

# Reactive Processing of Polyethylenes on a Single Screw Extruder

SHEELA KUMARI ISAC, K. E. GEORGE

Department of Polymer Science and Rubber Technology, Cochin University of Science and Technology, Kochi 682 022, India

Received 12 May 2000; accepted 20 August 2000

**ABSTRACT:** The modification of low density polyethylene, linear low density polyethylene, and their blend by dicumyl peroxide at the time of the extrusion on a single screw extruder is reported. The study shows that the optimum conditions of modification can be determined on a torque rheometer and these can then be applied for actual extrusion. A low level of crosslinking can be introduced by reactive extrusion for improving the heat stability without adversely affecting the processing behavior. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 2545–2549, 2001

**Key words:** LDPE; LLDPE; reactive extrusion; DCP modification

## INTRODUCTION

Blends of low density polyethylene (LDPE) and linear low density polyethylene (LLDPE) are widely used for making films. LLDPE has a greater degree of stiffness and better strength than LDPE, a more regular crystalline structure, higher melting point, and better fracture resistance. However, the shear viscosity of LLDPE is usually greater compared with LDPE, causing difficulties in the formation of films. The addition of small amounts of LDPE to LLDPE results in reduced haze and better bubble stability. LDPE/LLDPE films can be made in thinner gages than that of LDPE alone with acceptable properties in conventional extruders used for LDPE alone.<sup>1–5</sup>

In certain processing applications, the available polyethylene resins are not always optimum in terms of processability or mechanical properties of the finished product. Crosslinking of polymers improves their mechanical stability at high

temperature, mechanical properties, and resistance to creep. Polyolefines are sometimes modified with organic peroxides to alter their processability and mechanical properties.<sup>6,7</sup> These peroxides can either induce crosslinking or initiate chain scission which leads to many changes in the properties of the polymer. It is known that the effectiveness of the chemical crosslinking of polyethylenes can be increased by the use of coagents. Radical processes occurring in their presence lead to the formation of a three-dimensional network, the links in which are different from the usual C—C links and confer special properties on the polymer materials. Thus coagents not only improve the effectiveness of the crosslinking reactions but also improve the properties of the final products.<sup>8</sup>

Reactive extrusion is a recent technique in which modification and shaping of a polymer are done simultaneously and the extruder itself acts as the reactor.<sup>9–13</sup> For this report, our purpose was to study the modification of LDPE, LLDPE, and their blend with dicumyl peroxide (DCP) during their processing in a single screw extruder. The effect of using a coagent in the peroxide modification was also investigated.

Correspondence to: K. E. George (kegeorge@cusat.ac.in).

*Journal of Applied Polymer Science*, Vol. 81, 2545–2549 (2001)  
© 2001 John Wiley & Sons, Inc.

## EXPERIMENTAL

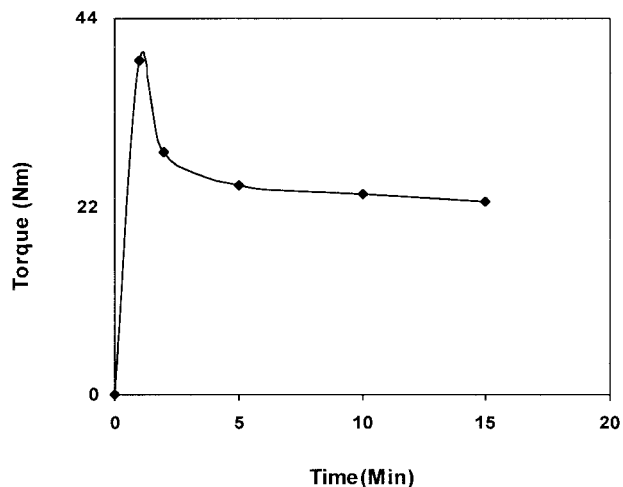
### Materials

The grades of LDPE and LLDPE used for the study were: LDPE, indothene 24FSO40, melt index 4 g/10 min, density 0.922 g/cm<sup>3</sup> (supplied by IPCL, Baroda, India); LLDPE, indothene LL20FSO10, melt index 1.0 g/10 min, density 0.920 g/cm<sup>3</sup> (supplied by IPCL); DCP used was commercial grade with 40% purity; triallyl cyanurate (TAC) used was commercial grade.

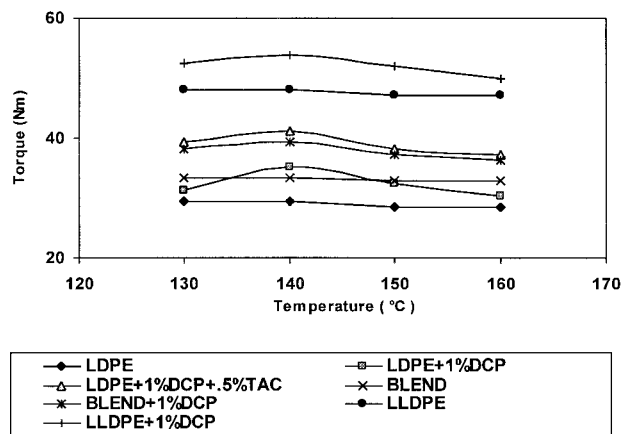
Conditions for reactive extrusion were first determined on a Brabender plasticorder mixer model PL3S equipped with roller type rotors, having a capacity of 40 g. Different mixing conditions were generated by varying the temperature and rpm. DCP at concentrations of 0.5, 1.0, and 1.5% of the total weight of the polymers was used as the crosslinking agent. DCP was added along with the polymers. The dosage of TAC used as the coagent was varied from 0.25 to 1% of the amount of the polymers. Reactive extrusion was done on a laboratory general purpose plastic extruder attached to a Brabender plasticorder model PL 2000 with an L/D ratio of 25 and a compression ratio of 2 and fitted with a ribbon die. The temperatures of the barrel and the die, rpm of the screw, and DCP and TAC concentrations were fixed as per the results obtained from the mixer.

### Characterization and Testing

The gel content of the extrudate was determined from extraction in boiling toluene for 8 h accord-



**Figure 1** Torque versus time curve of the LDPE/LLDPE blend in the presence of DCP at 140°C, at 60 rpm.

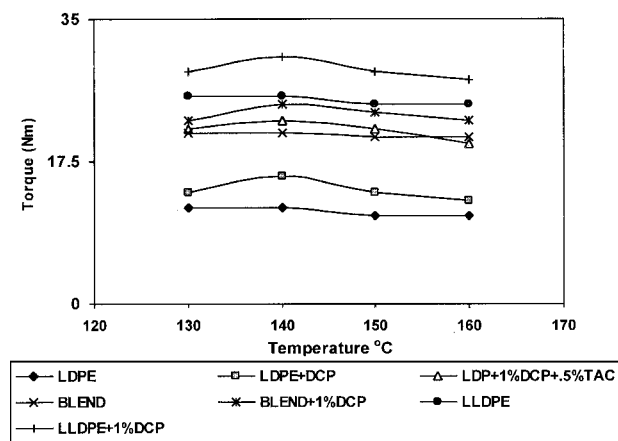


**Figure 2** Maximum torque versus temperature curves of unmodified and modified LDPE, LLDPE, and their blend, at 60 rpm.

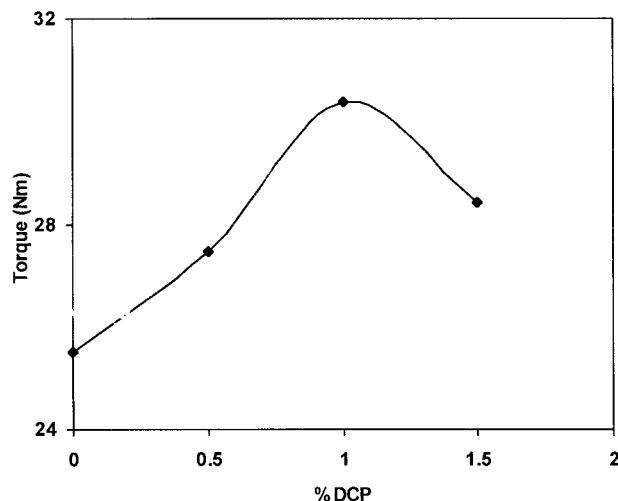
ing to ASTM D 2765. The tensile properties were determined according to ASTM D 638 using a Zwick tensile testing machine model 1445 using a stretching rate of 50 mm/min. The flow behavior of the polymers was determined on a Goettfert capillary rheometer using a die of 1 mm diameter and an L/D ratio 30. The thermogravimetric analyses were done on a Dupont 2000 thermal analyzer at a heating rate of 10°C/min in air, from room temperature to 700°C.

## RESULTS AND DISCUSSION

Figure 1 shows a typical torque versus time graph obtained from the Brabender mixer for the 50:50 LDPE/LLDPE blend containing 1% DCP at



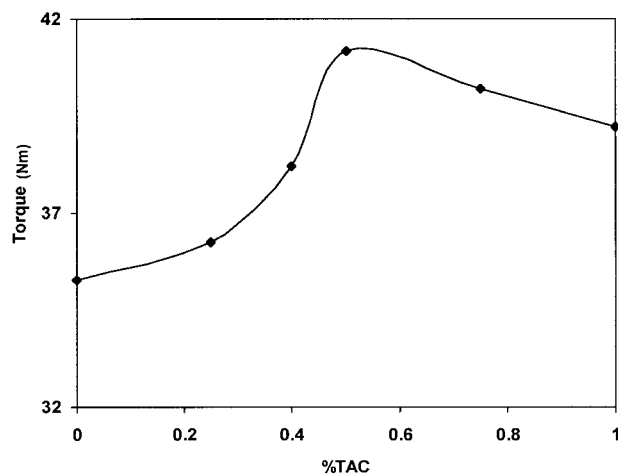
**Figure 3** Stabilized torque versus temperature curves of unmodified and modified LDPE, LLDPE, and their blend at 60 rpm.



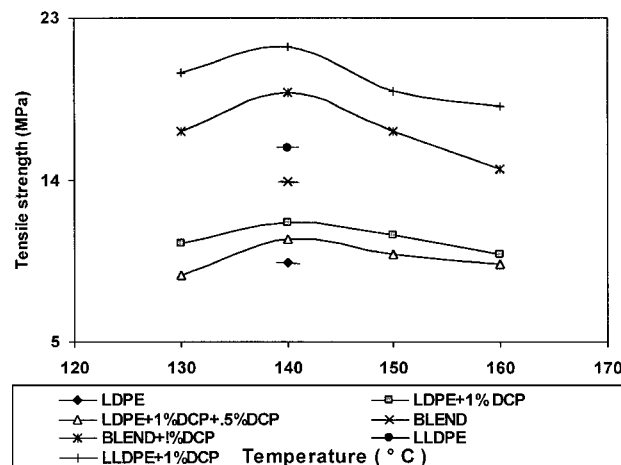
**Figure 4** Variation of stabilized torque of LLDPE with DCP content at 140°C, at 60 rpm.

140°C. The torque rises initially because of melting/crosslinking of the polymer, reaches a maximum, and then decreases and stabilizes. The maximum and/or stabilized torque attained may give indication of the extent of melting and crosslinking of the polymer. The extent of melting/crosslinking was assessed both from the maximum and stabilized torques.

Figure 2 shows the variation of maximum torque with temperatures for LDPE, LLDPE, and their blend with and without DCP and TAC. A temperature of 140°C registers the highest torque for all the combinations. This is probably because of better crosslinking efficiency at this temperature at the conditions used. Figure 3 shows the variation of stabilized torque with mixer temper-

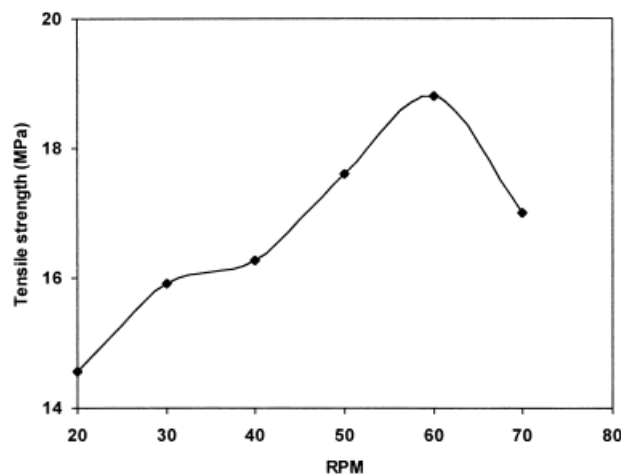


**Figure 5** Variation in the maximum torque of LDPE + 1% DCP with TAC content at 140°C, at 60 rpm.

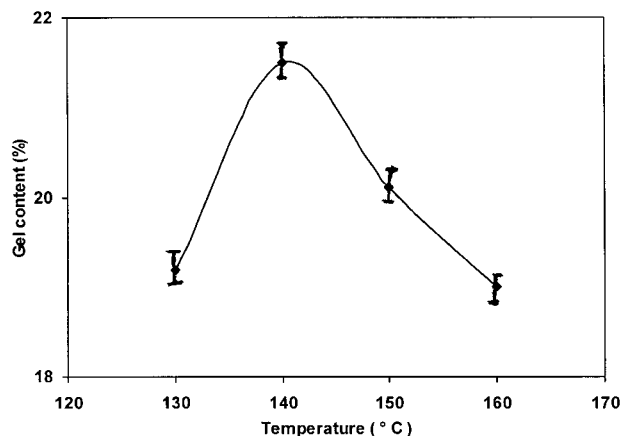


**Figure 6** Variation of tensile strength with temperature of extrusion for unmodified and modified LDPE, LLDPE, and their blend, at 60 rpm.

ature. For pure polymer without any DCP, the torque is almost parallel to the x-axis as expected. The increase in the torque for the compositions containing DCP is obviously attributable to crosslinking. Because 140°C again registers the maximum torque for DCP-modified LDPE, LLDPE, and their blend, this temperature was chosen as optimum for DCP modification in the case of these polymers. LLDPE and its blend show a higher degree of crosslinking than that of LDPE. This may be attributed to a larger number of tertiary carbon atoms in LLDPE than in LDPE.<sup>14</sup> This figure also shows the efficiency of adding coagent (TAC) for DCP modification. Figure 4 shows the variation of stabilized torque of LLDPE with DCP content. The stabilized torque in-



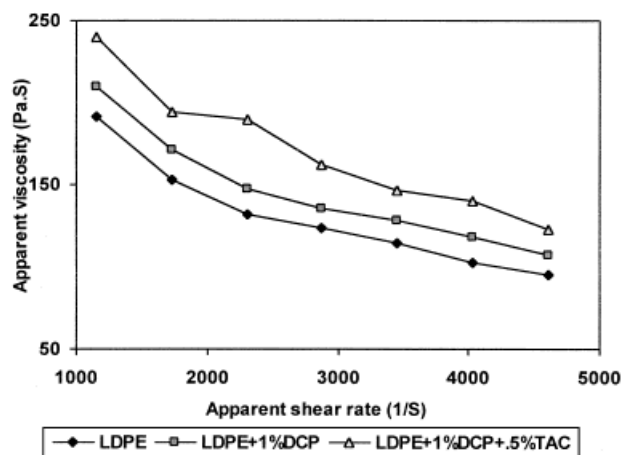
**Figure 7** Variation of tensile strength with rpm of modified LDPE/LLDPE blend at 140°C.



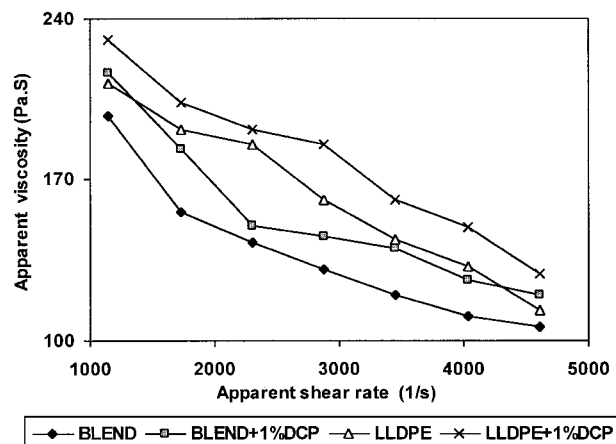
**Figure 8** Variation of gel content of DCP-modified LDPE extruded at different temperatures, at 60 rpm.

creases with DCP content, reaches a maximum, and then decreases, indicating there is an optimum DCP concentration.<sup>8</sup> Maximum torque is observed for 1% DCP. The same behavior was observed in the case of LDPE and LDPE/LLDPE blend at different temperatures. So 1% DCP was chosen as the optimum concentration. Similarly, the optimum concentration of TAC was found to be 0.5% (Fig. 5).

To study the correlation between the mixer parameters for DCP modification with those of the extruder parameters, reactive modification of polyethylenes and their blend was done on a laboratory extruder at different temperatures and rpms at different DCP concentrations. The tensile properties of the extruded film were measured. Figure 6 shows the variation of tensile strength with temperature of extrusion for LDPE, LLDPE,



**Figure 9** Flow curves of unmodified and modified LDPE at 170°C.



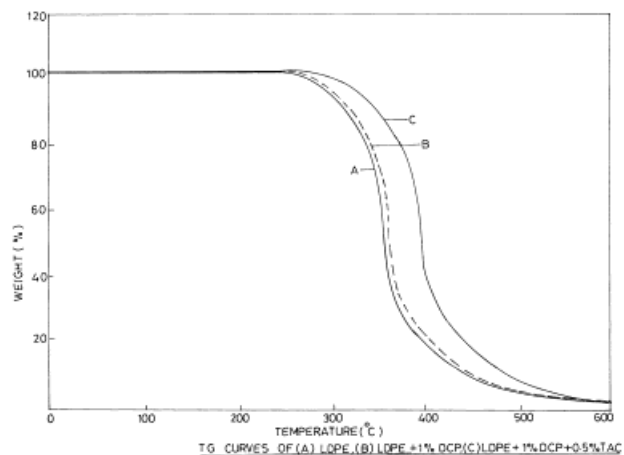
**Figure 10** Flow curves of unmodified and modified LLDPE and LDPE/LLDPE blend at 170°C.

and their 50:50 blend at 60 rpm. Maximum tensile strength is obtained at 140°C as in the case of the mixer showing that this temperature is the optimum for DCP modification at the conditions used. The extrusion behavior also shows that the results obtained from the mixer can be used for fixing the extrusion characteristics. Figure 7 shows the variation of tensile strength with rpm in the case of the 50:50 blend with 1% DCP at 140°C. A maximum value of tensile strength is obtained at 60 rpm. This shows that the shear rate/residence time under these conditions give the best choice for DCP modification. Figure 8 shows the variation of gel content with mixing temperature for LDPE. Maximum value of gel content is obtained at 140°C, confirming that maximum crosslinking occurs at this temperature.

Figures 9 and 10 show the variation of viscosity at different shear rates, at 170°C. An increase in viscosity is obtained on DCP addition as expected. The increase in viscosity is attributed to the introduction of crosslinks between the chains. However, the increase in viscosity is only marginal and hence may not affect the processability. The gel content of LDPE is compared with that of LLDPE and the 50:50 LDPE/LLDPE blend in Ta-

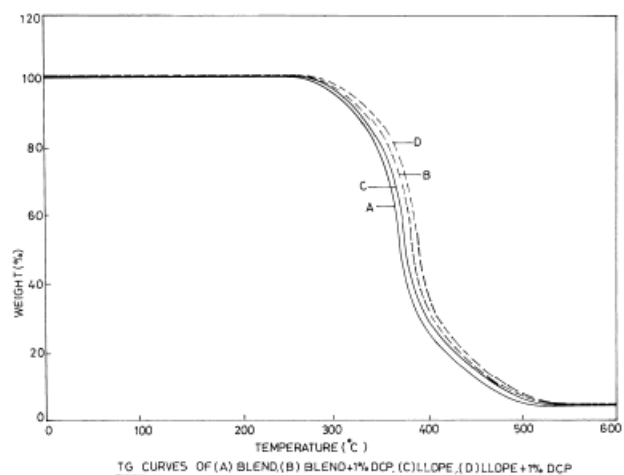
**Table I** Gel Content Values at 140°C

Material	Gel Content (%)
LDPE + 1% DCP	21.5
LDPE + 1% DCP + 0.5% TAC	25.6
Blend + 1% DCP	24.4
LLDPE + 1% DCP	26.2



**Figure 11** Thermogravimetric curves of unmodified and modified LDPE.

ble I. LLDPE gives a higher crosslink density than LDPE. Gel content, which relates to the three-dimensional network structure, increases with LLDPE content, indicating that the LLDPE phase forms a relatively denser network structure. The addition of the coagent is found to improve the crosslink density. Figures 11 and 12 show the TG curves of LDPE, LLDPE, and their blend. DCP modification shows marginal improvement in thermal stability as expected. The LLDPE phase shows a higher improvement in decomposition temperature than that of LDPE, probably because of the higher crosslink density (Table II).



**Figure 12** Thermogravimetric curves of unmodified and modified LLDPE and LDPE/LLDPE blend.

**Table II** The Temperature of Derivative Weight Percent Peak

Material	Peak Temperature
LDPE alone	373.8
LDPE + 1% DCP	378.1
LDPE + 1% DCP + 0.5% TAC	400
Blend alone	380.3
Blend + 1% DCP	391.0
LLDPE alone	383.5
LLDPE + 1% DCP	394.8

## CONCLUSIONS

This study shows that a single screw extruder can be used for reactive extrusion of polyethylenes. The optimum reaction conditions, viz., temperature, shear, and time can be determined on a torque rheometer and then this information can be used in actual extrusion.

## REFERENCES

1. Siegman, A.; Nir, Y. *Polym Eng Sci* 1987, 27, 1182.
2. La Mantia, F. P.; Acierno, D. *Eur Polym J* 1985, 21, 811.
3. Datta, N. K.; Birley, A. W. *Plast Rubber Process Appl* 1983, 3, 237.
4. Klecenova, T.; Szweczyk, P. *Int Polym Sci Technol* 1988, 15, 68.
5. Klecenova, T.; Birley, A. W. *Plast Rubber Process Appl* 1990, 13, 197.
6. Woods, D. W.; Busfield, W. K.; Ward, I. M. *Plast Rubber Process Appl* 1988, 9, 155.
7. De Boer, J.; Pennings, A. J. *Polymer* 1982, 23, 1944.
8. Kalafski, L.; Zhiznevskii, V. M. *Int Polym Sci Technol* 1986, 13, ref PM 86/12/17; transl. serial no. 10287.
9. Gaylord, N. G.; Mehta, M.; Kumar, V.; Tazi, M. *J Appl Polym Sci* 1989, 38, 359.
10. Greco, R.; Musto, P.; Riva, F.; Maglio, G. *J Appl Polym Sci* 1989, 37, 789.
11. Brown, S. B.; Orlando, C. M. in *Encyclopedia of Polymer Science and Engineering*; Kroschwitz, J. I., Ed., Wiley: New York, 1988; Vol. 14, p. 169.
12. Biesenberger, J. A.; Dey, S. K.; Brizzolara, J. *Polym Eng Sci* 1990, 30, 1493.
13. Berghaus, U.; Michaeli, W. *Soc Plast Eng ANTEC Tech Pap* 1990, 36, 1929.
14. Romanini, D. *Polym Plast Technol Eng* 1982, 19, 201.