

# Rheological Behavior of Controlled-Rheology Polypropylenes Obtained by Peroxide-Promoted Degradation During Extrusion: Comparison Between Homopolymer and Copolymer

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**ABSTRACT:** In the present work, experimental studies of the free-radical-initiated molecular weight degradation of polypropylene in a modular self-wiping corotating twin-screw extruder are investigated. The control of the molecular weight distribution of polypropylene resins by peroxide degradation is widely used in the polymer industry. It allows one to adjust the viscosity of these resins to the level required for processing applications. The purpose of this work was to characterize the influence of peroxide degradation on the rheological behavior of a polypropylene homopolymer and a block polypropylene/polyethylene copolymer, which includes an addition of a low percentage of polyethylene (around 7%). The homopolymer exhibits a classical behavior: When the peroxide amount is increased, we observe a decrease in the viscosity corresponding to a decreasing molecular weight and a pronounced shift toward more Newtonian behavior. The rheological behavior of the copolymer is influenced by the presence of the polyethylene phase which greatly modifies the viscoelastic properties and increases the viscosity when the polypropylene matrix is highly degraded. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 1243–1252, 2001

**Key words:** rheology; polypropylene; copolymer; peroxide degradation; reactive extrusion; molecular structure

## INTRODUCTION

Polypropylene (PP) resins produced in most industrial polymerization processes have a broad molecular weight distribution and a high molecular weight. To adjust the molecular weight distribution and to improve the mechanical properties of the polypropylene, the polymer can be mod-

ified in reactive extrusion operations using peroxide-initiated scission reactions.<sup>1,2</sup> The process is initiated by free radicals formed from the thermal decomposition of an organic peroxide, which leads to significant polymer degradation by  $\beta$ -scissions because of the low stability of the tertiary hydrogen atoms of macroradicals.<sup>3</sup> In the present work, we present experimental studies of the free-radical-initiated molecular weight degradation of two PPs [a PP homopolymer and a block copolymer of polyethylene (PE) and PP] and the modification to their rheological behaviors.

Until now, studies involving peroxide-induced modifications have been focused on the behavior

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of PP homopolymers<sup>4-7</sup> and on mechanical blends of PP and PE.<sup>8-12</sup> Only recently have a few studies appeared on the behavior of PP/PE copolymers.<sup>13,14</sup> For the PP homopolymer, the main mechanism involved in the presence of free radicals is  $\beta$ -scission, that is, the rupture of the main chain by hydrogen abstraction. As a result, the molecular weights decrease, the molecular weight distribution becomes narrower,<sup>4</sup> the viscoelastic properties decrease,<sup>6,7</sup> and the melt becomes more Newtonian.<sup>4</sup> On the contrary, a peroxide attack on PE leads to chain branching and to crosslinking by macroradical recombination.<sup>15,16</sup> Consequently, during mechanical blending of PP and PE in the presence of peroxide, both mechanisms will affect the two phases differently. At a high PE content (more than 60%) and very high peroxide content (3%), a totally crosslinked material is obtained.<sup>11</sup> For lower peroxide contents (0.5%), PE is partially crosslinked, with a gel fraction inferior to 10%.<sup>12</sup> For low PE concentrations (less than 25%) and moderate peroxide contents (less than 1%), the blend behaves as a "solid" suspension, with a low viscous PP matrix in which are embedded crosslinked or highly branched PE droplets.<sup>8,10</sup> In the case of copolymers, the PE content is low (usually less than 10%). However, as small changes in the molecular structure can affect considerably the viscoelastic behavior, it is important to characterize such materials and to compare their properties to those of similar homopolymers. This was the purpose of the present article.

## EXPERIMENTAL

### Materials

Two kinds of commercial PPs provided by Appryl were studied: The first one is a standard homopolymer and the second one is a block copolymer which includes an addition of a low percentage of PE (around 7%). The homo- and copolymer have melt flow indices of 4.5 and of 6 g/10 min (2.16 kg/230°C), weight-average molecular weights of 301,600 and of 256,100 g/mol, and polydispersity indices of 6.4 and 5.4, respectively. The peroxide used was 2,5-dimethyl-2,5-di(*t*-butylperoxy) hexane (DHBP, Trigonox 101, Akzo Chemie, Amersfoort, The Netherlands).

### Sample Preparation

The reactive experiments are made in a laboratory corotating self-wiping twin-screw extruder

(Model 30/34, Leistritz). The polymer and copolymer pellets are fed via a weighted feeding system. The peroxide is injected into the extruder by a volumetric piston feed pump. The DHBP is previously diluted in 1,2,4-trichlorobenzene to obtain a good precision on the pump flow rate, even for concentrations less than 1000 ppm (i.e., 0.1 wt %). In all cases, the output rate of the piston pump is adjusted according to the flow rate of PP and its regularity is controlled by the loss in weight of the beaker containing the peroxide. In all cases, the total throughput is 12 kg/h, and the screw speed, 200 rpm.

Left-handed and neutral kneading disc blocks assure the melting of the polymer. The injection of DHBP is housed in an unfilled section, just after the melting zone. The reaction area includes kneading disc blocks designed to improve the mixing and homogenization between free radicals and PP and right-handed conveying screw elements. A devolatilization zone is placed prior the pumping zone. At this level, the degradation reaction of PP is stopped by the elimination by a vacuum pump of all volatile reactants. The barrel regulation temperature is fixed at 250°C. We chose a relatively high barrel temperature to be sure that the degradation reaction is finished upon reaching the devolatilization zone, due to the very short half-lifetime of peroxide at this temperature.

By using various amounts of peroxide (0.01–0.5 wt %), we obtain a series of polymers and copolymers with different molecular weight distributions. Samples are collected at the die exit, after 15 min of steady-state extrusion conditions (stable die pressure). Extrudates are quenched in water before being cut into pellets. The samples are dried under a vacuum, at 80°C during a 24-h period, to eliminate all possible residual peroxide.

### Characterization

The molecular weight distributions are analyzed by size-exclusion chromatography (SEC). The samples are dissolved at 145°C in the 1,2,4-trichlorobenzene, at a polymer concentration of 0.8 g/L, with the addition of an antioxidant to prevent any degradation.

The rheological behavior of the different samples is measured in a Rheometrics mechanical spectrometer (RMS-800), using 25-mm-diameter parallel-plate geometry, in the oscillatory mode. The dynamic measurements are carried out in the linear domain for frequencies ranging from 0.1 to

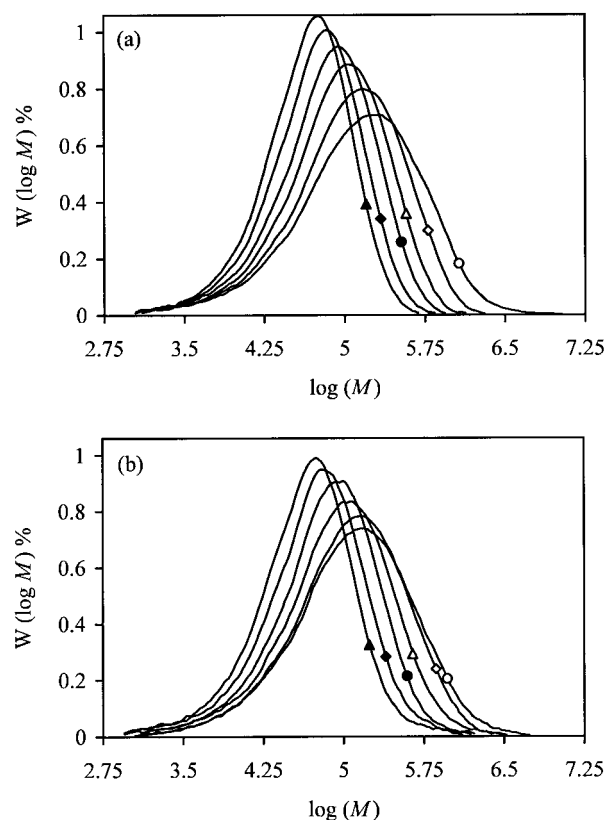
100 rad/s and at five temperatures (185–245°C). Time sweep tests are made at different temperatures and at a frequency of 1 rad/s to check the thermal stability of the samples.

A Perkin–Elmer differential scanning calorimeter (DSC-7) is used for crystallization and thermal analyses. Samples are beforehand heated up to a temperature corresponding to the thermodynamic equilibrium temperature of PP (around 208°C). They are then kept for 10 min at this temperature to reduce the products to the same reference state and to ensure that all the crystalline part is melted. Then, to impose the same thermal history, the samples are first heated from 50 to 200°C at a heating rate of 10°C/min. For the isothermal crystallization experiments, they are cooled from 200 to 50°C; melting endotherms are then obtained by reheating the samples up to 200°C (the sweeping rate is fixed at 10°C/min for each cooling and heating).

## RESULTS AND DISCUSSION

### Molecular Weight Distribution

The molecular weight distributions obtained by SEC are presented in Figure 1. The weight-average molecular weights ( $\bar{M}_w$ ) range between 301,600 and 62,970 g/mol for the homopolymer and between 256,100 and 74,430 g/mol for the copolymer. We first observe that the distributions of the virgin PP and the extruded one (without peroxide) are very close, which means that, in the processing conditions used, mechanical and thermal degradations are limited. As expected, irrespective of the material, we note that increasing the peroxide concentration narrows the molecular weight distribution and decreases the presence of the high molecular weight species.<sup>4</sup> For example, with 0.5% peroxide,  $\bar{M}_w$  is reduced by 79 and 71% for the homo- and the copolymer, respectively. The degradation of the homopolymer is more important than for the copolymer. Indeed, the polydispersity decreases from 6.4 to 2.5 for the homopolymer and from 5.4 to 3.4 for the copolymer (Table I). It is worth noticing the presence of high residual masses for the copolymer, even for the more degraded products (Fig. 2). For the homopolymer, masses above 800,000 g/mol disappear as soon as the peroxide concentration is higher than 0.15%. For the copolymer, even with 0.5% peroxide, these high molecular weight species are still present, at a level of approximately



**Figure 1** Effect of peroxide concentration on the molecular weight distribution—comparison between the (a) homopolymer and (b) copolymer: (○) virgin PP; (◇) 0.01%; (△) 0.06%; (●) 0.15%; (◆) 0.35%; (▲) 0.5%.

0.3% of the total mass. Similar observations can be made on the GPC curves presented by Dionisi et al.<sup>13</sup> on a copolymer with 16% ethylene. We will see later on that these species play a major role in the rheological behavior of the copolymer.

### Rheological Behavior

Measurements were carried out on the various samples. The results of the time sweep tests show that the complex viscosity,  $\eta^*$ , and the storage,  $G'$ , and loss,  $G''$ , moduli are constant with time (duration of tests: 30 min; temperatures: 185, 215, and 245°C), whatever the homo- or copolymer. Concerning the effect of the frequency, Figures 3 and 4 show the result of the time–temperature superposition, for the elastic and loss moduli (reference temperature of 215°C) as function of the weight-average molecular weights.

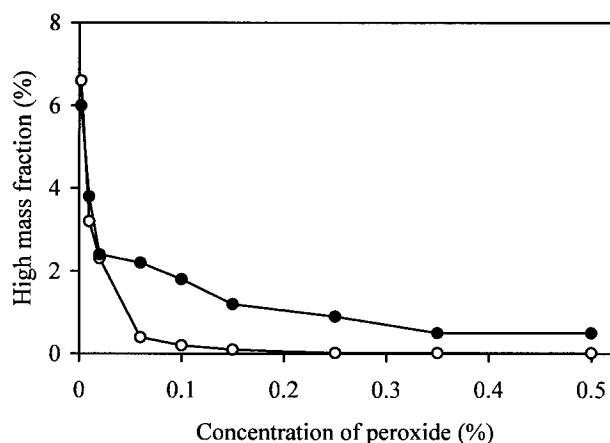
For the homopolymer, the results are in close agreement with the literature.<sup>4,5,17,18</sup> We observe the usual decrease in viscosity with decreasing

**Table I** GPC Results: Average Molecular Weights of the Two PPs

% DHBP	Homopolymer (PP 3050 BN 1)				Copolymer (PP 3060 MN 5)			
	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_z$	$\bar{M}_w/\bar{M}_n$	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_z$	$\bar{M}_w/\bar{M}_n$
Virgin PP	47,050	301,600	1,125,000	6.4	47,110	256,100	850,500	5.4
Extruded PP	46,070	271,200	779,000	5.9	43,230	250,800	820,900	5.8
0.01%	45,870	209,300	482,300	4.6	44,800	210,400	559,700	4.7
0.02%	40,590	190,500	425,800	4.7	41,850	181,400	456,000	4.3
0.06%	36,210	135,600	278,100	3.7	36,680	168,900	612,300	4.6
0.1%	34,730	114,800	224,800	3.3	36,130	150,100	488,900	4.2
0.15%	33,570	104,900	202,600	3.1	30,000	116,900	285,400	3.9
0.25%	29,140	87,480	175,500	3.0	29,810	104,700	305,000	3.5
0.35%	27,170	78,760	148,300	2.9	23,980	89,290	218,900	3.7
0.5%	25,220	62,970	112,600	2.5	21,800	74,430	231,700	3.4

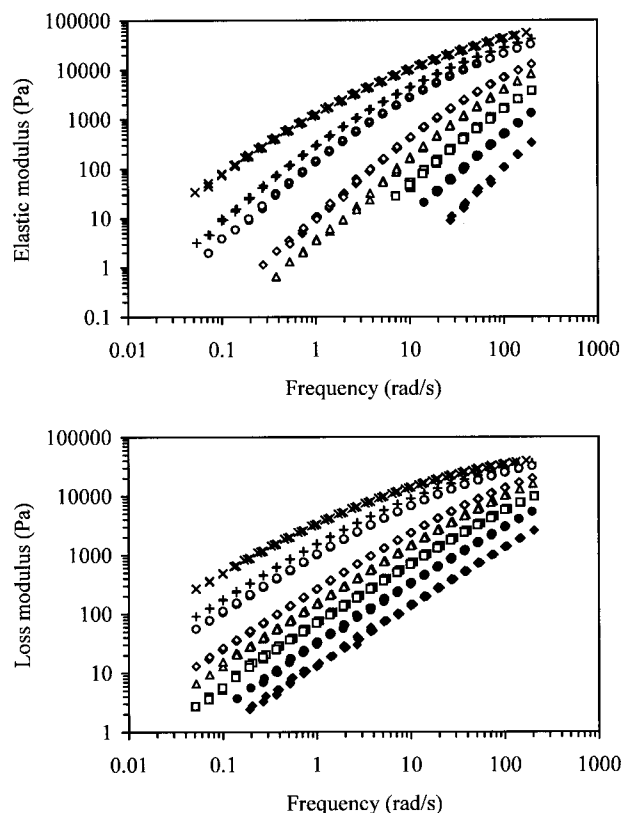
molecular weight and a pronounced shift toward more Newtonian behavior [Fig. 5(a)]. With 0.5% peroxide, we obtain a very low viscous material, with a constant viscosity of 12 Pa s.

For the copolymer [Figs. 4 and 5(b)], these tendencies are verified only for low amounts of peroxide, that is, below 0.1 wt %. When increasing this amount, and thus decreasing the molecular weight, we observe the onset of a low-frequency plateau for  $G'$  and at a lesser extent for  $G''$ . Consequently, the complex viscosity tends to increase, first at low frequency, and then on the whole range of frequencies. For the more reacted samples, the copolymer has the behavior of a yield stress fluid, that is, the complex viscosity tends to infinite at low frequencies. As the time sweep tests have shown that the rheological properties of the copolymer were constant with time, these

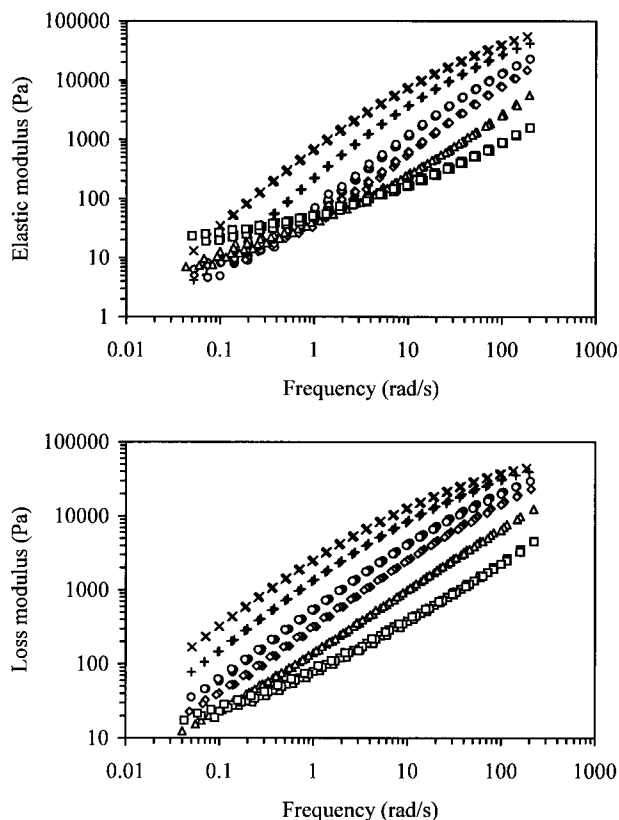


**Figure 2** Evolution of high mass fraction (superior of 800,000 g/mol) in function of the peroxide concentration: (○) homopolymer; (●) copolymer.

increases in viscosity are not produced by an evolution of the samples during the measurements, but reflect the true behavior of the products. Such behavior was previously observed on mechanical



**Figure 3** Storage and loss moduli master curves at 215°C of PP homopolymers with different weight-average molecular weight  $\bar{M}_w$ : (×) 301,600; (+) 209,300; (○) 190,500; (◇) 135,600; (△) 114,800; (□) 104,800; (●) 78,760; (◆) 62,970.



**Figure 4** Storage and loss moduli master curves at 215°C of PP/PE copolymers with different weight-average molecular weight  $\bar{M}_w$ : (×) 256,100; (+) 210,400; (○) 168,900; (◇) 150,100; (△) 104,700; (□) 74,430.

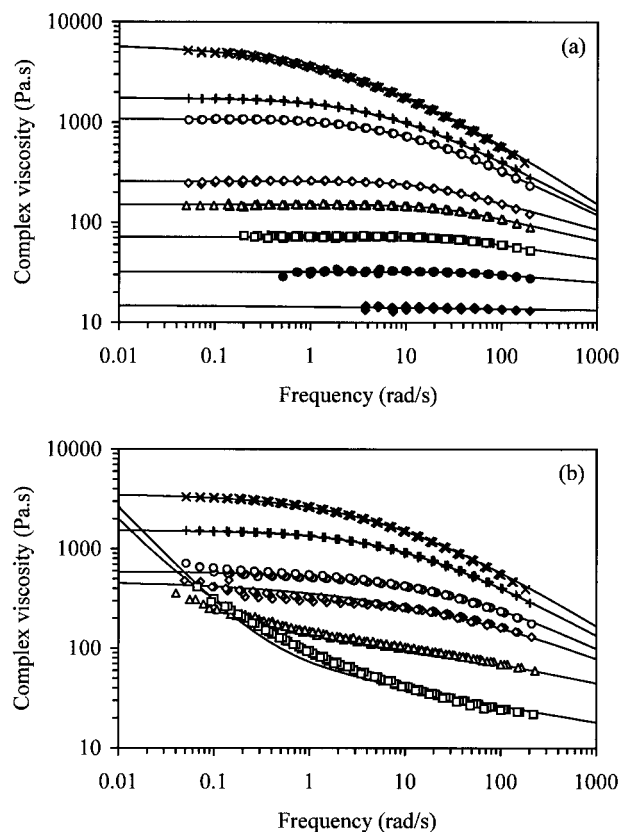
PP/PE blends by Yu et al.<sup>8</sup> (25% PE, 1% peroxide), Graebing et al.<sup>10</sup> (10% PE, 0.04% peroxide), and Dionisi et al.<sup>13</sup> on a PP/PE copolymer with 16% PE.

As explained in the Introduction, in a PE/PP mixture, there is competition between the PP chain degradation by  $\beta$ -scission and the creation of high molecular weight species with long branches in the PE. In the present work, the increase in the complex viscosity can be explained by the presence of the PE phase, which is highly viscous and which is dispersed in a less viscous PP matrix.<sup>13</sup> This PE phase can be constituted either by “solid” crosslinked particles or by high molecular weight highly branched species. In fact, we do not have a globally crosslinked material because, whatever the molecular weight and even for the most degraded product,  $G'$  is always lower than is  $G''$ . The results of SEC analyses show the presence of high residual masses, which indicates the presence of long chains (Fig. 2). To evaluate an eventual degree of crosslinking, the amount of

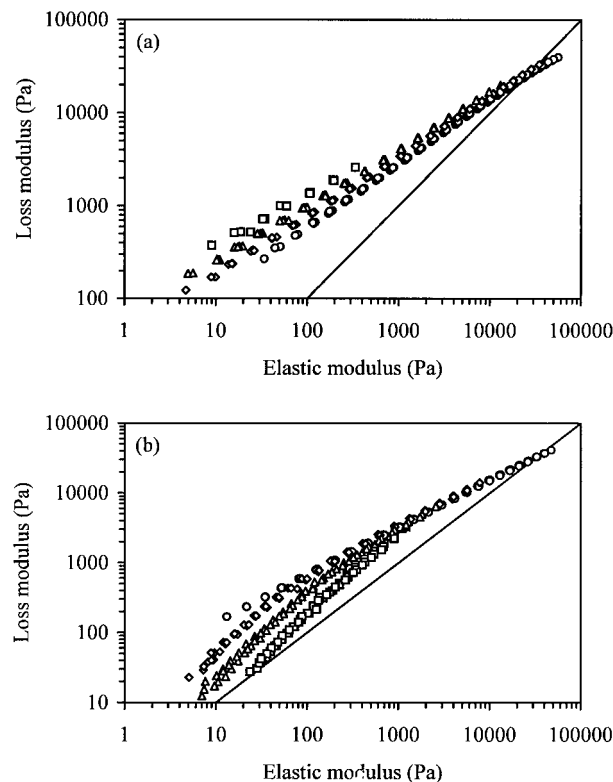
the gel content is determined in all PP/PE copolymer samples by Soxhlet extraction in xylene for a 24-h period. But, in all cases, the samples are gel-free, even for the most degraded products. So we can conclude that the formation of the high molecular weight species is not due to the crosslinking of the PE phase, but rather to the branching of PE chains.

### Cole–Cole Plots and Relaxation Times

Modified Cole–Cole plots ( $G''$  as a function of  $G'$ ) allow one to observe the general behavior of the samples when the peroxide amount is increased<sup>8</sup>: Values above (respectively, under) the equimoduli line ( $G' = G''$ ) indicate that the behavior is dominated by viscosity (respectively, elasticity). For



**Figure 5** Complex viscosity master curves at 215°C for different (a) PP homopolymers and (b) PP/PE copolymers. Symbols are experimental points corresponding to the different weight-average molecular weight values: (a) (×) 301,600; (+) 209,300; (○) 190,500; (◇) 135,600; (△) 114,800; (□) 104,800; (●) 78,760; (◆) 62,970. (b) (×) 256,100; (+) 210,400; (○) 168,900; (◇) 150,100; (△) 104,700; (□) 74,430. Full lines are the theoretical fits using Carreau-type models.

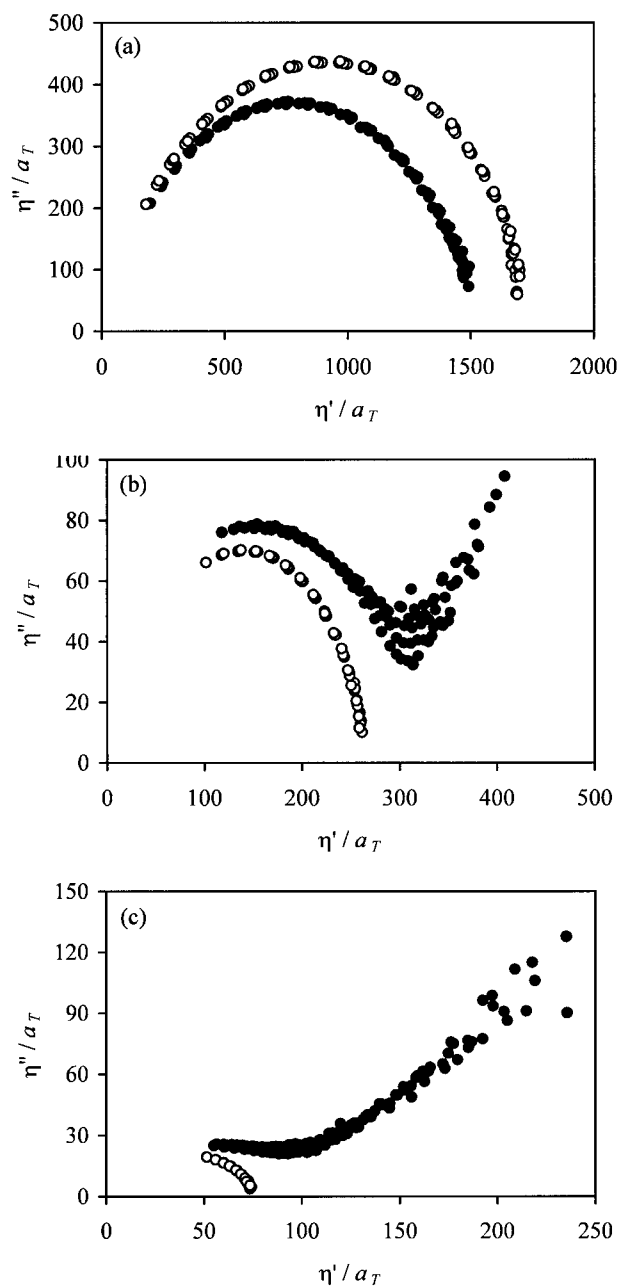


**Figure 6** Modified Cole–Cole plots (reference temperature of master curves: 215°C) for (a) the homopolymer and (b) the copolymer: (a) (○) 301,600; (◇) 209,300; (△) 135,600; (□) 62,970. (b) (○) 256,100; (◇) 150,100; (△) 104,700; (□) 74,430.

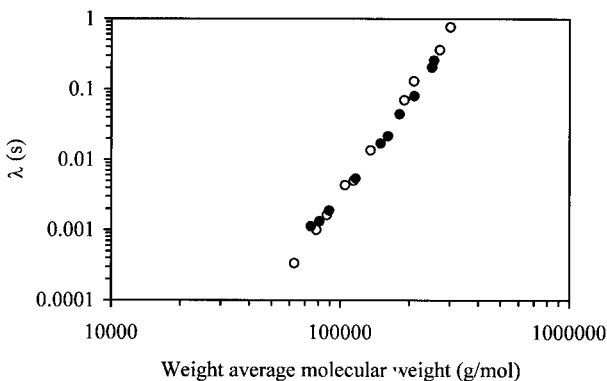
the homopolymer [Fig. 6(a)], the action of peroxide moves the curves in the viscous domain: Degraded samples are much less elastic. On the contrary, for the copolymer [Fig. 6(b)], the curves tend to be closer to the elastic domain and degraded samples are now much more elastic. Low-frequency regions are principally affected by these changes. Classical Cole–Cole plots ( $\eta'$  as a function of  $\eta''$ ) allow one to underline these differences (Fig. 7). For equivalent weight-average molecular weights, low-degraded samples of the homo- and copolymer have the same classical behavior, described by portions of circles. But when the peroxide content is increased, a second arc of a circle appears for the copolymer. It is characteristic of the presence of the PE phase and of the interactions between PP and PE. As the degradation of the PP progresses, the contribution of the PE becomes more and more important. For the most degraded sample, the behavior of the PE phase is totally predominant.

From these Cole–Cole plots, we can deduce the average relaxation time of the PP phase, which is

equal to the inverse of the maximal frequencies corresponding to the horizontal tangents at the top of circles (for the copolymer, we obviously consider only the first arc of a circle). It can be observed that decreasing the molecular weight decreases the relaxation time, whatever the homo- or copolymer (Fig. 8). Relaxation times of the PP phase are quite identical for the homo- and



**Figure 7** Cole–Cole plots (reference temperature of master curves: 215°C) for (○) the homopolymer and (●) the copolymer: (a)  $\bar{M}_w \approx 210,000$ ; (b)  $\bar{M}_w \approx 140,000$ ; (c)  $\bar{M}_w \approx 105,000$ .



**Figure 8** Evolution of the average relaxation time with the weight-average molecular weight: (○) homopolymer; (●) copolymer.

copolymer and vary with the molecular weight according to a power law:

$$\lambda_{PP} = \alpha \bar{M}_w^\beta \quad (1)$$

with  $\beta = 4.9$  for the homopolymer and  $\beta = 4.4$  for the copolymer. These values are higher than those given by Bernreitner et al.<sup>5</sup> ( $\beta = 2.75$ ). This is because the former were deduced from a fit of the viscosity data by a Carreau-type law. As we will see later on, these characteristic times are shorter than those deduced from Cole–Cole plots.

For the copolymer, the second part of the Cole–Cole plots shows the existence of a second relaxation mechanism, linked to the PE phase and characterized by much higher relaxation times. This is often observed for polydisperse polymers<sup>19</sup> and immiscible polymer blends.<sup>20</sup> Such a mechanism was also shown by Dionisi et al.<sup>13</sup> on a peroxide-degraded PE/PP copolymer.

From the Cole–Cole plot analysis, we can also deduce a parameter describing the width of the relaxation-time spectrum. The results show that the spectrum is narrower when the molecular weight decreases and is broader for the copolymer than for the homopolymer. These results are in agreement with the literature.<sup>6,10,13</sup>

It is interesting to correlate the width of the molecular weight distribution measured by SEC with the rheological parameters, which are usually easier to obtain. Zeichner and Patel<sup>21</sup> proposed to correlate the polydispersity index ( $\bar{M}_w/\bar{M}_n$ ) with the inverse of the crossover modulus, defined as the crossover point  $G_C$  between  $G'$  and  $G''$ . Figure 9 confirms the correlation of the rheological polydispersity index from dynamic exper-

iments ( $I_{RP} = 10^5/G_C$ ) with the polydispersity index determined from SEC measurements. We obtain the following linear relationships:

For the homopolymer:

$$I_{RP} = 0.536 + 0.874 \frac{\bar{M}_w}{\bar{M}_n} \quad (r^2 = 0.987) \quad (2)$$

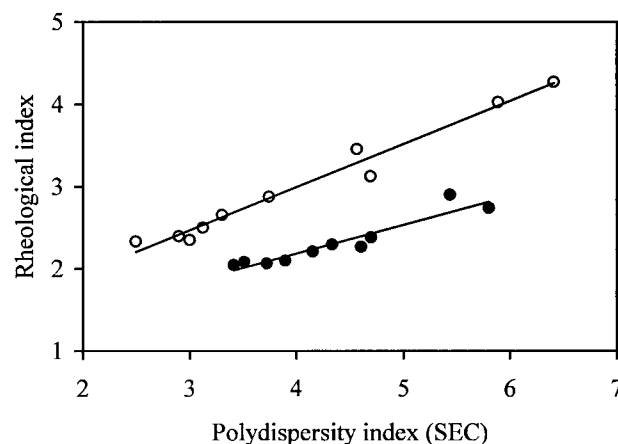
For the copolymer:

$$I_{RP} = 0.788 + 0.349 \frac{\bar{M}_w}{\bar{M}_n} \quad (r^2 = 0.894) \quad (3)$$

Increasing the peroxide amount leads to an increased crossover modulus and to a narrower molecular weight distribution for both materials. Similar relationships for peroxide-degraded PP were previously published by Bernreitner et al.,<sup>5</sup> Tzoganakis,<sup>6</sup> and Ryu.<sup>22</sup>

### Studies in Differential Scanning Calorimetry

The samples used for the crystallization and thermal analysis and the corresponding molecular weights are indicated in Table II. For both the homo- and copolymer, a very slight enhancement of the crystallization temperature is observed with decreasing molecular weight, but the form of the peaks remains unchanged. The melting endotherms of the reacted samples are separated into two peaks; this effect is more pronounced for the copolymer. This phenomenon depends on the



**Figure 9** Relationship between polydispersity indexes defined from the crossover points ( $I_{RP}$ ) and measured from SEC measurements (the solid lines are the linear regression fit of the data): (○) homopolymer; (●) copolymer.

**Table II** Sample Reference Used for Thermal and Crystallization Analysis

Reference	Homopolymer (PP 3050 BN 1)			Copolymer (PP 3060 MN 5)		
	% DHBP	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	% DHBP	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
1	0%	301,600	6.4	0%	256,100	5.4
2	0.01%	209,300	4.6	0.01%	210,400	4.7
3	0.06%	135,600	3.7	0.1%	150,100	4.2
4	0.35%	78,760	2.9	0.5%	74,430	3.4

sweep rate: At low heating rates, it is more pronounced than at high heating rates. The first peak is characteristic of the melting of crystals formed during the crystallization, and the second one, of crystals formed during the reorganization and recrystallization of metastable crystals.<sup>23,24</sup> When the molecular weight decreases, a double crystalline population is, hence, observed, characteristic of the  $\alpha$ -phase. This can be explained by the fact that the phenomena of the reorganization and recrystallization of crystals can occur easily and faster during the melting phase, due to the higher mobility of the molecules and of the lower relaxation time.

For the copolymer, the DSC thermograms show a shift of the crystallization peaks of PE to lower temperatures (from 100.2 to 98.1°C) with a decreasing molecular weight and a more pronounced shift of the melting temperatures (from 116.7 to 111.9°C). This decrease of temperature indicates that the size of the PE crystals decreases with the molecular mass. We also observe a very slight reducing of the area under the PE peaks when increasing the peroxide concentration: from  $-0.86$  to  $-0.71$  J/g for the crystallization peaks and from  $+1.25$  to  $+1.09$  J/g for the melting peaks. Similar observations were made by Braun et al.<sup>11</sup> on peroxide-degraded PP/PE blends.

During the cooling time in this range of rate, the PP phase first crystallizes, followed by the PE phase: Hence, it is the PP matrix which first stabilizes, and the PE chains, the next. If the PE phase was crosslinked, we would observe a modification followed by a disappearance of crystallization and melting peaks, but that is not the case here. So, the specific rheological behavior observed for the copolymer is due to the presence of noncrosslinked PE chains which have a very viscous behavior in relation to the PP matrix. These results confirm the negative results of the gel content.

## Rheological Models

One of the aims of this work was to characterize the influence of peroxide degradation on the rheological behavior of an homopolymer and a block copolymer, in order to use these results to obtain a predictive model of the degradation in a twin-screw extruder. By coupling a thermomechanical model of the twin-screw extrusion process, a kinetic model of the considered reactions and the rheological behavior, it is possible to calculate the changes in molecular weight along the extruder, during the peroxide-controlled degradation.<sup>2,25</sup> For that purpose, we assume the validity of the Cox–Merz rule and we use, as did Bernreitner et al.,<sup>5</sup> Carreau-type laws to describe the change in viscosity with the shear rate. In the literature, we also find polynomial expressions of the viscosity,<sup>4</sup> classical power laws,<sup>4</sup> or viscoelastic integral equations.<sup>7</sup>

For the homopolymer, we have

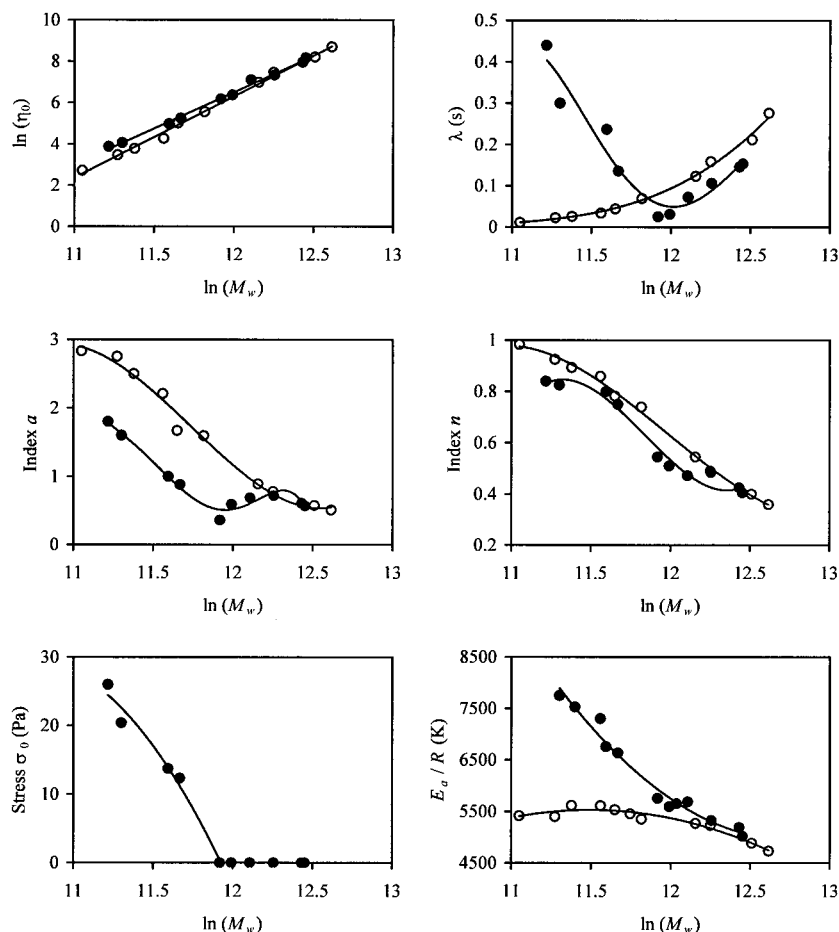
$$\eta = \eta_0 a_T [1 + (\lambda \dot{\gamma} a_T)^\alpha]^{(n-1)/\alpha} \quad (4)$$

$$a_T = e^{E_a/R[1/T-1/T_0]} \quad (5)$$

where  $a_T$  is the shift factor;  $E_a$ , the activation energy; and  $R$ , the gas constant.  $T_0$  is the reference temperature (215°C) at which are determined the plateau viscosity,  $\eta_0$ , the characteristic time,  $\lambda$ , and the indices,  $n$  and  $\alpha$ . All these parameters are assumed to be only functions of the weight-average molecular weight  $\bar{M}_w$ .

The determination of the parameters  $\eta_0$ ,  $\lambda$ ,  $n$ , and  $\alpha$  is done using a home-made identification software which minimizes the differences between the measured and calculated viscosities. For each molecular weight, the set of initial values is selected in function of the experimental values. If changing parameters of the initial set one at a time gives different solutions, the solution adopted is the set which gives the best min-





**Figure 10** Evolution of the  $\eta_0$ ,  $\lambda$ ,  $n$ ,  $\alpha$ ,  $\sigma_0$ , and  $E_a/R$  of the Carreau-type laws with the weight-average molecular weight: (○) homopolymer; (●) copolymer.

imization of the objective function. The result of the superposition of the experimental and calculated curves is shown in Figure 5.

For the copolymer, we selected a Carreau–Yasuda law with a yield stress ( $\sigma_0$ ), to account for the increase of viscosity at a low shear rate:

$$\eta = \frac{\sigma_0}{\dot{\gamma}} + \eta_0 a_T [1 + (\lambda \dot{\gamma} a_T)^a]^{(n-1)/a} \quad (6)$$

Figure 10 shows the evolution of each factor of the homo- and copolymer laws, in function of the weight-average molecular weight. The limit viscosity,  $\eta_0$ , which is characteristic of the Newtonian plateau, varies linearly with the logarithm of  $\bar{M}_w$  (with a slope of 3.9 for the homopolymer and of 3.5 for the copolymer when the plateau exists). For flexible polymer chains, at high molecular weights, the zero shear viscosity usually increases with a 3.4 power of the molecular

weight.<sup>26</sup> In fact, this value is a function of the polydispersity. Values of 3.7 were reported by Minoshima and White,<sup>18</sup> and of 3.3, by Bernreiter et al.<sup>5</sup>

For the homopolymer, the characteristic time  $\lambda$  increases when increasing the molecular weight, while  $n$  and  $\alpha$  decrease continuously. Indeed, we have a more and more Newtonian behavior,  $n$  being close to 1 for the lowest molecular mass. Tzoganakis et al.<sup>4</sup> reported also an increase in the power-law index when degradation increases.

For the copolymer, the tendencies are the same only for the power-law index  $n$ . The evolution of the indices  $\alpha$  and  $\lambda$  is less regular, as their identification is more difficult to realize when there is no more a Newtonian plateau, for low frequencies and low molecular weights. We note that the characteristic time  $\lambda$  (average relaxation time) increases for the more degraded products; this increase is linked to the second relaxation mech-

anism evidenced on the Cole–Cole plots. We observe also that the characteristic times deduced from the Carreau law are different from those defined using the Cole–Cole plots.

The values obtained for the apparent yield stress,  $\sigma_0$ , reach about 20–25 Pa for the lowest molecular weights. Finally, we observe that the activation energy, which is calculated by the shift of the viscosity curves, decreases when increasing the molecular weight. This phenomenon is more pronounced for the copolymer (64.4–41.7 kJ/mol) than for the homopolymer (44.9–39.3 kJ/mol). This result could be another indication of the presence of long branches in the copolymer.<sup>27</sup>

## CONCLUSIONS

In this study, we prepared a series of differently degraded samples of both a homopolymer and a block copolymer that were processed in the presence of peroxide. The rheological behavior of a degraded PP is highly dependent on its composition. The homopolymer exhibits a classical behavior, with a monotonic decrease in viscosity with decreasing molecular weight. Oppositely, the copolymer shows a more unexpected behavior, particularly at low frequencies. It can be explained by the presence of long residual chains of PE, probably branched, dispersed in an almost Newtonian PP matrix, highly degraded and with a very low viscosity.

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## REFERENCES

1. Tzoganakis, C.; Vlachopoulos, J.; Hamielec, A. E. *Polym Eng Sci* 1988, 28, 170.
2. Berzin, F.; Vergnes, B.; Delamare, L.; Dufossé, P. *Polym Eng Sci* 2000, 40, 344.
3. Fritz, H.-G.; Stöhrer, B. *Int Polym Proc* 1986, 1, 31.
4. Tzoganakis, C.; Tang, Y.; Vlachopoulos, J.; Hamielec, A. E. *Polym Plast Technol Eng* 1989, 28, 319.
5. Bernreitner, K.; Neissl, W.; Gahleitner, M. *Polym Test* 1992, 11, 89.
6. Tzoganakis, C. *Can J Chem Eng* 1994, 72, 749.
7. Barakos, G.; Mitsoulis, E.; Tzoganakis, C.; Kajiwara, T. *J Appl Polym Sci* 1996, 59, 543.
8. Yu, D. W.; Xanthos, M.; Gogos, C. G. *Adv Polym Tech* 1991, 10, 163.
9. Chodak, I.; Janigova, I.; Romanov, A. *Makromol Chem* 1991, 192, 2791.
10. Graebing, D.; Lambla, M.; Wautier, H. *J Appl Polym Sci* 1997, 66, 809.
11. Braun, D.; Richter, S.; Hellmann, G. P.; Rätzsch, M. *J Appl Polym Sci* 1998, 68, 2019.
12. Andreopoulos, A. G.; Tarantili, P. A.; Anastassakis, P. *JMS Pure Appl Chem A* 1998, 35, 751.
13. Dionisi, R. A.; Failla, M. D.; Villar, M. A.; Quinzani, L. M.; Valles, E. M. *Macromol Symp* 1998, 129, 127.
14. Berzin, F.; Vergnes, B.; Dufossé, P.; Delamare, L. In *Progress and Trends in Rheology V*; Emri, I.; Cvelbar, R., Eds.; Steinkopff: Darmstadt, 1998; p 377.
15. Suwanda, D.; Balke, S. T. *Polym Eng Sci* 1993, 33, 1585.
16. Ghosh, P.; Dev, D.; Chakrabarti, A. *Polymer* 1997, 38, 6175.
17. Tzoganakis, C.; Vlachopoulos, J.; Hamielec, A. E. *Polym Eng Sci* 1989, 29, 390.
18. Minoshima, W.; White, J. L.; Spruiell, J. *Polym Eng Sci* 1980, 20, 1166.
19. Belaribi, C.; Marin, G.; Monge, P. *Eur Polym J* 1986, 6, 487.
20. Cassagnau, P.; Montfort, J. P.; Marin, G.; Monge, P. *Rheol Acta* 1993, 32, 156.
21. Zeichner, G. R.; Patel, P. D. In *Proceedings of the 2<sup>nd</sup> World Congress of Chemical Engineering*, Montreal, 1981; Vol. 6, p 333.
22. Ryu, R. H. Ph.D. Thesis, Stevens Institute of Technology, 1991.
23. Guerra, G.; Petraccone, V.; Corradini, P.; De Rosa, C.; Napolitano, R.; Pirrozzini, B. *J Polym Sci* 1984, 22, 1039.
24. Yadav, Y. S.; Jain, P. C. *Polymer* 1986, 27, 721.
25. Berzin, F. Ph.D. Thesis, Ecole des Mines de Paris, 1998.
26. Ferry, J. D. *Viscoelastic Properties of Polymers*; Wiley: New York, 1969.
27. Dealy, J. M.; Wissbrun, K. F. *Melts Rheology and Its Role in Plastics Processing Theory and Applications*; Chapman & Hall: London, 1995.