

Reactive Processing of LLDPEs in Counterrotating Nonintermeshing Twin-Screw Extruder. III. Methods of Peroxide Addition

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SYNOPSIS

An ethylene-octene linear low-density polyethylene (LLDPE) was treated with peroxide in a reactive extrusion system. A counterrotating nonintermeshing twin-screw extruder (System 2) was contrasted with a corotating intermeshing twin-screw machine (System 1). In System 2, the peroxide solution was pumped into the melted polymer, while it entered with the polymer pellets in the feed section of System 1. Molecular structure changes and the rheological behavior of peroxide-modified resins are similar in both operations but System 2 is much more effective. Much lower peroxide levels were needed in System 2. However, reactions in this setup were also more difficult to control. The presence of microgel was clearly evident in System 2 products but not in those made in System 1. The results of such reactive extrusion processes depend critically on the method of the peroxide feed and mixing conditions. Reaction conditions that favor optimum economy and peroxide efficiency are those which may compromise product homogeneity. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The quality of mixing in reactive extrusion processes affects the product properties, processability, and cost. Several studies on the simulation of mixing in corotating intermeshing twin-screw configurations¹⁻³ and in counterrotating nonintermeshing twin-screw configurations⁴⁻⁷ have been reported. However, the advantage of one over the other continues to be debated.^{8,9} Also, the formulations of the mixtures studied have often not been reported and there is no evidence on the effect of mixing on the reaction kinetics. Recently, Rauwendaal¹⁰ described some important aspects of the mechanism of mixing and the characteristics of the most commonly used devices in polymer mixing operations.

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 (LLDPE). The present article consists of the third study in our laboratory into the reactive processing of LLDPE with very low levels of peroxides. The first study¹¹ showed that the molecular weight averages tend to increase with increasing peroxide concentration. Also, the reacted samples tended to have broader molecular weight distributions, which are related to a higher degree of long-chain branching. However, the sensitivities of the molecular characterization techniques like SEC and ¹³C-NMR analyses were inadequate to distinguish fine differences in long-branch contents of the virgin and peroxide-modified PEs in the peroxide concentration region of particular interest.

The second study in this series¹² demonstrated that rheological properties were a more sensitive indicator of chemical modification in LLDPEs. As showed by complex viscosity measurements, low-frequency Newtonian behavior in virgin resins was replaced by 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

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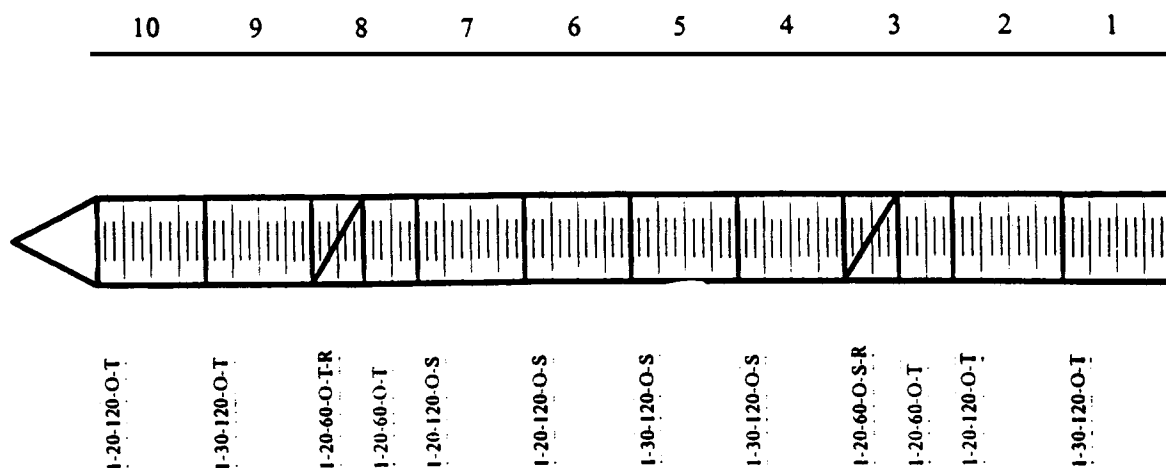


Figure 1 Screw configuration used in System 2.

products as compared to virgin resins. In addition, the use of a modified Cole-Cole plot¹³ to assess variations in molecular structure indicated that long-chain branching was induced in LLDPE when treated with peroxide in a reactive extrusion process. 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 used, the improvements in the elongational flow properties of the products were at the expense of their drawdown ability. The second study¹² also showed that the effectiveness of this process was highly dependent on the extrusion conditions. The quality of mixing, the temperature, and the method of dispersing the peroxide are important variables in this process.

This article describes the behavior of a selected LLDPE upon peroxide treatment when the reactant is metered directly into the polymer melt. Since mixing

affects the material properties, processability, and cost, it is expected that the nature of the peroxide feed and the extrusion system would affect these results. The earlier research employed a corotating intermeshing twin-screw extruder for reactive processing. In the present work, we report results with a counterrotating, nonintermeshing twin-screw machine.

EXPERIMENTAL

Materials

The same LLDPE described in the previous study¹¹ and designated as Resin B was used in this investigation. Therefore, the molecular characteristics of the virgin resin can be eliminated as the variable in the comparison of the observed molecular structure and processability differences of peroxide-modified samples generated in the present system to those of

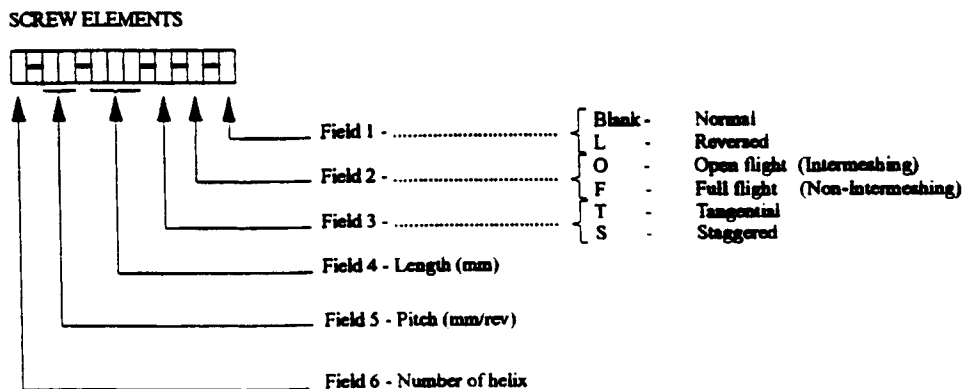


Figure 2 Screw elements used in counterrotating nonintermeshing configuration. Screw elements are coded according to the system of the manufacturer (Leistritz).

products produced in the previous process.^{11,12} The organic peroxide, 2,5-dimethyl-2,5-di(*t*-butylperoxy)hexane (Lupersol™ 101) used for the chemical reactions of LLDPE resins under investigation was also the same as before.

Extruder Reactor

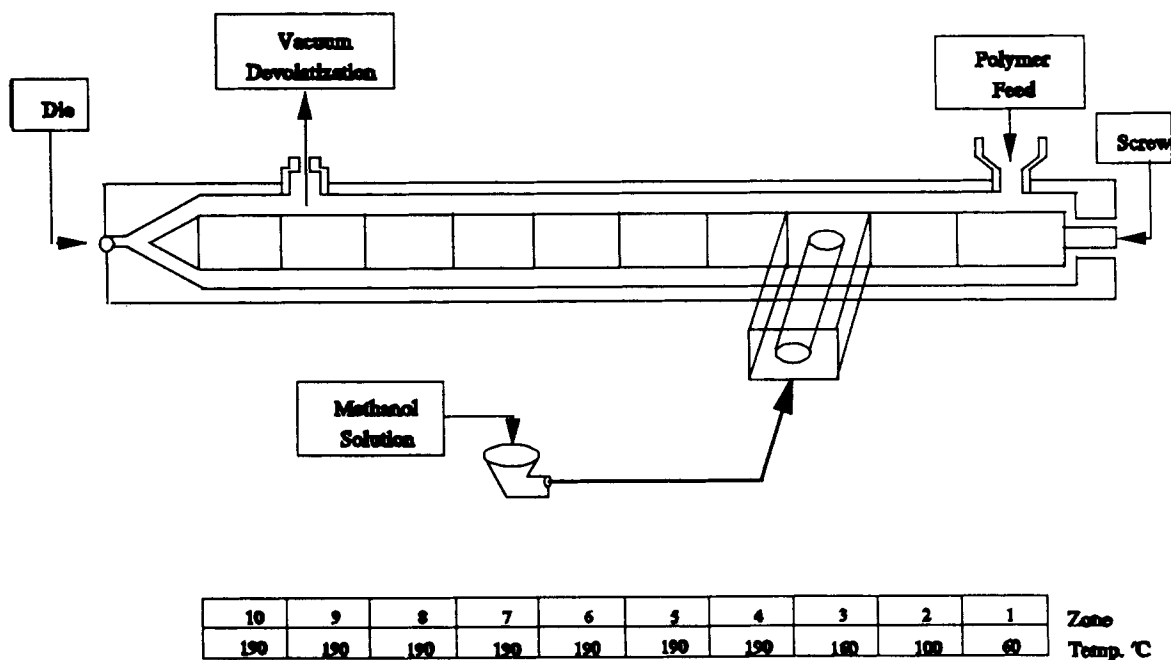
The reactive modification of selected resins was carried out on a modular Leistritz twin-screw extruder. In this particular study, the twin-screw extruder was used as a counterrotating nonintermeshing extruder (CRNI) labeled System 2. Figures 1 and 2 show the screw configuration and the screw elements used in this system. The feeding (1–2) and the pumping (9) zones used matched screw flight configurations, but the melting and mixing zones (3–8) used staggered screw flight configurations. The zone 3 to zone 8 section was melt-sealed at both ends, each by a reverse flight element. In the previous study,¹¹ the Leistritz twin-screw extruder was used as a corotating intermeshing extruder (CRI) labeled System 1–Set 2.

Table I Molecular Weight Averages of Sample Set B[n] Generated in System 2

Resin	M_z (10^{-3})	M_w (10^{-3})	M_n (10^{-3})	M_w/M_u
B	370	73	24	3.0
B[0.03]	412	93	28	3.3
B[0.07]	600	142	27	5.2

Methodology

For the sake of comparison, the selected virgin resin was extruded at the same reaction conditions, but no peroxide was added to the extruder. Figure 3 illustrates the experimental setup used in this system. The screw speed remained constant at 90 rpm, and output was controlled at a throughput of 30 g/min with a calibrated feeder. While the methanol solution of peroxide was introduced into a feed port in the same zone as the polymer feed in the corotating intermeshing extruder (CRI),¹¹ in the present system, the solution was metered downstream into the



Zone 1-2: Plastification of the LLDPE Raw Material.

Zone 3: Liquid Feed, Melting and Intensive Mixing.

Zone 4-7: Reaction of LLDPE with Peroxide and Continuous Mixing.

Zone 8-10: Pressure Build-Up (Reverse Flight Elements) and Devolatilization.

Figure 3 Experimental setup used in System 2.

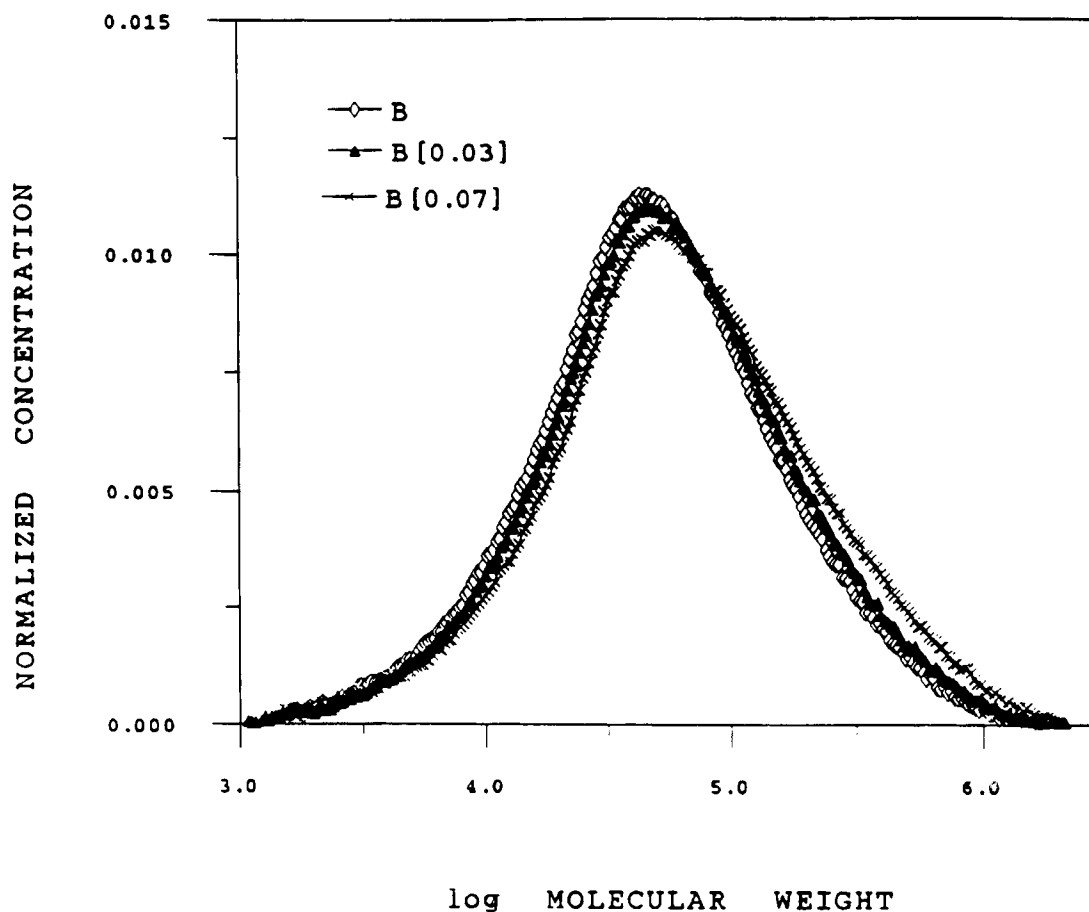


Figure 4 Molecular weight distributions of Samples Set $B[n]$ generated in System 2 from SEC using a continuous viscometer detector.

polymer melt. As in the CRI extruder work,¹¹ a low temperature, ranging from 60 to 100°C, was employed in the first two zones of the extrusion barrel to ensure proper mixing of the reactants before the reaction took place. The barrel temperature in zones 4–10 was the same as used in the previous set up (CRI). It should be noted that the range of peroxide concentration (0.01–0.07% w/w) used in the present CRNI extruder was much lower than that in the CRI extruder (0.05–0.15% w/w).¹¹ This is because the peroxide was used more efficiently in the experiment reported here. The residence time was measured as described in the previous study. The residence time in this system was approximately 3 min, which correlates to six times the half-life of the selected peroxide. However, as expected, the residence time distribution was broader in System 2,¹⁴ since this is characteristic of nonintermeshing twin-screw extruder configurations. Kamath and Palys¹⁵ suggested that in the reactive modification of PE by organic peroxide a residence time of approximately six times the half-life of the peroxide was required to ensure a complete re-

action in the extruder. Bremner¹⁶ confirmed that a reaction time of five half-lives resulted in practically complete decomposition of the peroxide.

Devolatilization was accomplished at zone 9 with the aid of a vacuum pump to remove any gaseous products. The extrudate was cooled, dried, and granulated.

Molecular Characterization and Rheological Properties

The methods of analysis employed in this study were the same as detailed in the previous studies.^{11,12}

RESULTS

Molecular Characterization

Samples are assigned two code numbers: The first corresponds to the resin under investigation, and, the second, in brackets, to the peroxide concentra-

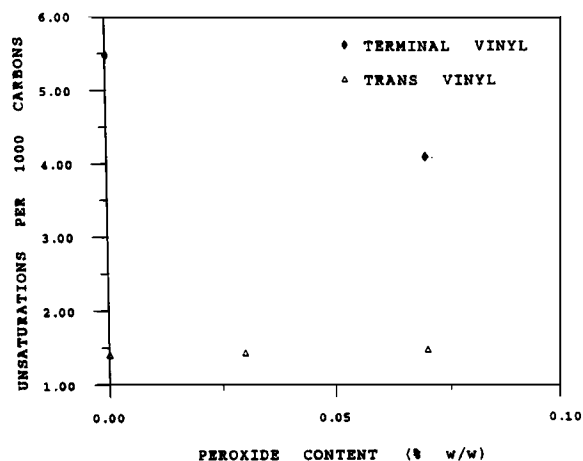


Figure 5 Vinyl unsaturation contents of Samples Set B[n] generated in System 2.

tion. The molecular weight distributions of virgin and unreacted (without peroxide) extruded Resin B in System 2 measured from SEC using a continuous viscometer detector were identical. Therefore, the extrusion process itself can be eliminated as a variable in the consideration of the observed molecular structure differences of peroxide-modified samples generated in the corotating intermeshing extruder (CRI), System 1–Set 2, compared to the reactive extrusion products prepared in the present study (CRNI), System 2.

Table I lists the molecular weight data for Resin B before and after peroxide reaction in the present system (CRNI). These measurements were made by SEC using a continuous viscometer and low-angle light-scattering (LALLS) molecular weight detectors.¹⁷ M_n and M_w were determined from continuous viscometer data, and M_z , from LALLS data. Just as for the resins generated in the CRI extruder,¹¹ the M_w of peroxide-modified samples generated in the present system (CRNI) increases as the peroxide concentration is increased. A more significant effect is revealed by the M_z values. In both cases, the products have broader molecular weight distributions compared to those of unreacted resins.

Figure 4 shows that the molecular weight distribution is shifted toward the high molecular weight end with increasing peroxide concentration. It should be noted that the highest peroxide concentration used in System 2 was 0.07% (w/w), while 0.15% (w/w) was used in the CRI extruder.¹¹ Since experiments in the present system used half of the peroxide concentration as compared to that in the CRI extruder, the changes in the molecular weight distribution are more significant for the reactive extrusion products generated in the present system

than that in the previous corotating extruder system where the peroxide was added to the polymer pellets. The lower peroxide levels in the present system reflect the more efficient nature of this peroxide feed and the reactive extrusion system.

A similar procedure described in the previous article¹¹ was used to determine the long-chain branching (LCB) frequency of Resin B before and after peroxide reaction in the present system. The level of LCB in the virgin Resin B is undetectable over the entire observed molecular weight range. As shown earlier¹¹ for the reactive extrusion products generated in System 1–Set 2, the level of LCB in peroxide-modified resin B produced in System 2 increased with increasing peroxide concentration.

Similarly to the samples prepared in the CRI extruder,¹¹ the amount of terminal unsaturations in peroxide-modified resins generated in the present reactor extrusion system decreases as the peroxide concentration is increased (Fig. 5). Simultaneously, the number of *trans* unsaturations tend to increase slightly with peroxide concentration. Again, these results demonstrate that the coupling reaction involving terminal unsaturation is a major contributor to chain extension in the reactive processing of selected LLDPEs.¹⁸

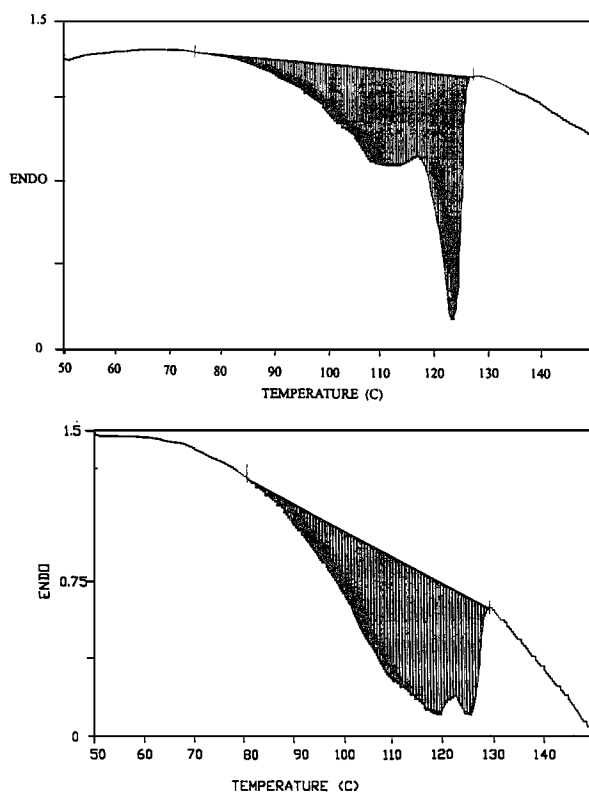


Figure 6 (a) DSC endotherm of Resin B. (b) DSC endotherm of Resin B[0.07].

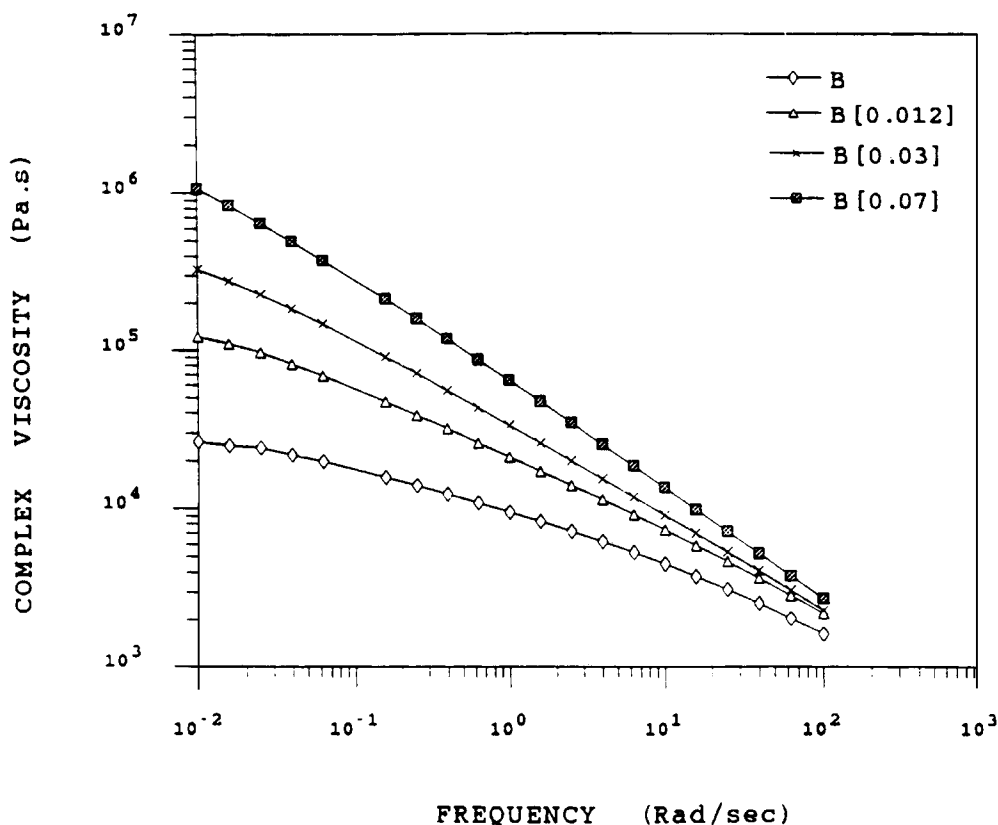


Figure 7 Complex Viscosity as a function of frequency of Sample Set $B[n]$ generated in System 2 (this study) at 190°C .

Figure 6 illustrates the thermal behavior of Resin B before and after the reaction in the present system. As shown in the previous investigation, the intensity of the peak pertaining to the linear polymer fraction decreases with increasing peroxide concentration, while the peak at the lower temperature pertaining to the branched material becomes broader. These results confirm the increase of the chain irregularities for the reactive extrusion products generated in the present system as compared to unreacted Resin B.

For all the reactive extrusion products generated in the present system, the branching content was not evaluated, since the 32.2 ppm resonance from 3B_6 carbon was unresolvable from the main CH_2 resonance at 29.99 ppm due to NMR line broadening. Since inspection of peroxide-modified sample tapes generated on a single-screw extruder indicates the presence of microgel in all selected resins, this could be a possible explanation for the line broadening as measured by the NMR technique.

Rheological Properties

Rheological analyses are performed to determine the differences in the flow behavior of reactive extrusion

products as compared to unreacted extruded ones. Figure 7 contains the plots of complex viscosity as a function of frequency for unreacted extruded resins and reactive extrusion products generated in the CRNI extruder. The low-frequency complex viscosity of the peroxide-modified samples generated in this system increases as the peroxide concentration is increased. Again, the pseudoplastic nature is more significant for Resins B[0.01], B[0.03], and B[0.07] as compared to that of Resin B. The conditions used in System 2 were more effective in enhancing the reaction, since half of the peroxide concentration used in the present system (CRNI) than in the previous set up (CRI)¹¹ gives similar complex viscosity values for the peroxide-modified samples. These results are in agreement with the previously noted molecular weight measurements.

Figure 8 illustrates the contribution of the elastic component and the viscous component in the viscoelasticity of Resin B[0.01] generated in System 2, as compared to Resin B. The sample codes are assigned to the resin under investigation, and G' and G'' , to identify the storage component and loss component, respectively. The peroxide concentration follows in brackets. The elastic component G' in

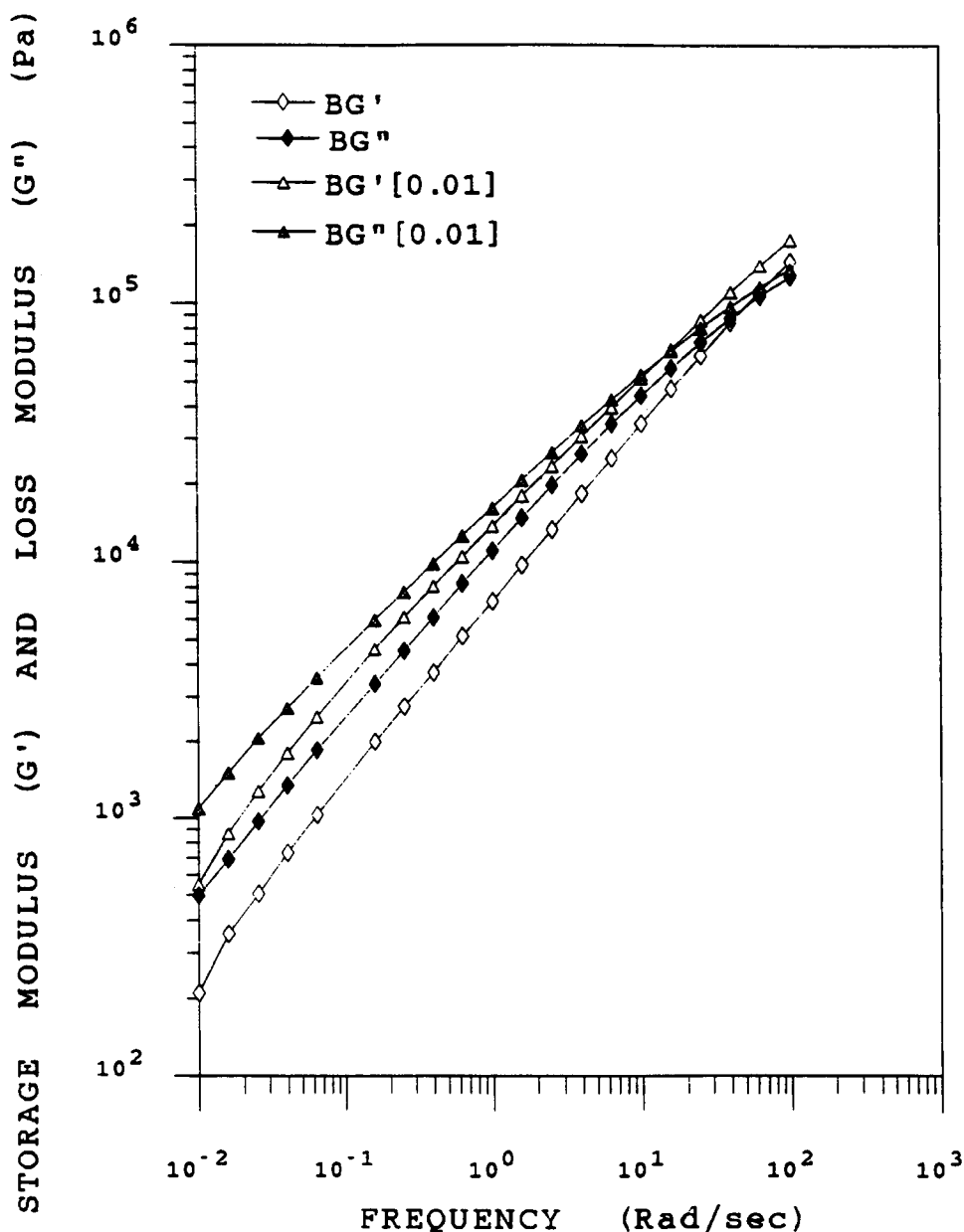


Figure 8 Storage modulus (G') and loss modulus (G'') of Resins B and B[0.01] in System 2 as a function of frequency at 190°C.

Resin B dominates at the highest frequency, above approximately 100 rad/s, while the elastic component G' in Resin B [0.01] becomes more predominant than the viscous response G'' at lower frequencies, above approximately 16 rad/s.

The effect of peroxide treatment on the contribution of the elastic response to the viscoelastic behavior was more significant for peroxide-modified resins generated in the present system (CRNI) than for reactive extrusion products prepared in the CRI extruder.¹¹ The $G'-G''$ crossover for Resin B [0.03] occurred at a higher frequency of approximately 0.06 rad/s, while the elas-

tic response, G' , was dominant over the entire observed frequency range for Resin B [0.07].

Since similar viscoelastic behavior is shown upon peroxide treatment by products generated in the former¹¹ and in the latter systems, it appears that the presence of microgel in all products generated in the CRNI extruder does not affect their viscoelastic behavior. Nakajima and Harrell¹⁹ reported similar results about the effects of the presence of gel on the viscoelasticity of elastomers. These authors suggest that the manifestation of the microgel in the viscoelastic properties, which

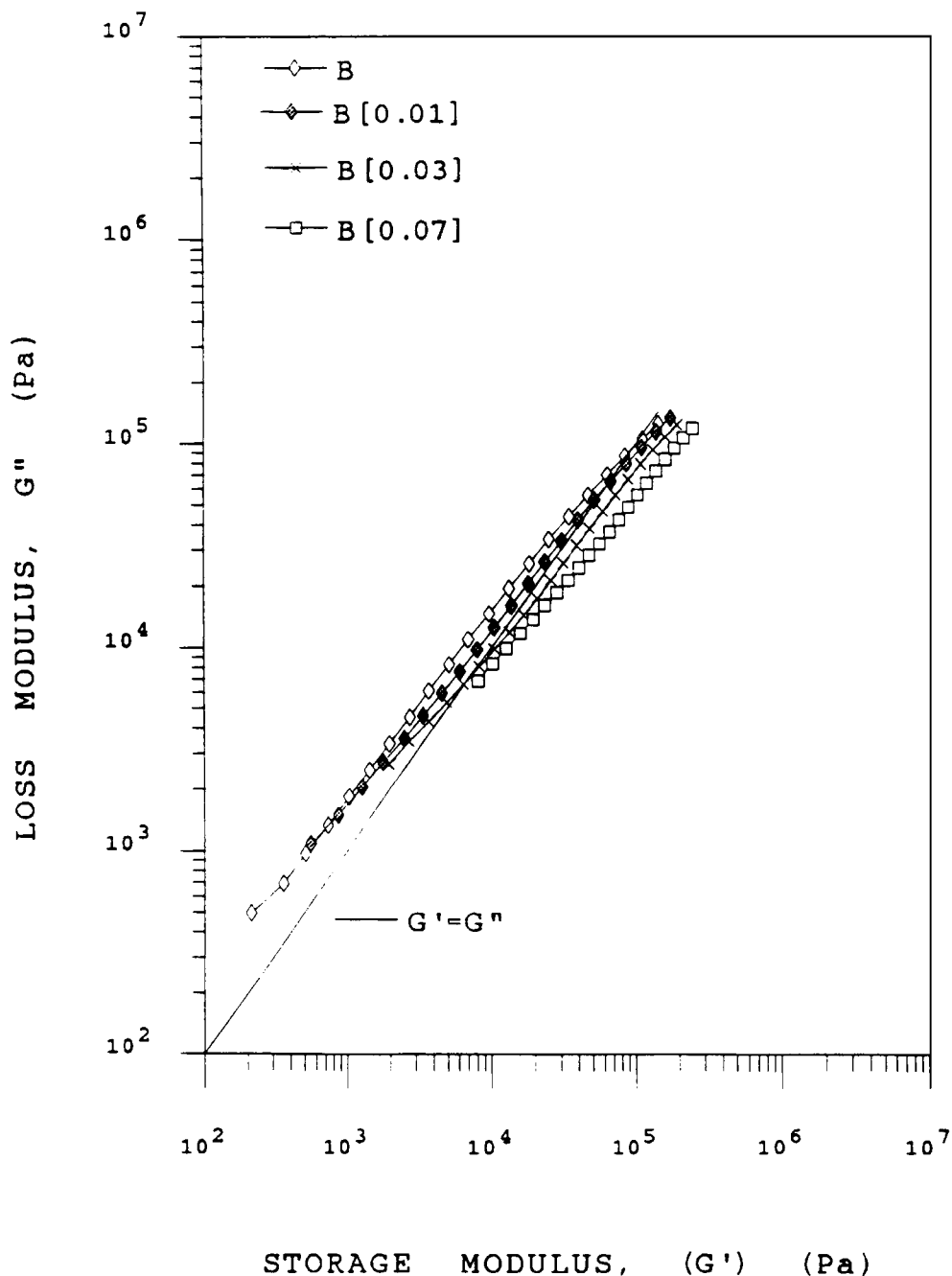


Figure 9 Loss modulus (G'') as a function of storage modulus (G') of Sample Set $B[n]$ generated in System 2 at 190°C .

are dependent on the magnitude of the normal force, disappears for samples when these are well compacted and loaded into the measuring device.

A modified Cole-Cole (mCC) method, generated by plotting the loss modulus G'' as a function storage modulus G' in a log-log scale, as a tool to represent the relative contribution of the G' response to that of G'' for reactive extrusion products generated in

the CRNI extruder is illustrated in Figure 9. Similar to the samples generated in the previous set up CRI extruder,¹¹ the contribution of the elastic response to the viscoelasticity behavior of peroxide-modified samples generated in the present study is more predominant than that of the unreacted extruded Resin B. This method is consistent with the previous rheological measurements, suggesting that the elas-

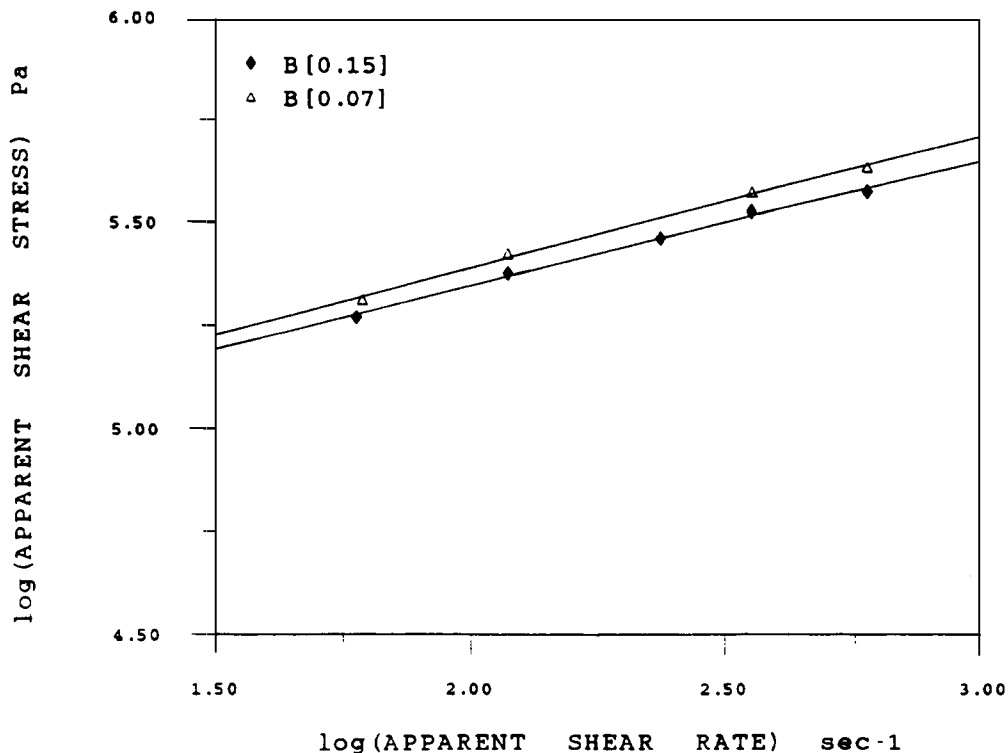


Figure 10 Apparent flow curves of Resin B[0.15] in System 1–Set 2 and Resin B[0.07] in System 2; cylindrical die, L/D of 20 at 190°C.

tic component is more predominant over the viscous response for peroxide-modified resins generated in the CRNI extruder than that for the products generated in the CRI extruder¹¹ at the same level of peroxide concentration. Since an increase in the degree of long-chain branching is reflected in the shift of the mCC plot toward lower G'' values,¹³ these results suggest that the degree of long-chain branching in selected LLDPE increases upon peroxide treatment.

A comparison of the higher shear rate apparent flow curves between Resin B[0.15] generated in the CRI extruder, System 1–Set 2 (Ref. 11) and Resin B[0.07] generated in the CRNI extruder was done using the same L/D capillary die of 20 (Fig. 10). It is interesting that the apparent shear stress for Resin B[0.07] (System 2) is higher than that for Resin B[0.15] (from System 1) at all apparent shear rates under investigation. These results are in agreement with the flow analyses at low shear rates.

In addition to the flow analyses at high shear rate, the die swell behavior is illustrated in Figure 11 for reactive extrusion products generated in System 2, which exhibit a similar trend as compared to that of the resins prepared in the CRI¹¹ extruder. The

extrudate swell tends to decrease with increasing peroxide concentration.

In addition to the shear viscosity measurements, the extensional viscosity of peroxide-modified LLDPE samples generated by reactive extrusion are investigated, since the elongational flow properties play an important role in applications, such as in tubular film operation. The elongational flow properties was evaluated on the Rheometrics extensional rheometer.

The extensional viscosity of Resin B and its products are displayed in a double logarithmic scale as a function of time at 170°C (Fig. 12). The elongational flow analyses of these resins were generated at the same Hencky strain of 3.1 and at different constant strain rates $\dot{\epsilon}_0$. For all selected strain rates, the extensional viscosity first rises and then falls after passing through a broad maximum. Resin B does not exhibit the strain-hardening behavior which is reported to be typical of LDPE. Strain hardening is shown by a rapid increase in the extensional viscosity with the strain. The sharp drop of the extensional viscosity at a longer time, i.e., higher strain, indicates that the polymer melt is unable to be stretched any further and it breaks. The increase of the elongational viscosity tends to be

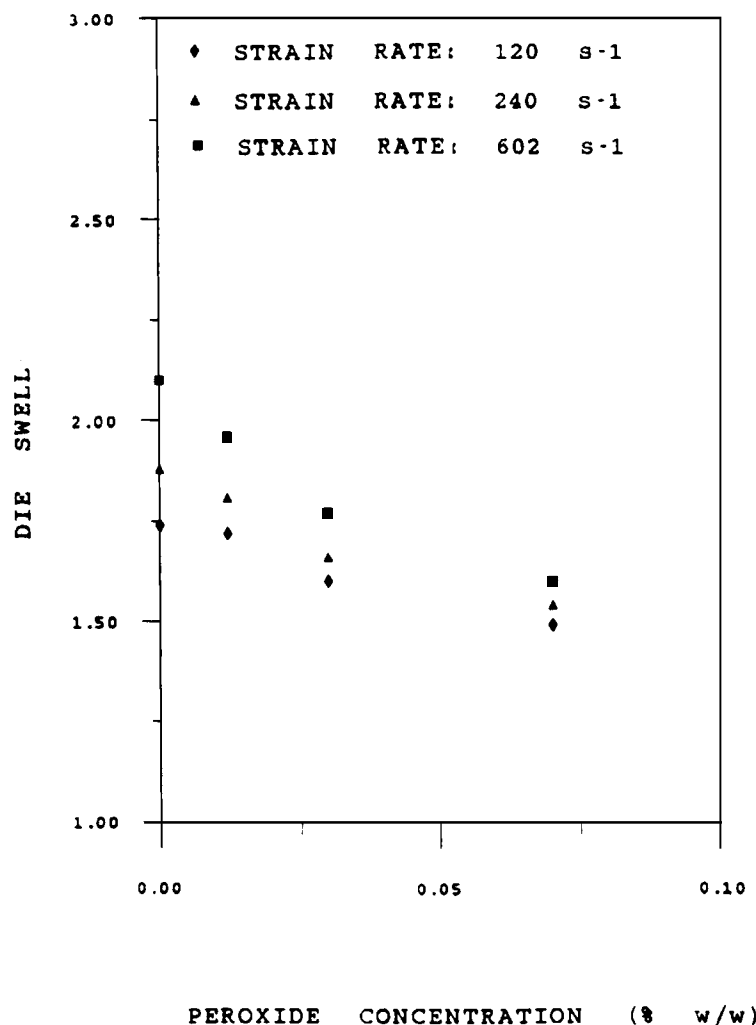


Figure 11 Die swell as a function of peroxide concentration of Sample Set B[n] generated in System 2; cylindrical die, L/D of 7.

more pronounced for Resins B[0.01] and B[0.03] as compared to Resin B. As for resin generated in the CRI extruder,¹¹ the increase of the extensional viscosity seems to be at the expense of the drawdown ability. At a strain rate of 0.07 s^{-1} , Resin B[0.01] broke at a strain of approximately 1.8, while Resin B[0.03] broke at a strain of approximately 1.0. A similar trend is shown at a higher strain rate where Resin B[0.01] broke at a strain of approximately 2.0, while Resin B[0.03] broke at a strain of approximately 0.7. These results are consistent with the creation of long-chain branches in the peroxide-modified LLDPEs.

CONCLUSIONS

The nature of the peroxide feed and the extrusion system are important variables in the reactive pro-

cessing of selected LLDPEs. The present system used a counterrotating nonintermeshing twin-screw extruder with peroxide injected into the PE melt. The peroxide action was more effective in this case than in the CRI extruder with peroxide added to the PE granules.¹¹ However, the extrusion process conditions used in the present system were not successful in generating homogeneous products. The presence of microgel is undesirable since this would interfere with the drawdown ability of these resins in film-blowing operations, as shown by a drastic reduction of the drawdown ability of resins B after reaction in the present system. The formation of microgel during the reactive process might be attributed to insufficient mixing, aggravated by the superior ability of the present extruder configuration to affect peroxide decomposition. It is to be expected that the sensitivity of the products to the extrusion

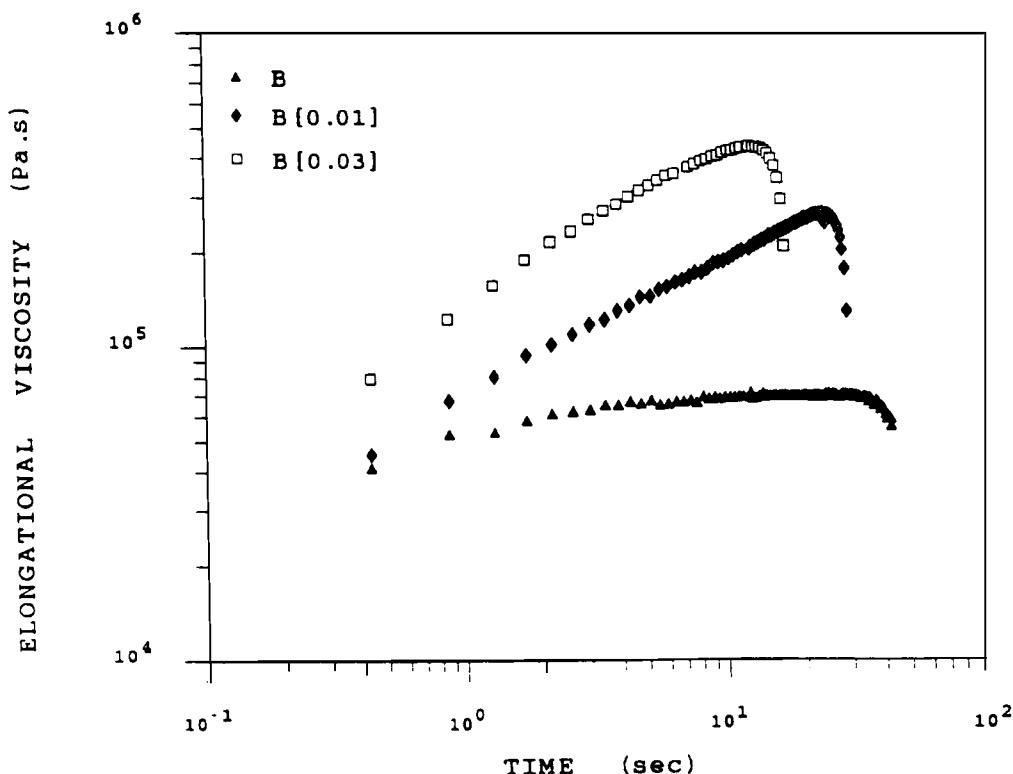


Figure 12 Extensional viscosity as a function of time of Resin B at 170°C.

mixing and peroxide addition details will vary also with the reactivity of the barefoot LLDPE. Resin B, used here, is quite reactive since it contains a fairly high level of terminal unsaturation.¹¹

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REFERENCES

1. D. Bigio and L. Erwin, *SPE Antec*, **47**, 45-48 (1985).
2. H. E. H. Meijer and P. H. M. Elemans, *Polym. Eng. Sci.*, **28**(5), 275 (1988).
3. A. D. Gotsis and D. M. Kalyon, *SPE Antec Proc.*, **47**, 44 (1989).
4. L. P. B. M. Janssen, in *Mixing in Polymer Processing*, C. Rauwendaal, Ed., Marcel Dekker, New York, 1991.
5. D. M. Kalyon and D. W. Yu, *Polym. Eng. Sci.*, **28**(23), 1542 (1988).
6. D. Bigio and W. Baim, *Adv. Polym. Tech.*, **11**(1), 11 (1992).
7. J. H. Conner and D. I. Bigio, *SPE Antec Proc.*, **50**, 1328 (1992).
8. C. Tucker and R. J. Nichols, *SPE Antec Proc.*, **45**, 117 (1987).
9. G. Menges and T. Bartilla, *Polym. Eng. Sci.*, **27**(16), 1216 (1987).
10. C. J. Rauwendaal, in *Mixing in Polymer Processing*, C. Rauwendaal, Ed., Marcel Dekker, New York, 1991.
11. M. G. Lachtermacher and A. Rudin, *J. Appl. Polym. Sci.*, **58**, 2077 (1995).
12. M. G. Lachtermacher and A. Rudin, *J. Appl. Polym. Sci.*, to appear.
13. E. R. Harrell and N. Nakajima, *J. Appl. Polym. Sci.*, **29**(3), 995 (1984).
14. J. L. White, W. Szydlowski, K. Min, and M. Kim, *Adv. Polym. Technol.*, **7**, 295 (1987).
15. V. R. Kamath and L. H. Palys, Technical Data, Atochem North America Inc., 1990 (presented at October 17-18, 1990 Retec at Mt. Laurel Resort Pocono Mountains, PA).
16. W. T. Bremner, PhD Thesis, Department of Chemistry, University of Waterloo, 1992.
17. S. Pang and A. Rudin, *J. Appl. Polym. Sci.*, **46**, 763 (1992).
18. T. Bremner and A. Rudin, *Plast. Rubb. Process. Appl.*, **13**, 61 (1990).
19. N. Nakajima and E. R. Harrell, *Rubb. Chem. Technol.*, **53**, 14 (1980).

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