

# Reactive Processing of LLDPEs with Peroxides in Counter-rotating Nonintermeshing Twin-Screw Extruder. IV. Effects of Molecular Structure of LLDPEs

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## SYNOPSIS

The effects of reactive extrusion with peroxide have been compared for two linear low-density polyethylenes (LLDPEs). Resin C is a butene copolymer, while Resin B is an octene-ethylene copolymer. Both have similar molecular weight distributions, but Resin B is significantly richer in terminal vinyl groups. Under the same reactive extrusion conditions, Resin B is much more reactive. Resin C is easier to process in this system, producing products clean of microgel. Concurrently, however, a given peroxide level produces less molecular weight enhancement and long-branch formation in Resin C. Reactive extrusion with peroxide is suitable to effect improvements in the processability of LLDPEs for film applications, provided that the choice of peroxide and the process details are tailored to the characteristics of the particular LLDPE. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

The scope of this research was to examine the effects of reactive peroxide treatment on the molecular structure and rheological properties of linear low-density polyethylenes (LLDPEs). The present article consists of the fourth study in this research.<sup>1-3</sup> This article examines the effects of the molecular characteristics of the virgin LLDPE on the action of peroxide in reactive processing. Peroxide levels were kept very low to minimize or eliminate crosslinking reactions.

The first study<sup>1</sup> showed that the molecular weight averages tend to increase with increasing peroxide concentration. Also, the reacted samples tend to have a broader molecular weight distribution, which seems to be related to a higher degree of long-chain branching. However, the sensitivities of the molecular characterization techniques like SEC and <sup>13</sup>C-NMR analyses were inadequate to distinguish dif-

ferences in the long-branch content of the virgin and peroxide-modified PEs in the peroxide concentration region of present interest. This was the case despite differences in thermal behavior and in the number of unsaturated groups. The second study<sup>2</sup> demonstrated that the rheological properties were a more sensitive indicator of chemical modification in LLDPEs. As showed by complex viscosity measurements, the low-frequency Newtonian behavior in virgin resin was replaced by a non-Newtonian power law behavior in peroxide-modified samples generated at all selected extrusion conditions. This result was correlated with lower power law index values for reactive extrusion products as compared to virgin resins. In addition, the use of a modified Cole-Cole plot<sup>4</sup> to assess variations in molecular structure suggested that long-chain branching was induced in LLDPE when treated with reactive extrusion peroxide. The changes in the molecular characteristics of LLDPEs upon peroxide treatment affected not only their shear flow properties but also their elongational flow behavior. However, at the highest peroxide concentration, the improvements in the elongational flow properties are at the expense of the drawdown ability. The second study<sup>2</sup> also showed that the effectiveness of this process was

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**Table I** Molecular Characteristics of Resins B and C

Resin	Molecular Weight Averages				Branch Concentration <sup>a</sup>		
	$M_z$ ( $10^{-3}$ )	$M_w$ ( $10^{-3}$ )	$M_n$ ( $10^{-3}$ )	$M_w/M_n$	Ethyl	Hexyl or Longer	Long Chain (>6 Carbons in Chain)
B	370	73	24	3.0	—	—	—
C	390	79	24	3.3	37	15	0.08

<sup>a</sup> Branch content is given per 1000 backbone carbons.

highly dependent on the extrusion conditions. The quality of mixing, the temperature, and the method of dispersing the peroxide were important variables in this process. The third study<sup>3</sup> demonstrated that the nature of peroxide feed and the extrusion system are important variables of the reactive process of selected LLDPEs. The peroxide solution in the third study was metered into the molten polymer, whereas it was fed into the polymer pellets in the earlier system. However, the extrusion process conditions used in the more reactive system were not successful in generating homogeneous products. The presence of microgel was observed and this is undesirable since this would interfere with the drawdown ability of these resins in film-blowing operations.

In this article, the behavior of an ethylene-butene copolymer upon reactive extrusion peroxide treatment is compared to that of the ethylene-octene copolymer described in the previous work,<sup>1-3</sup> under the same extrusion conditions.

## EXPERIMENTAL

### Extruder Reactor and Methodology

The counterrotating nonintermeshing twin-screw configuration (CRNI), labeled System 2, and the extrusion conditions are the same as detailed in the previous study.<sup>3</sup>

**Table II** Characteristics of Resins B and C

Resin	Terminal Unsaturations <sup>a</sup>	Trans Unsaturations	$\Delta H_{\text{melt}}$ <sup>b</sup> (J/g)
B	5.56	1.43	85
C	1.42	1.42	77

<sup>a</sup> Concentrations are given in unsaturations per 1000 carbons.<sup>5</sup>

<sup>b</sup> Enthalpy of melting from DSC measurements.

## Materials

Two commercial LLDPEs with an MFI of 1.0 were involved in this study. The material (supplied by the Exxon Co.) selected in the present study was an ethylene-butene copolymer in granular form and was designated as Resin C. The ethylene-octene copolymer, labeled Resin B, was used in the previous work.<sup>1-3</sup> The molecular weight averages and distributions were similar for the two PEs. The organic peroxide used for the chemical reactions of LLDPE resins under investigation was the same as before.<sup>1-3</sup>

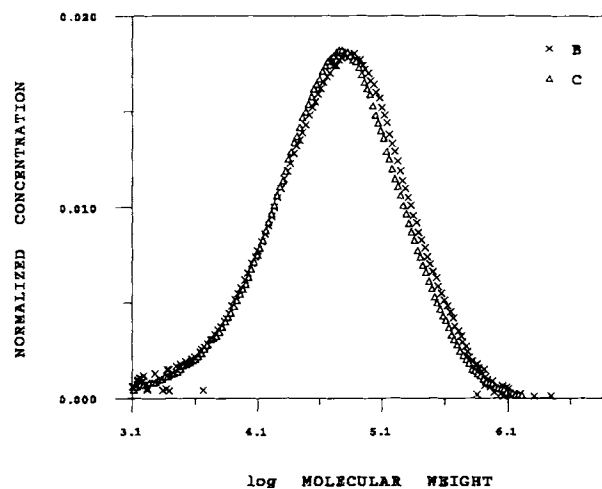
## Methodology

The methodology used in this investigation was the same as described in the previous studies.<sup>1-3</sup>

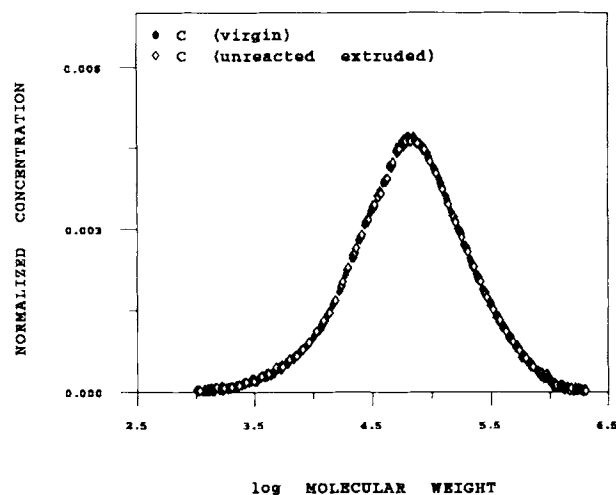
## RESULTS

### Molecular Characterization

Samples are assigned two code numbers: the first corresponding to the resin under investigation, and the



**Figure 1** Molecular weight distributions of Resins B and C from SEC using a continuous viscometer.



**Figure 2** Molecular weight distributions of Resin C virgin and unreacted extruded, from SEC using universal calibration.

second, in brackets, to the peroxide concentration. Tables I and II list some of the molecular characteristics and rheological properties pertaining to Resins B and C. The molecular weight distributions of these two resins are illustrated in Figure 1. The molecular weight averages and distributions are similar for these two resins. Branching data quoted in Table I indicates that while ethyl branches are the type of short-chain branching (SCB) present in Resin C hexyl branches are found in Resin B. Resin C has a higher amount of SCB of approximately 37 SCB/1000 backbone carbons compared to 14–15 SCB/1000 backbone carbons for B. Resin C has approximately 0.08 long-chain branches (LCB)/1000 C's, which is within the range of the LCB content in commercial LLDPE (less than 0.1 LCB/1000 C's).

Table II shows the terminal vinyl and *trans* unsaturation of the selected resins. The concentration of pendant vinyl unsaturations was not evaluated, because the band at  $888\text{ cm}^{-1}$  assigned to this type of unsaturation is obscured by the peak at  $850\text{ cm}^{-1}$  assigned to the terminal methyl of a branch of  $C_4$  or longer. Resin C has significantly lower terminal unsaturation compared to Resin B. However, these two resins have a similar number of *trans* vinyls. In addition, Resin C has a lower enthalpy of melting  $\Delta H_{\text{melt}}$  measured by the DSC endotherms (Table II). This is consistent with the higher branch content in Resin C.

Infrared bands are assigned to terminal vinyl ( $909\text{ cm}^{-1}$ ), pendant vinyl ( $888\text{ cm}^{-1}$ ), and *trans* unsaturation ( $964\text{ cm}^{-1}$ ).<sup>6</sup> The formation of unsaturated groups in PE depends primarily on the termination step in the polymerization reaction.<sup>7</sup>

**Table III** Molecular Weight Averages of Sample Set C[n]

Resin	$M_z$ ( $10^{-3}$ )	$M_w$ ( $10^{-3}$ )	$M_n$ ( $10^{-3}$ )	$M_w/M_n$
C	390	79	24	3.3
C[0.01]	441	116	32	3.6
C[0.03]	490	126	33	3.8

Figure 2 shows the molecular weight distribution overlays of virgin and unreacted extruded Resin C measured from SEC. These distribution curves show no appreciable differences between the two samples. Therefore, the extrusion process itself can be eliminated as a variable in the rationalization of observed molecular structure differences of Resins B and C after peroxide reaction in the CRNI extruder.

Table III lists the molecular weight data for Resin C before and after the peroxide reaction.  $M_n$  and  $M_w$  were determined from SEC with a continuous viscometer detector, and  $M_z$ , from LALLS data. As shown in the previous studies,<sup>1–3</sup> the  $M_w$  of peroxide-modified Resin C increases as the peroxide concentration is increased. A more significant effect is revealed by the  $M_z$  values. These results are expected, since the  $M_z$  average is more suitable to estimate the high molecular weight material in a polymer sample. In addition, the reactive extrusion products C have a broader molecular weight distribution as compared to that of unreacted resins.

Similarly to Resin B,<sup>1</sup> the molecular weight distribution of Resin C is shifted toward the high molecular weight end with increasing peroxide concentration. The effect of the peroxide concentration on the molecular weight averages of peroxide-modified samples C (Table IV) generated in the CRNI extruder is demonstrated by comparing the area of the normalized distribution curve at the highest molecular weight (above  $10^5$ ) fraction of Resin C to that

**Table IV** Higher Molecular Weight Fractions of Resins C[n] and B[n]

Sample	Molecular Weight Above $10^5$ (Weight Fraction) (Continuous Viscometer)
C	22
C[0.03]	23
C[0.07]	25
B	22
B[0.03]	29
B[0.07]	33

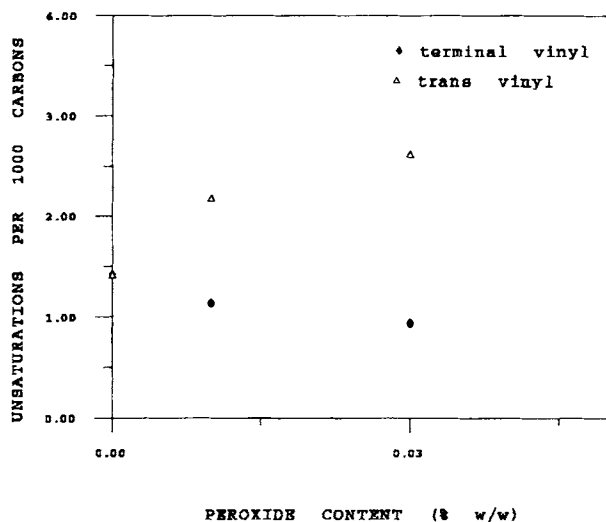


Figure 3 Vinyl unsaturation contents of Samples Set C[n] generated in System 2.

of reactive extrusion products. As expected, the weight fraction of the highest molecular weight end ( $> 10^5$ ) increases as the peroxide concentration is increased. A similar trend was shown for Resins B<sup>1</sup>;

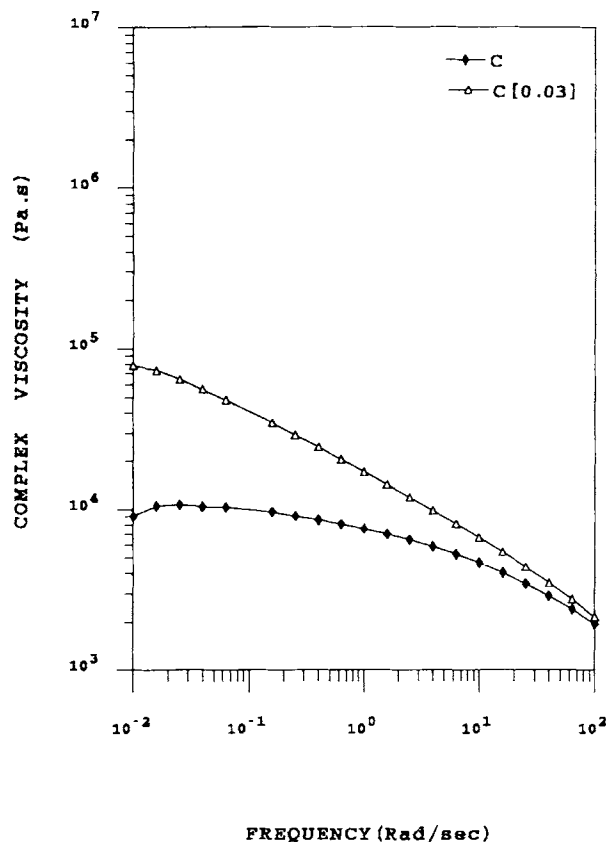


Figure 4 Complex viscosity as a function of frequency for Sample Set C[n] generated in System 2 at 190°C.

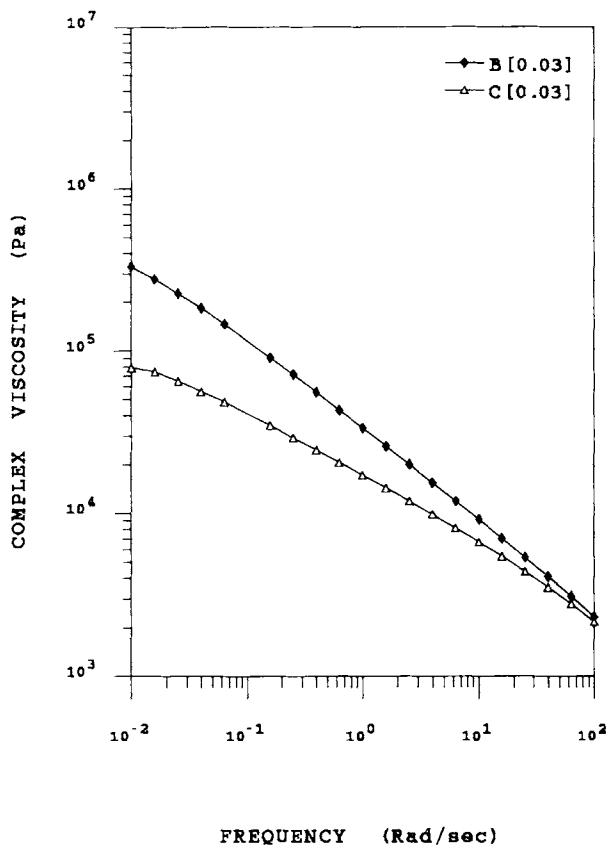


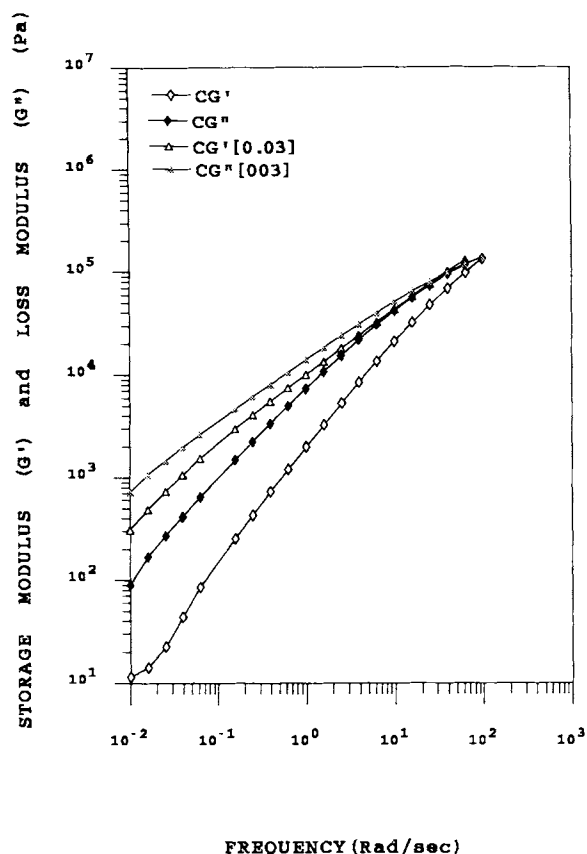
Figure 5 Complex viscosity as a function of frequency for Resins C[0.03] and B[0.03] generated in System 2 at 190°C.

however, the action of peroxide was more drastic for Resin B than for Resin C. These results show that polymer chain extension takes place in the presence of peroxide free radicals during reactive processing.

As well as for Resin B,<sup>1</sup> the amount of terminal unsaturations in peroxide-modified resins C decreases as the peroxide concentration is increased (Fig. 3). Simultaneously, the number of *trans* unsaturations tends to increase slightly with the peroxide concentration. Again, these results demonstrate that the coupling reaction involving terminal unsaturation is a major contributor to chain extension in the reactive process of LLDPE.<sup>8</sup>

The DSC traces of Resin B were strongly affected by peroxide treatment in the present system.<sup>3</sup> Resin C, on the other hand, exhibited no changes in DSC behavior after reactive extrusion.

It is interesting that, contrary to all reaction products of Resin B generated in the CRNI extruder,<sup>3</sup> the qualitative inspection of peroxide-modified samples C tapes generated on a single-screw extruder indicated the absence of microgel in all selected Resin C samples after peroxide treatment. In ad-



**Figure 6** Storage modulus ( $G'$ ) and loss modulus ( $G''$ ) of Sample Set C[n] as a function of frequency at 190°C.

dition, the analysis of gel content indicates that the amount of insoluble material is negligible in all selected samples of Resin C.

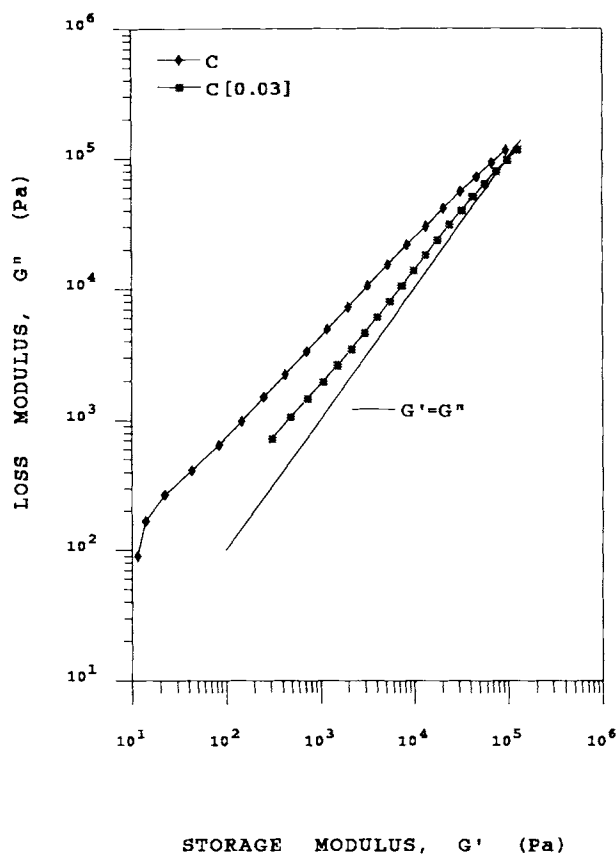
The examination of branches of six carbon atoms or longer and ethyl branches by the NMR technique did not reveal significant changes in branch content of Resin C upon peroxide treatment.

### Rheological Properties

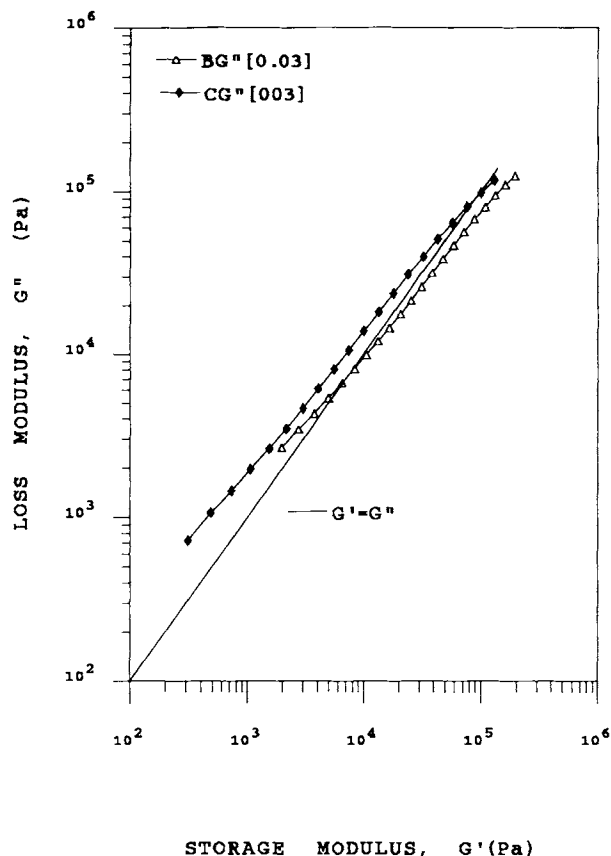
Rheological analyses were performed to determine the differences in flow behavior of reactive extrusion products as compared to unreacted extruded ones. Figure 4 illustrates the plot of complex viscosity as a function of frequency for Resin C before and after peroxide treatment in the CRNI extruder. As with peroxide-modified samples B,<sup>2</sup> the low-frequency complex viscosity of reactive extrusion products C increases as the peroxide concentration is increased. Again, Resin C[0.03] exhibits a more pronounced shear-thinning nature as compared to the unreacted Resin C. A comparison of the low-frequency viscosity of Resin B[0.03] and Resin C[0.03] (Fig. 5)

shows that the changes in the rheological properties of the unreacted Resin B upon peroxide treatment are more significant than those of unreacted Resin C. These results can be explained by the lower amount of terminal unsaturation in Resin C than in Resin B. Bremner and Rudin<sup>8</sup> suggested that the terminal unsaturation has a major contribution as a highly reactive site in the chemical modification of PEs. Suwanda<sup>9</sup> reported that the presence of terminal unsaturation in the virgin material enhances the molecular weight increase in peroxide-modified PEs, whereas the presence of branches in the virgin material favors degradation.

Figure 6 illustrates the contribution of the elastic component and the viscous component in the viscoelasticity of Resin C[0.03] as compared to Resin C. The sample codes are assigned to the resin under investigation, and  $G'$  and  $G''$  identify the storage component and loss component, respectively. The peroxide concentration follows in brackets. The viscous component  $G''$  in Resin C dominates over the entire frequency range, while the elastic component



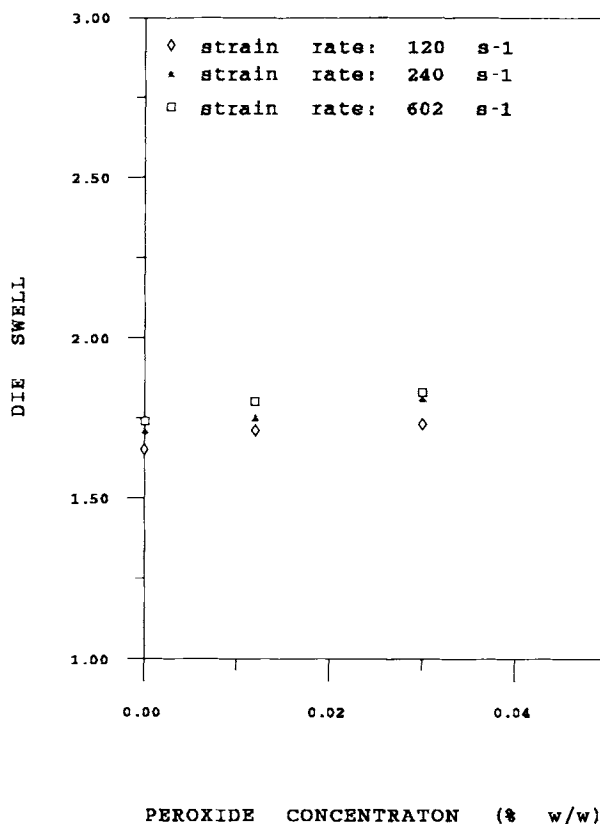
**Figure 7** Loss modulus ( $G''$ ) as a function of storage modulus ( $G'$ ) of Sample Set C[n] generated in System 2 at 190°C.



**Figure 8** Loss modulus ( $G''$ ) as a function of storage modulus ( $G'$ ) of Resins C[0.03] and B[0.03] generated in System 2 at 190°C.

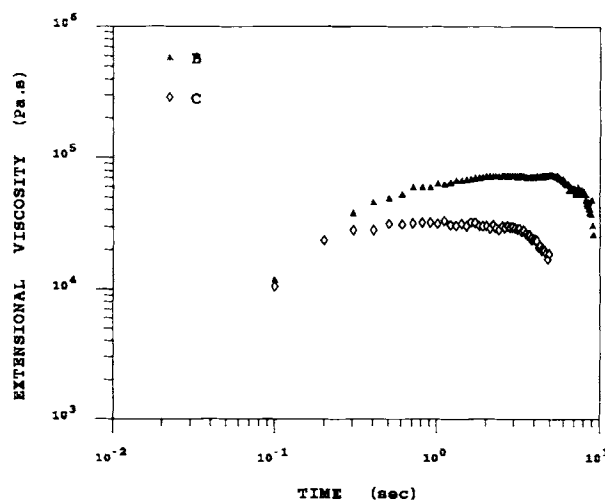
$G'$  in Resin C[0.03] becomes more predominant than the viscous response  $G''$  at lower frequencies, above approximately 40 rad/s. The action of peroxide in increasing the relative contribution of the elastic response is more significant for Resin B (Ref. 2) as compared to Resin C. Therefore, the  $G'-G''$  crossover for Resin B[0.03] is seen at a lower frequency of approximately 0.06 rad/s,<sup>2</sup> while the elastic response  $G'$  is dominant above approximately 40 rad/s for Resin C[0.03] (Fig. 6).

A modified Cole-Cole plot,<sup>10</sup> generated by plotting the loss modulus  $G''$  as a function of storage modulus  $G'$  in a log-log scale, for reactive extrusion products C generated in the present system is illustrated in Figure 7. A shift of the plot toward lower  $G''$  values indicates that the contribution of the elastic component to the viscoelasticity of Resin C[0.03] is more significant than that of Resin C. However, a comparison of the viscoelastic behavior of Resins B[0.03] and Resin C[0.03] demonstrates that the peroxide action is more drastic for Resin B than that for Resin C (Fig. 8). These results agree with

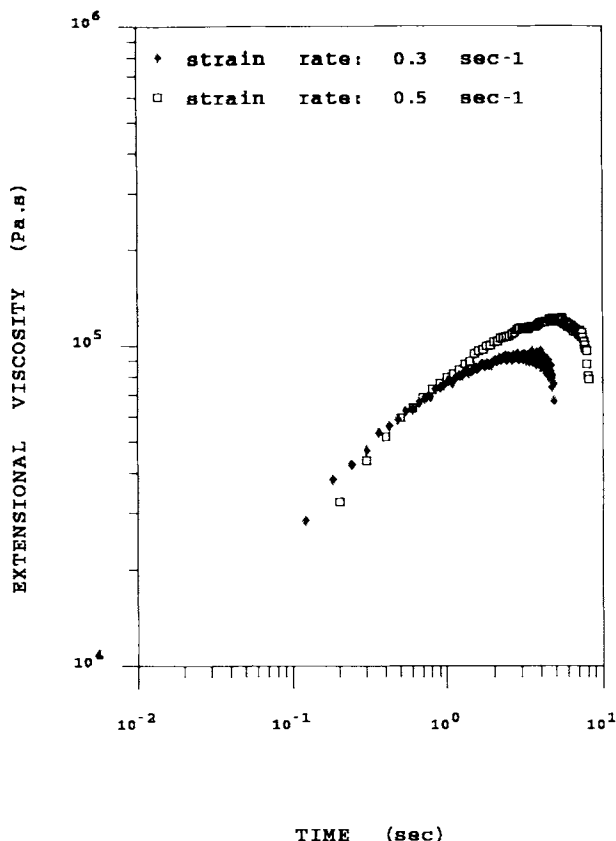


**Figure 9** Die swell as a function of peroxide concentration of Sample Set C[n] generated in System 2; cylindrical die,  $L/D$  of 7.

previously mentioned rheological measurements. Again, these findings can be explained by the differences in the amount of terminal unsaturations between these two virgin resins.



**Figure 10** Extensional viscosity as a function of time of Resins B and C; strain rate of 0.3 s<sup>-1</sup> at 170°C.



**Figure 11** Elongational flow behavior of Resin C[0.03] at 190°C.

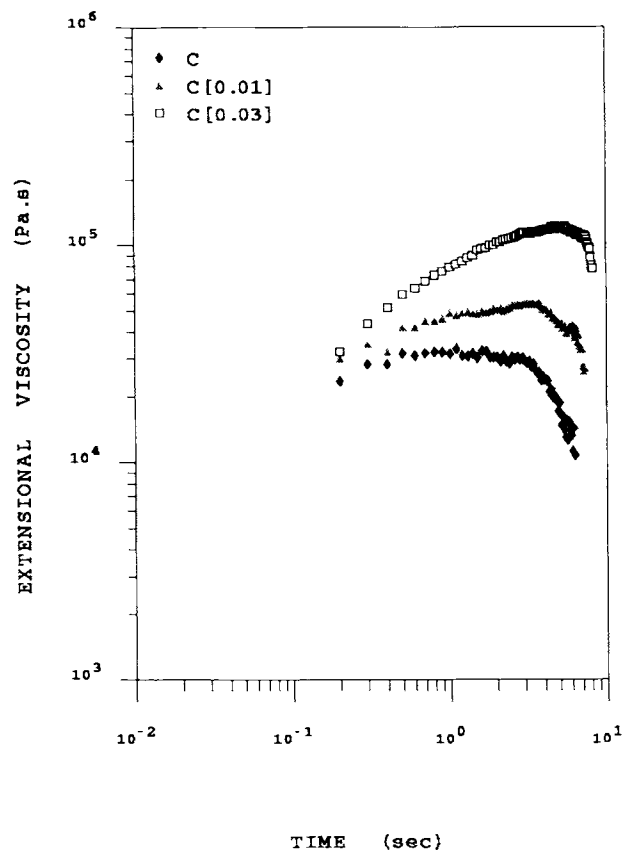
The response of the polymer melts at high shear rates were determined by capillary flow measurements. These results (not shown) are in agreement with the complex viscosity measurements.

The extrudate swell behavior of reactive extrusion products C is shown in Figure 9. Contrary to peroxide-modified samples B,<sup>2</sup> the extrudate swell of reactive extrusion products of Resin C tends to increase slightly with increasing peroxide concentration. This is probably because the presence of microgel in peroxide-treated B materials in the same system<sup>2</sup> reduces melt elasticity, by analogy with the behavior of filled thermoplastic systems.<sup>11,12</sup>

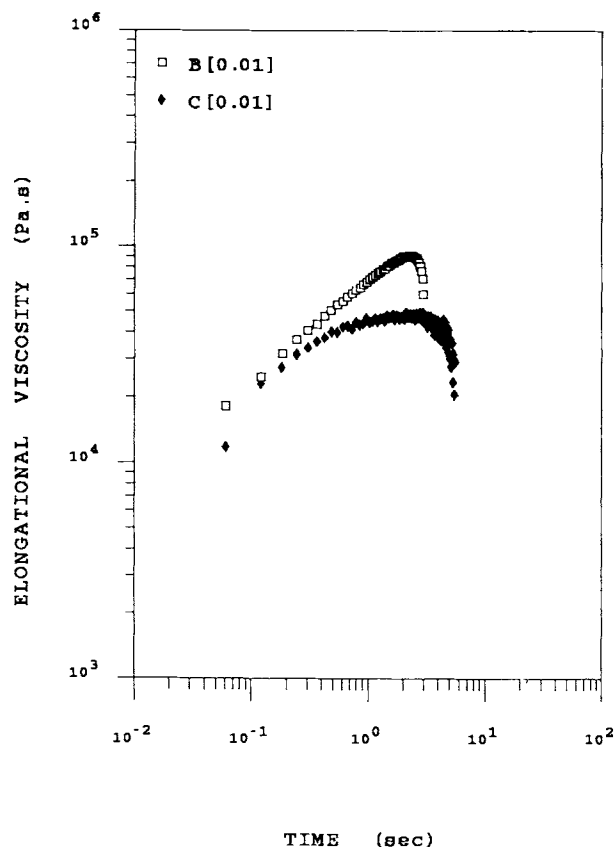
In addition to the shear viscosity measurements, the extensional viscosity of peroxide-modified LLDPE samples generated by reactive extrusion were investigated, since the elongational flow properties play an important role in applications, such as in tubular film operation. As the presence of microgel in all Resin B reactive extrusion products generated in the CRNI extruder limits their drawdown ability, the nonisothermal spinning technique described in the previous work<sup>2</sup> could not be employed in the present investigation. To

compare the elongational flow behavior of peroxide-modified LLDPE samples of Resin C to that of reactive extrusion products of Resin B generated in the same system, the extensional viscosity of all the resins were measured on an isothermal uniaxial extensional rheometer (Rheometrics, RER 900).

The extensional viscosities of Resins B and C are displayed in a double logarithmic scale as a function of time at 170°C at a strain rate of 0.5 s<sup>-1</sup> (Figs. 10 and 11). The elongational flow analyses of these two resins are generated at the same Hencky strain of 3.1, and strain rates  $\dot{\epsilon}_0$ . For all selected strain rates, the extensional viscosity first rises and then falls after passing through a broad maximum. Resins B and C do not exhibit the strain-hardening behavior. Strain hardening is shown by a rapid increase in the extensional viscosity over a small increase in strain rate. The sharp drop of the extensional viscosity at a longer time, i.e., at a higher strain, indicates that the polymer melt is unable to be stretched any further and it breaks. Figure 11 shows the elongational



**Figure 12** Extensional viscosity as a function of time of Sample Set C[n]; strain rate of 0.3 s<sup>-1</sup> at 190°C.



**Figure 13** Extensional viscosity as a function of time of Resins C[0.01] and B[0.01]; strain rate of  $0.5 \text{ s}^{-1}$  at  $190^\circ\text{C}$ .

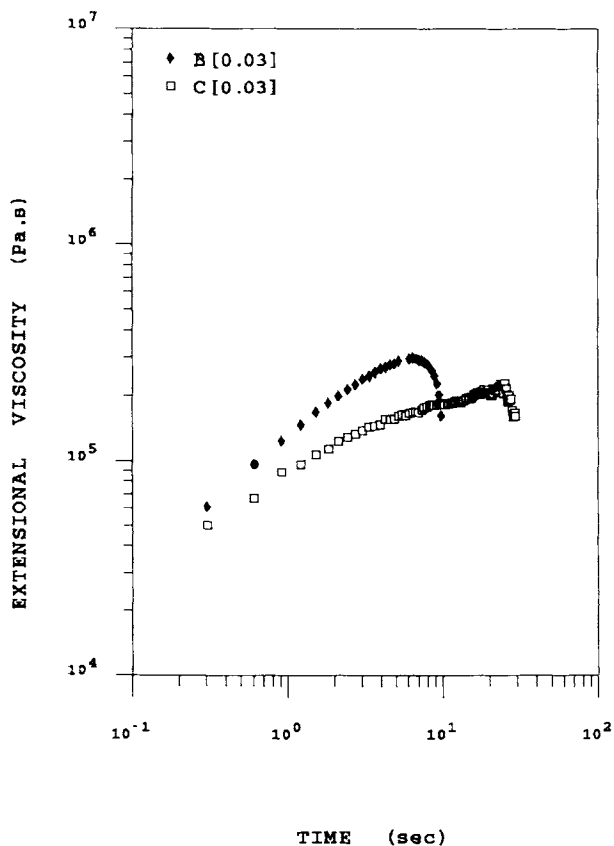
flow properties of Resin C[0.03] measured at two different strain rates. Figure 12 demonstrates that the extensional viscosity of Resin C increases with increasing peroxide concentration in the reactive extrusion process. In addition, a steeper increase of the extensional viscosity of Resin C[0.03], as compared to Resin C, indicates a higher tendency of peroxide-modified resin for strain hardening. A comparison of the elongational flow properties of Resin B[0.01] to that of Resin C[0.01] at strain rate of  $0.5 \text{ s}^{-1}$  (Fig. 13) shows that the changes in the elongational flow behavior are more significant for the former resin. This result is in agreement with the previous shear viscosity measurements. In addition, Resin B[0.01] breaks at approximately a strain of 1.0, while the Resin C[0.01] breaks at a strain of approximately 2.0. This result could be a manifestation of the presence of microgel in peroxide-modified samples of Resin B generated in System 2. A similar trend is shown for Resin B[0.03] and Resin C[0.03] at a higher strain rate of  $0.1 \text{ s}^{-1}$  (Fig. 14). The former resin breaks at a

strain of approximately 0.6, while the latter sample breaks at a strain of approximately 2.5.

## CONCLUSIONS

The results obtained in this study indicate that Resins B and C exhibit similar rheological behavior upon peroxide treatment. However, the amount of changes in selected samples, as well as the molecular characteristics of reacted products, are significantly affected by the molecular structure of the virgin material. This implies that the peroxide concentration needed during reactive processing is very dependent on the molecular characteristics of the virgin material.

While the presence of microgel was found in Resin B after peroxide reaction in the same system,<sup>3</sup> homogeneous products of Resin C were generated at the same peroxide level. These results are in agreement with previous studies,<sup>3,13</sup> suggesting that the terminal vinyls are a major contributor as reactive sites in a free-radical mechanism.



**Figure 14** Extensional viscosity as a function of time of resins C[0.03] and B[0.03]; strain rate of  $0.1 \text{ s}^{-1}$  at  $190^\circ\text{C}$ .



Also, the lower number of terminal vinyls in Resin C accounts for the less drastic peroxide action. For example, Resin C[0.03] has a higher elongational viscosity and a higher tendency to exhibit strain hardening than does unreacted Resin C. However, these changes are smaller than in Resin B[0.03] generated in the same system. Therefore, for Resin C, a higher peroxide concentration is necessary to be used for achieving desired processability improvements in film extrusion.

Another approach to provide a better control of the changes in LLDPE upon peroxide treatment through reactive processing could be the use of organic peroxides that exhibit a lower hydrogen abstraction ability. This may be particularly advantageous with resins with high concentrations of terminal unsaturations. Since precise metering of the system components are necessary for controlling the reaction during reactive process, this alternative would provide an easier control of the polymer modification with change in peroxide level.

All differences between the behaviors of Resins B and C have been assigned here to variations in molecular structure and particularly to differences in terminal vinyl content. This is in accord with similar differences that have been noted in the same and other contexts.<sup>5,13</sup> A note of caution is in order, however, since the stabilizer packages used in Resins B and C are both proprietary and could conceivably also affect the course of reactive extrusion with peroxides.

The results gathered from this investigation suggest that improvements in the processability of LLDPEs can be achieved by peroxide treatment in reactive extrusion processes. It is expected that these modifications will result in a better performance in film-blowing applications, if the reactive extrusion process is tailored to the characteristics of the particular LLDPE.

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## REFERENCES

1. M. G. Lachtermacher and A. Rudin, *J. Appl. Polym. Sci.*, to appear.
2. M. G. Lachtermacher and A. Rudin, *J. Appl. Polym. Sci.*, to appear.
3. M. G. Lachtermacher and A. Rudin, *J. Appl. Polym. Sci.*, to appear.
4. N. Nakajima and E. R. Harrell, in *Current Topics in Polymer Science*, R. M. Ottenbrite, L. A. Utracki, and S. Inoue, Eds., Hanser, Munich, 1987, Vol. 2, p. 149.
5. T. Bremner, S. Haridoss, and A. Rudin, *J. Appl. Polym. Sci.*, **32**, 939 (1992).
6. J. Haslam, H. A. Willis, and D. C. M. Squirrel, Butterworth, London, 1972, pp. 369-370.
7. U. Zucchini and G. Cecchin, *Adv. Polym. Sci.*, **51**, 101 (1983).
7. S. Pang and A. Rudin, *J. Appl. Polym. Sci.*, **46**, 763 (1992).
8. T. Bremner and A. Rudin, *Plast. Rubb. Process. Appl.*, **13**, 61 (1990).
9. D. Suwanda, PhD Thesis, Department of Chemical Engineering, University of Toronto, 1992.
10. E. R. Harrell and N. Nakajima, *J. Appl. Polym. Sci.*, **29**, 995 (1984).
11. M. Minwaga and J. L. White, *J. Appl. Polym. Sci.*, **20**, 501 (1976).
12. T. Nishimura and T. Katooka, *Rheol. Acta*, **23**, 401 (1984).
13. R. T. Johnston and E. J. Slone, *Polyolefins*, Society of Plastics Engineers, Houston, TX. 1991, Vol. 7, p. 207.

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