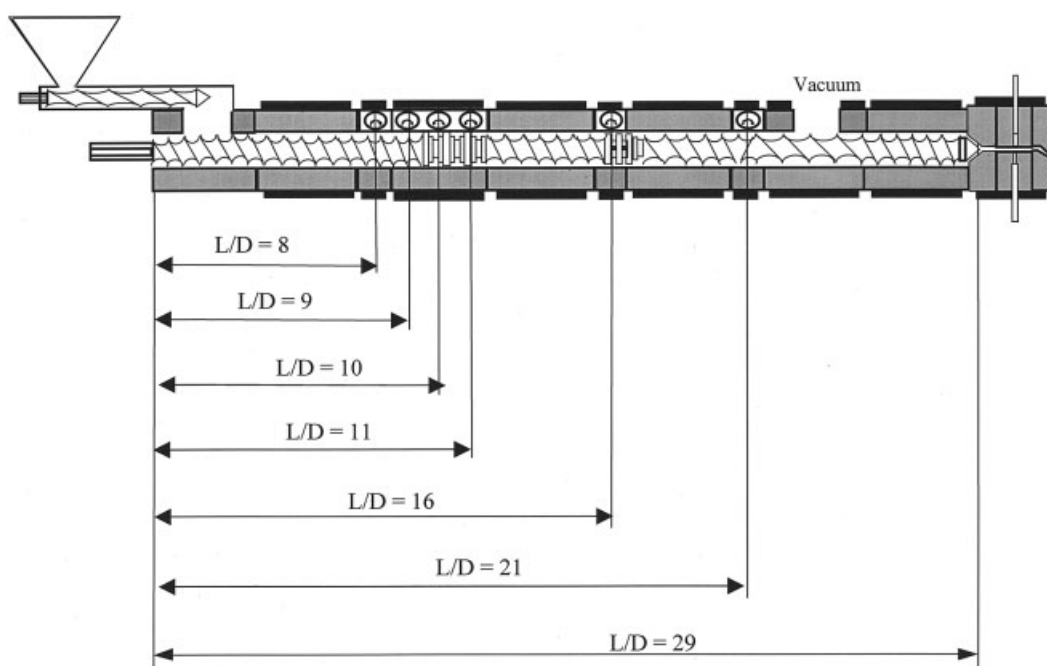


Figure 2 Extruder layout and sampling locations.

TABLE I
Processing Conditions and Peroxide Concentration

Temperature profile (°C)	Screw speed (rpm)	Peroxide concentration (phr)
200	75	0
200	15	0
220	75	0
200	75	0.1
200	75	0.05
200	15	0.05
220	75	0.05

dure induced similar results in comparison with feeding the peroxide after melting the polymer.¹³ Given that the peroxide was used in powder form, this procedure was adopted because of its simplicity. The baseline processing conditions (screw speed of 75 rpm and barrel temperature of 200°C) were varied to a condition with little shear (screw speed of 15 rpm) and another with higher temperature (220°C). No special precautions were taken against the presence of oxygen. Samples for subsequent off-line characterization were quickly collected along the extruder axis using a series of sampling devices (see Machado and Covas¹² for details) and were immediately quenched in liquid nitrogen, to avoid further reaction. The location of these sampling ports is also shown in Figure 2. They were selected to match positions where the screws work with high degrees of filling and where significant stresses develop. Each 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 essentially caused by a combination of heat transfer and mechanical stresses developed by the mixing block upstream.

The melt temperature was measured at the sampling points. Immediately after operating the sampling device to collect polymer material, the preheated needle of a thermocouple with a small time constant (1 s) was stuck into the molten volume and a measurement was made. The results are shown in Table II. The

validity of the technique has been demonstrated elsewhere.¹¹

Materials characterization

On-line capillary rheometry

The authors developed a concept of on-line capillary rheometry that allows the monitoring of the evolution of rheological properties of materials along the extruder,^{14,15} with a view to future real-time process control. The available prototype allows small sample volumes (typically 2–3 cm³) of material to be collected at any location along the barrel of the extruder where inner pressure develops. The sample can then be tested within 10–20 s of collection, or after equilibration at a set temperature (an autonomous temperature control system is available), information being gathered quantitatively regarding the shear viscosity (through conventional flow curves) and qualitatively regarding the extensional behavior (through the magnitude of the entry pressure drop¹⁵). In the case of the present work, where only point measurements at fixed shear rate were performed, the total test time (including sample collection and thermal stabilization at the set temperature) was about 40 s. The relatively long thermal stabilization time was necessary because the true melt temperatures were never equal to the set temperature for the experiments.

In the present work, capillary rheometry was used to assess its potential in discriminating between variations in processing conditions and/or peroxide content along the extruder. For that purpose, sample collecting and rheological testing were carried out at the same locations. To allow true values of the shear viscosity to be measured, two different circular dies were used in this work, both of 2 mm diameter, one of length to diameter ratio (L/D) = 1 and another of L/D = 8. The usual Bagley correction was then applied. In all experiments, the downstream wall shear rate was constant and equal to 8.6 s⁻¹. Test temperatures varied between 200 and 220°C.

TABLE II
Melt Temperatures for the Different Processing Conditions

Temperature/speed/peroxide	Length to diameter ratio					
	9	10	11	16	21	29
200/75/0	185.4	204.8	206.7	205.0	216.5	213.1
200/15/0	187.7	195.8	193.4	190.2	195.6	210.1
220/75/0	192.8	215.8	227.3	227.8	230.0	226.7
200/75/0.1	178.9	190.8	193.3	207.4	209.3	200.4
200/75/0.05	172.9	194.6	200.5	204.1	204.7	202.8
200/15/0.05	179.9	186.4	191.7	200.8	201.0	199.4
220/75/0.05	188.1	213.4	215.4	228.5	226.0	221.9

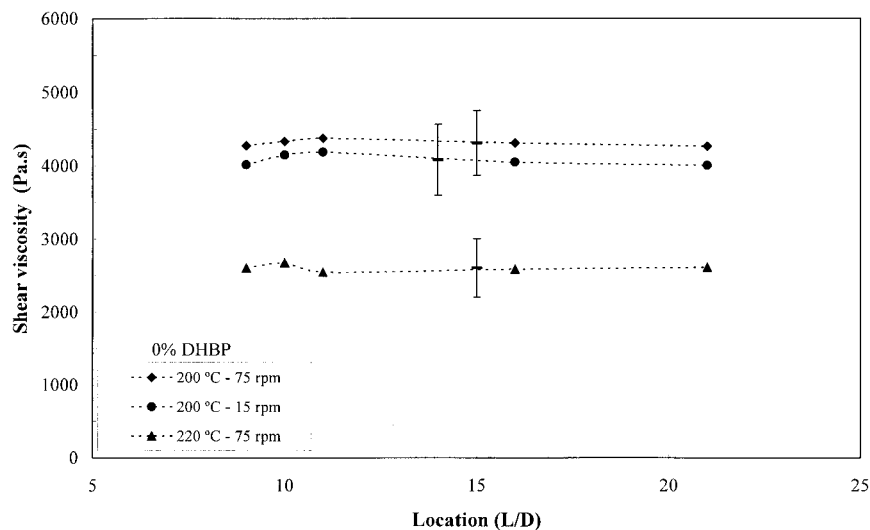


Figure 3 Shear viscosity of PP, under various operating conditions.

Size-exclusion chromatography (gel-permeation chromatography)

The molecular weight distribution (MWD) of the various samples was measured in a Waters Chromatograph GPC 150 CV (Waters Chromatography Division/Millipore, Milford, MA), with refractive index detector, using three Waters Styragel HT columns in the effective molecular weight range of 10^2 to 10^6 with 10 μm particle size. Samples were solubilized at 0.1 phr concentration in 1,2,4-trichlorobenzene (TCB) at 140°C and pumped at a flow rate of 1 mL/min. Calibration curves were obtained using 12 monodisperse polystyrene standards, ranging from 480 to 1,000,000 g mol^{-1} . The raw data were calculated with the Millennium 2010 software, with manual adjustment of the baseline.

For the purpose of calculating chain-scission distribution function (CSDF) functions, the GPC raw data {as $\log(\text{MW})$ versus $dw/d[\log(\text{MW})]$ } was exported as ASCII matrices from the Millennium 2010 software, and replotted using the CSDF macro developed in house running in the Excel software. Starting from the virgin PP data, this macro calculates the distance between a point in the initial curve (virgin PP) and the corresponding point in the degraded curve (for more details, see Canevarolo¹⁶).

RESULTS AND DISCUSSION

Direct visual observation of the polymer samples removed from the extruder with the sampling devices showed clearly that, under the processing conditions selected, melting was not yet complete at $L/D = 8$ (Fig. 2). However, just one L/D downstream an apparently homogeneous melt had already been formed (this very fast melting process has in fact been ob-

served for various other systems processed with similar screw configurations¹¹). Therefore, the ensuing discussion will include data on samples collected only from location $L/D = 9$ onward.

Behavior of PP homopolymer along the extruder

Figure 3 shows the evolution of the shear viscosity along the barrel of the extruder for the PP homopolymer. All the samples were left equilibrating long enough so that the melt temperatures resulting from varying screw speeds and temperatures (which are presented in Table II) would stabilize at 200 or 220°C (this was measured by a thermocouple inserted in the rheometer).

The shear viscosity of the melt does not change (within experimental error) along the extruder, which is not surprising, although at the low screw speed the higher corresponding local residence times could induce some thermal degradation (see, e.g., Machado et al.¹¹). However, it is also apparent that the rheometer is not sensitive enough to discern the influence of changing the screw speed, even if this produces an important viscous dissipation, as shown in Table II.

Influence of peroxide content

The influence of peroxide content on the evolution of shear viscosity along the barrel of the extruder for PP processed at 200°C and 75 rpm can be studied in Figure 4. As expected, the higher the peroxide content, the lower the shear viscosity. The decrease is of roughly one order of magnitude when 0.1% DHBP is added to PP. Also, the degradation reaction seems to occur very quickly and very early in the extruder. For example, when 0.05 phr DHBP was added to PP, by

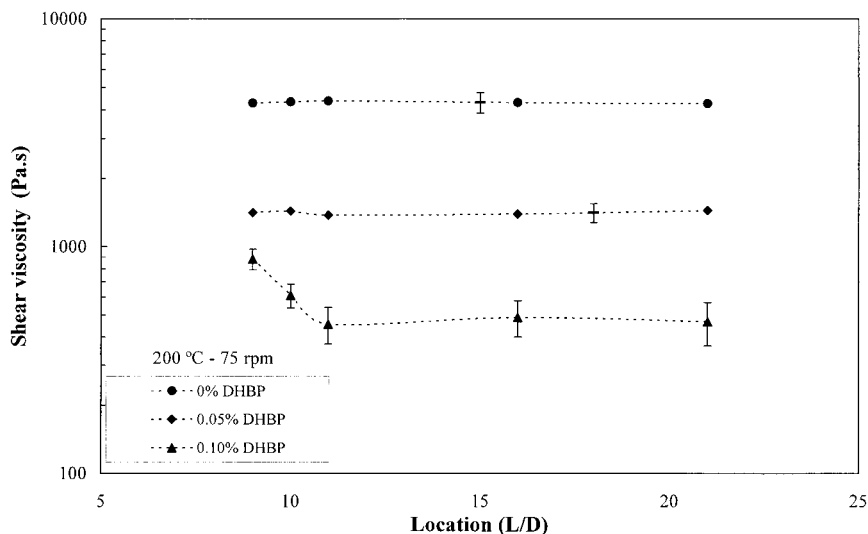


Figure 4 Effect of peroxide concentration on shear viscosity of PP + DHDP along the extruder.

the time the melt reached the first mixing block at L/D = 9 (one must emphasize that the material was still solid at L/D = 8) the reaction seems to have already largely finished. Even when the peroxide content was increased to 0.1 phr, the reaction was all but complete at the end of this mixing block (L/D = 11).

Figures 5 and 6 exhibit the evolution of the molecular weight distribution of PP along the extruder, for the two peroxide content levels (0.05 and 0.1 phr, respectively). The MWD curves are progressively shifted to the low molecular weight side, especially in the first part of the extruder (i.e., in the first mixing block), which is consistent with the viscosity data. This is obviously related with the peroxide decomposition, which is very fast under the conditions used, thus meaning that chain scission takes place mainly upon

melting of PP. However, unlike capillary rheometry, GPC is able to identify an evolution of the degradation process until the extruder outlet. These results highlight: (1) the relative lack of sensitivity of capillary rheometry to changes in molecular structure (in this case, essentially MWD) other than molecular weight and (2) the fact that capillary rheometry is probably not the best rheological characterization technique in this case because of the fact that a mechanical history is being imposed on the material, which may cause the reaction to continue occurring as it is being tested.

However, the influence of peroxide concentration can be identified qualitatively from the comparative analysis of the two figures. In agreement with the on-line rheological results, the higher the amount of peroxide, the more significant the differences on the

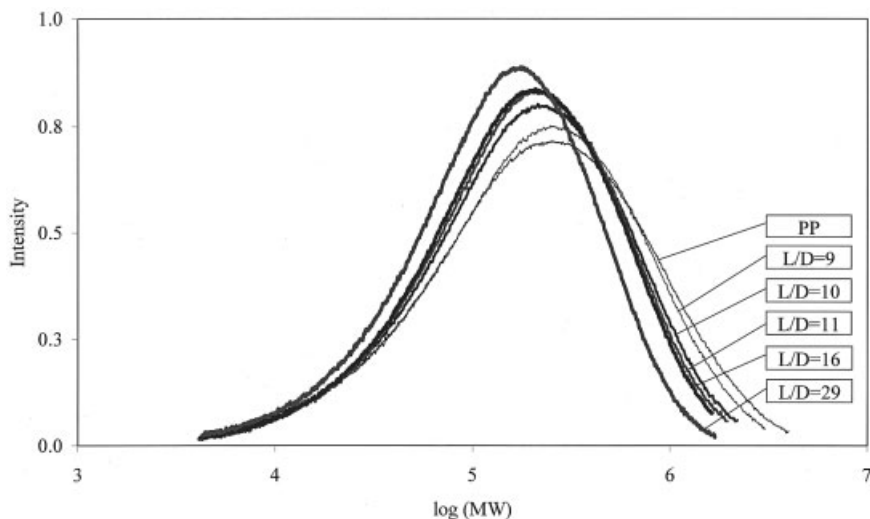


Figure 5 Molecular weight distribution of PP + 0.05 phr DHDP along the extruder (75 rpm, 200°C).

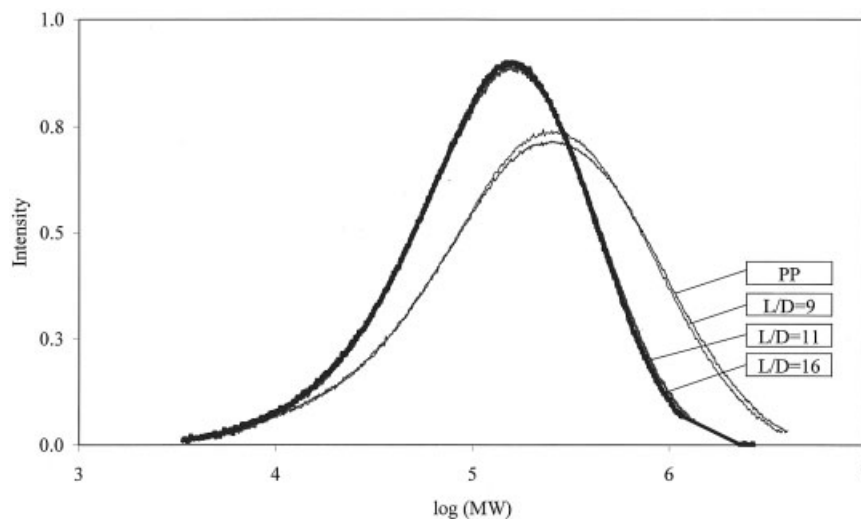


Figure 6 Molecular weight distribution of PP + 0.1 phr DHDP along the extruder (75 rpm, 200°C).

MWD curves, given the generation of more free radicals and the higher extent of the degradation.

To obtain more detailed information on the chain-scission process, the shift between the MWD curves for the homopolymer PP and those for the degraded material was calculated as a chain-scission distribution function (CSDF).¹⁶ The results for the curves of Figures 5 and 6 are presented in Figures 7 and 8, respectively. CSDF curves indicate the change in chain length throughout the scission process and so it becomes possible to detect whether any selectiveness in the chain-scission mechanism is occurring during the degradation process. CSDF curves generally start from near-zero values and assume different positive slopes. The greater the slope, the more important the effect of MW on the chain scission, given that increasing chain molecular weight increases not only the probability of entanglements, but also the chances for chain scission. The existence of negative values, as well as of scattered data at very low and very high

molecular weights should be taken cautiously because the low concentration of chains in these regions increases the uncertainty of the calculations.

In the present case a thermomechanical process develops catalyzed by the presence of peroxide, which increases the rate of β -scission. Starting from the low MW region, most CSDF curves of Figures 7 and 8 are initially almost flat, which points to the development of a random chain-scission process. At molecular weights of roughly 10,000 [$\log(\text{MW}) = 5$] a change in slope occurs, indicating a selective chain-scission process with more dramatic changes in the high MW region. This indicates that chain scission occurs in any MW, but is more effective at the high MW side. Moreover, when a hydrogen-abstracting agent (i.e., peroxide) is added, the chain-scission mechanism is monotonically activated as the chain length is increased.

During a thermomechanical degradation process the chain-scission rate will be affected by: (1) the level of tensile stress in the chain (which increases with

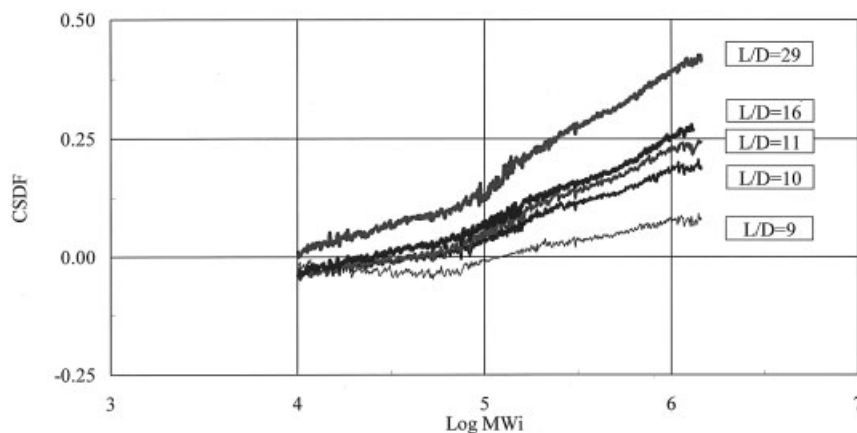


Figure 7 Chain-scission distribution function (CSDF) derived from the data of Figure 5 (PP + 0.05 phr DHDP).

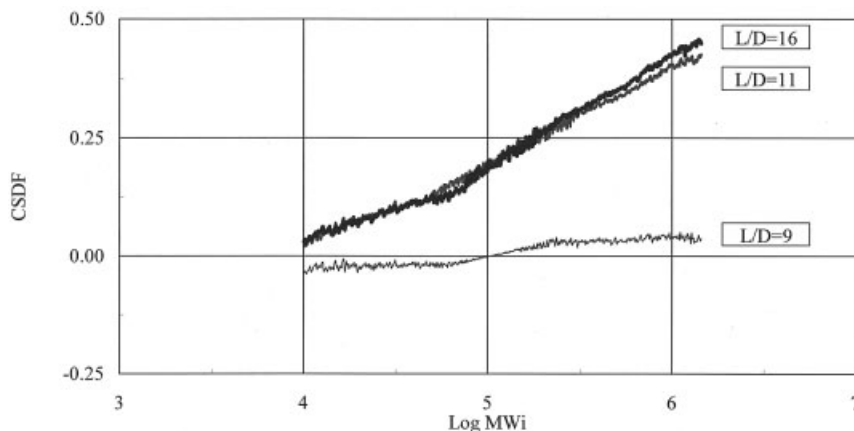


Figure 8 CSDF derived from the data of Figure 6 (PP + 0.1 phr DHDP).

shear rate and chain length) and (2) the concentration of hydrogen-abstrating agents promoting the β -scission mechanism. Whereas the first effect is molecular weight dependent, the second is not. However, in the presence of H-abstrating agents, the chain becomes so sensitive to scission that even chains subjected to a low stress level (shorter chains producing small amounts of entanglements) do show a MW dependency. Thus, the presence of peroxide can have a significant influence in the level of chain scission in thermomechanical PP degradation. Figure 7 shows the level of chain scission measured at various positions along the barrel, when PP was processed with 0.05 phr of peroxide. As expected, as the material progresses in the screw, the level of chain scission increases. Again, the greater changes occur between L/D values of 9 and 10 (i.e., in the first half of the first kneading block). When the peroxide concentration is raised to 0.1 phr

(Fig. 7 versus Fig. 8), the level of chain scission increases.

Influence of processing conditions

Figure 9 shows the influence of the processing conditions on the viscosity of the melt, for 0.05 phr DHBP. As shown by direct comparison with Figure 3, the behavior of PP + 0.05 phr DHBP mirrors that of PP, albeit for lower absolute values of the viscosity. As before, no changes along the extruder could be detected.

Because Figure 10 illustrates the evolution of the MWD of PP along the extruder at 15 rpm (barrel set at 200°C, 0.05 phr of peroxide), its direct comparison with Figure 5, which shows similar data for 75 rpm, yields the effect of screw speed. In both cases the MWD curves are shifted to the lower molecular

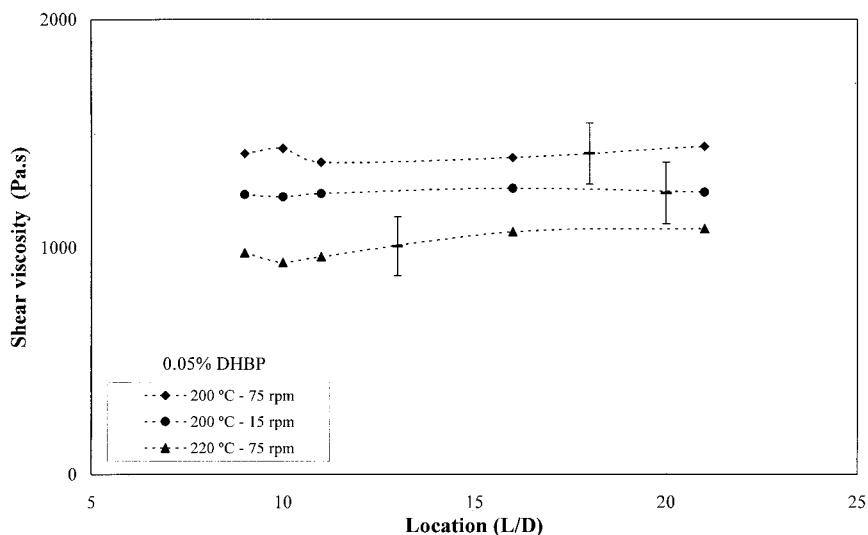


Figure 9 Shear viscosity of PP + 0.05 phr DHDP, under various operating conditions.

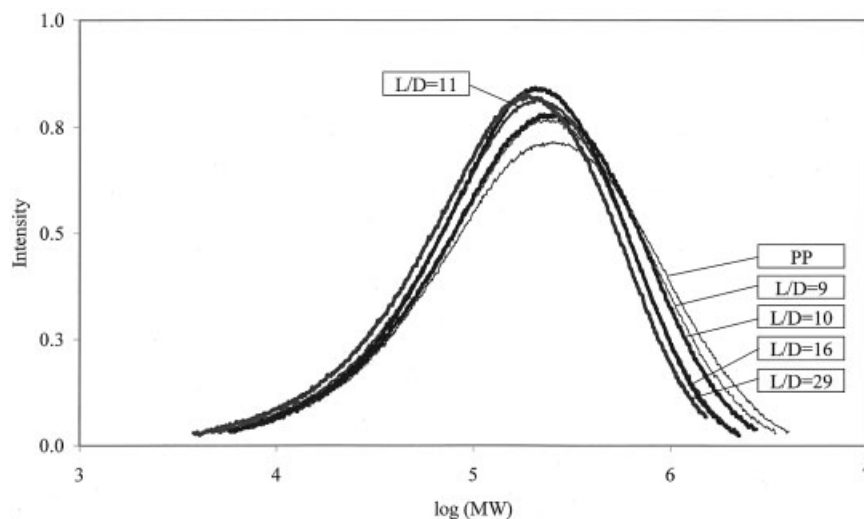


Figure 10 Molecular weight distribution of PP + 0.05 phr DHDP along the extruder (15 rpm, 200°C).

weight side, especially in the first part of the extruder. Nonetheless, for the lower screw speed the changes in MWD seem to occur slightly more slowly in the first mixing block than for the higher speed. The MWD of the extrudates is also distinct.

Figure 11 presents the evolution of the CSDF functions for the data of Figure 10. The effect of screw speed can be ascertained from its comparison with Figure 7. The rate and level of chain scission increase with screw speed, a change in slope being again perceived at $\log(\text{MW}) = 5$. This could be attributable to the higher temperature (3–10°C; see Table II) and stress levels that are reached under these processing conditions that are associated with higher peroxide decomposition rates and, consequently, with the rate of chain scission.¹¹ As seen above, this level of discrimination is not observed in the rheological experiments, not only because the differences induced in viscosity are close to the experimental error, but also because capillary rheometry is more sensitive to

changes in MW than to variations in MWD (the two variables actually imposing opposite effects on the viscosity).

The effect of temperature on the degradation reaction, for PP + 0.05 phr DHBP, is evident from the comparative analysis of Figure 12 (extrusion temperature of 220°C) with Figure 5 (extrusion temperature of 200°C). The shift of the MWD curves is much less apparent in the former case (i.e., higher extrusion temperature). This can be explained by the fast decomposition of the peroxide at 220°C (at this temperature the half-life of the peroxide is 1.2 s). Thus, probably most of the peroxide is decomposed before the polymer starts to melt and as a consequence a very small amount of peroxide is used as an initiator of the degradation reaction. Increasing the temperature to 220°C and keeping all other variables at the same values as the starting conditions, the level of chain scission in general drops significantly in all locations (Fig. 13). Thus, in this case the degradation follows roughly the

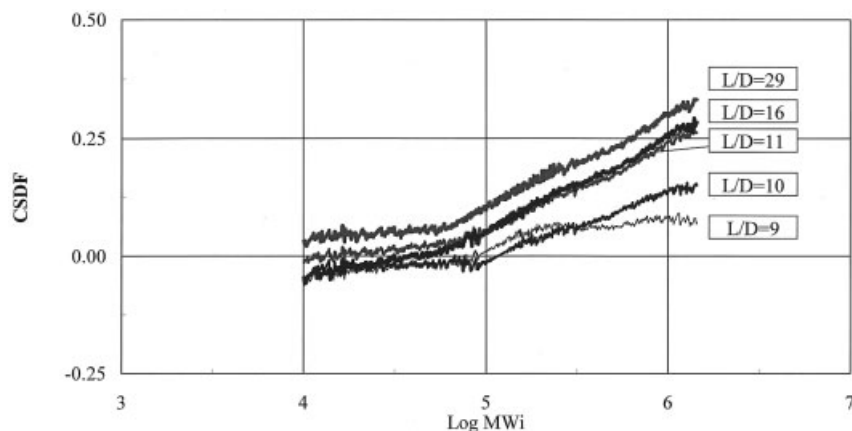


Figure 11 CSDF derived from the data of Figure 10 (PP + 0.05 phr DHDP, 15 rpm).

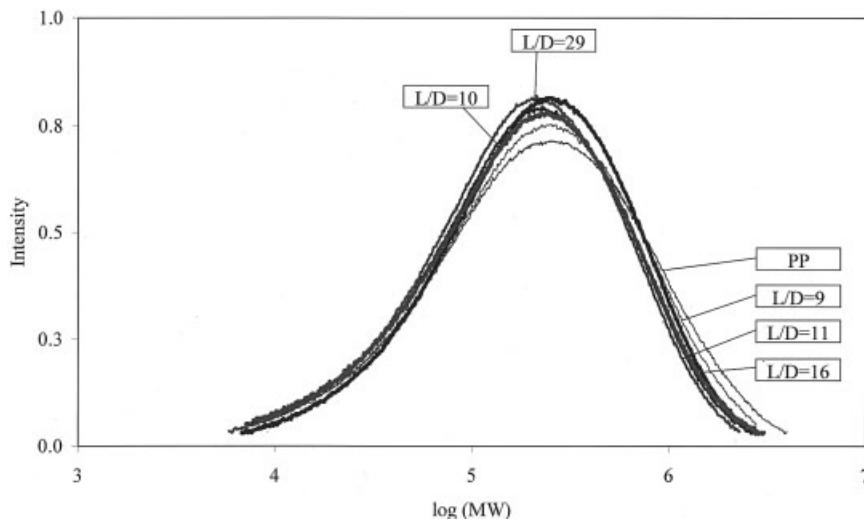


Figure 12 Molecular weight distribution of PP + 0.05 phr DHDP along the extruder (75 rpm, 220°C).

behavior shown by pure PP,¹⁶ having a low MW region of random chain scission followed by a MW-dependent mechanism above $\log(\text{MW}) = 5$ ($\text{MW} = 10,000$).

CONCLUSIONS

The evolution of the peroxide-induced degradation of polypropylene along the axis of a corotating twin-screw extruder, operating under various conditions, was monitored both on-line and off-line, using distinct experimental techniques. On-line capillary rheometry—which is simple to operate, can be automatized and, therefore, could be envisaged as a technique for process control—demonstrated its ability to detect changes in molecular weight (which are directly related to the percentage of peroxide), but was unable to discriminate between the variations in MWD occurring along the extruder axis for each specific recipe.

Therefore, future work should judge the possibility of developing a more precise on-line rheometry technique, such as rotational oscillatory measurements.

The various MWD curves of the samples collected along the extruder axis showed differences, and thus they are important tools to study the level of chain scission occurring during thermomechanical processes. To better highlight these (in some cases subtle) effects, the concept of chain-scission distribution function (CSDF) proved to be useful.

PP degradation occurs by chain scission, and depends on the level of stresses imposed by the screw elements, temperature, and concentration of hydrogen-abstracting agents (in this case, peroxide). The reaction is extremely rapid; that is, most of the degradation occurs in the first kneading block, upon melting, when the peroxide decomposes and abstracts one hydrogen from the PP chain, facilitating the β -scission mechanism.

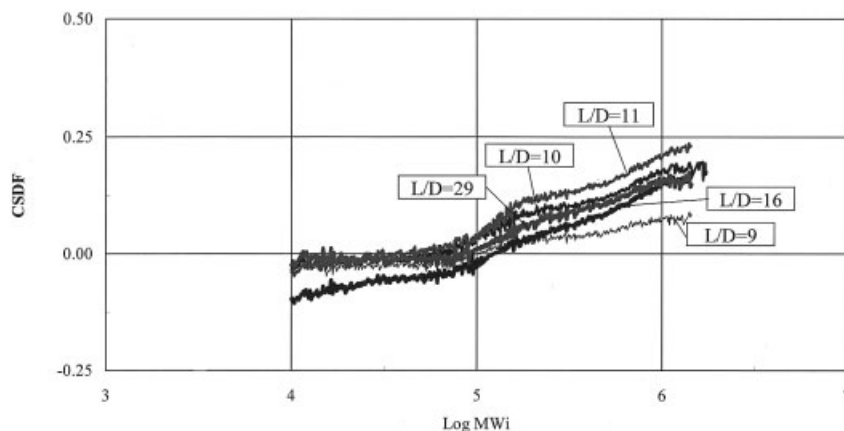


Figure 13 CSDF derived from the data of Figure 12 (PP + 0.05 phr DHDP, 220°C rpm).

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