Benzoyl Peroxide as a Crosslinking Agent for Polyethylene

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Synopsis

The efficiency of benzoyl peroxide (BPO) as a crosslinking agent for polyethylene (PE) was studied as a function of concentration and temperature in relation with the resin melt flow index and particle size. The investigation can lead to the selection of suitable materials and operating conditions for a proper crosslinking process. The decomposition characteristics of the initiator studied can be regulated in order to allow faster production rates when crosslinked PE are prepared by injection molding.

INTRODUCTION

The use of free radical initiators, especially peroxide compounds, is very common for the crosslinking of polymers having a saturated hydrocarbon structure. Thus, many authors studied the crosslinking of polyethylene (PE) with peroxides, selecting the suitable compounds and investigating process characteristics.[1]

One of the most extensively used peroxides is *bis*-a,a-dimethyl benzyl peroxide (dicumyl peroxide)[2-4] accompanied by di-tert butyl peroxide.[2,5,6] The use of peroxides with a higher thermal stability have also been studied, including 2,5 *bis*(tert-butyl-dioxy)-3-hexyne[7] or a,a-*bis*(tert-butyl-peroxy)-*p*-diisopropylbenzene.[1]

The initiators of lower thermal stability can also be found in the related literature[8,9] and some attention was paid to the dissociation of benzoyl peroxide (BPO)[10,11] as well as the effect of pressure on its decomposition rate.[12] A decrease in the rate of thermal decomposition with increasing pressure is known[13,14] and this influence is observed in the cases of liquid solvents and polymers.[15-17]

In our work, an attempt was made to define the efficiency of BPO as crosslinking agent for PE under normal processing conditions. The properties of the final product related with crosslinking techniques, for various polymer grades and particle sizes, can dictate the recommended parameters for an efficient process. Furthermore, the use of a low temperature decomposing initiator is accompanied by quick curing processes. Thus, BPO enhances the versatility of PE crosslinkable compounds suitable for molding. In fact, when crosslinked PE is to be produced by injection molding, the fast cure is advantageous for short molding cycles. As a consequence, production rate is

increased and dangers of premature crosslinking into the molding machine are eliminated.

EXPERIMENTAL

Materials

Five difference grades of "Carlona" PE (Shell Chemicals Co) were selected among the low density types since these materials are expected to be easily processed at lower temperatures. This results in a decreased decomposition rate of the peroxide when it is mixed with the molten resin, making possible the use of thermal-sensitive members.

The selected grades also varied in melt flow index, since this characteristic prescribes the melt viscosity, which also can influence the process.

The five PE grades are assigned five code numbers each, with the two first corresponding to the second and third decimal places of the density value and the rest to the melt flow index. For example, a grade presented as PE 18 020 has a density of 0.918 g/mL and a melt flow index of 20 g/10 min.

The organic peroxide used was chemical-pure benzoyl peroxide (Fluka A.G.). The solvents used were chemical-pure toluene and methanol (Merck A.G.).

Method

The crosslinking reaction was carried out in a 50 mL mixing chamber of PVL 151 Brabender plasticorder. The use of plasticorder offers the advantage of recording the mixing torque during mixing of the molten resin with peroxide, thus giving a first indication of the crosslinking reaction.

The gel content of the crosslinked PE samples was determined by extraction of the soluble material for 8 h in boiling toluene. Specimens prepared from crosslinked PE by compression molding were tested to determine their tensile strength according to ASTM D 638. Finally, the polymer size reduction (i.e., the transfer of pellets to powder) was carried out by dissolution and precipitation of the resin.

Thus, 150 g of PE were dissolved in 1,000 mL toluene, at 90°C and the solution added to 3 L of methanol under thorough stirring. The resulting precipitate was collected by filtering and washed twice with 1,000 mL methanol. After washing, the PE slurry was dried in an air-circulating oven at 50°C to give the PE powder.

RESULTS AND DISCUSSION

Rheological Investigation

The mixing torque value as a function of BPO concentration for PE 18 020 and PE 18 200 can be seen in Figure 1. The curves of Figure 1 are referred to the maximum torque (peak value) as well as the torque value after 10 min. In both cases, an increase of the torque with increasing peroxide concentration is evident at least until 5 phr. For PE 18 020, which presents higher viscosity and torque values, the increase rate is lower for BPO concentrations above 2 phr.
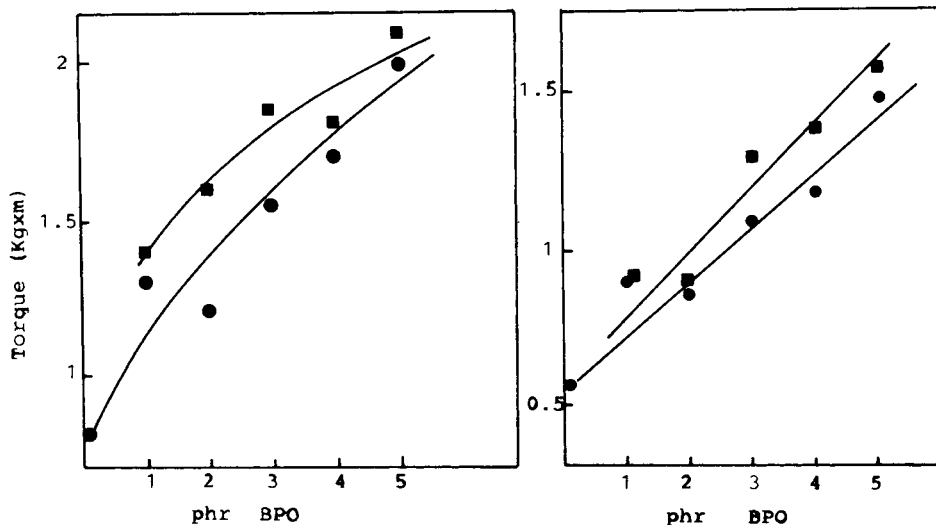
Fig. 1. The torque as a function of peroxide concentration for PE 18 020 at 120°C: (■) max torque; (●) torque at 10 min.
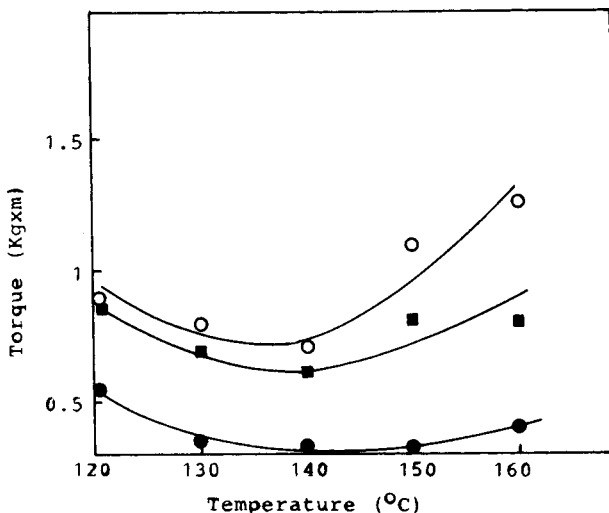

Fig. 2. The torque versus temperature for pure and mixed PE: (○) PE 18 200-BPO 2 phr, maximum; (■) PE 18 200-BPO 2 phr, 10 min.; (●) PE 18 200, 10 min.

The mixing torque as a function of reaction temperature, for mixtures of PE 18 020 or PE 18 200 with 2 phr BPO, is presented in Figures 2 and 3. The torque value for the polymer alone is also plotted in these figures. In general, an increase of the mixing torque with reaction temperature is evident, and this increase for the crosslinkable compounds is higher when considering the torque decrease with temperature, which normally occurs for the pure polymer. In the case of PE 18 200, the curves seem to reach a minimum for temperature 140°C. This point is also the limiting temperature value for the torque presented by the pure polymer. The above behavior indicates that for
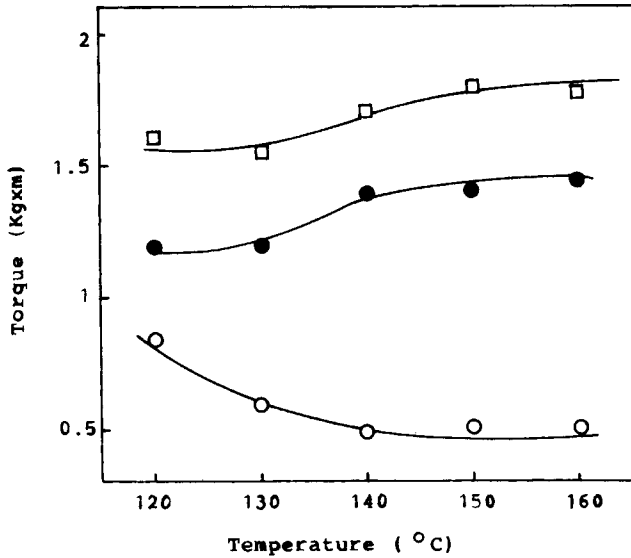
Fig. 3. The torque as a function of temperature for PE 18 020: (□) BPO 2 phr, maximum; (●) BPO 2 phr, 10 min; (○) pure PE 18 020.
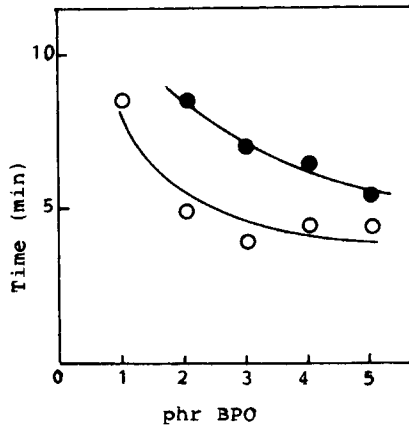

Fig. 4. The time for maximum torque as a function of peroxide concentration: (●) PE 18 020; (○) PE 18 200.

PE 18 200, temperatures below 140°C do not favor the crosslinking reaction to a degree that can surpass the decrease due to the temperature effect. In Figure 4 the time for maximum torque is plotted versus peroxide concentration for PE 18 020 and PE 18 200, processed at 120°C. A decrease of peak time with peroxide concentration up to a limiting value, for 2 phr BPO in PE 18 020, can be observed. Furthermore, the values referred to PE 18 020 are lower than those of PE 18 200.

The effect of melt flow index on the crosslinking reaction, as well as the peak time can be seen in Figure 5 and in Table I. In fact, the curves of Figure 5 indicate that low melt flow value, (i.e., high melt viscosity) favors the crosslinking reaction if the mixing torque is considered as an evaluation
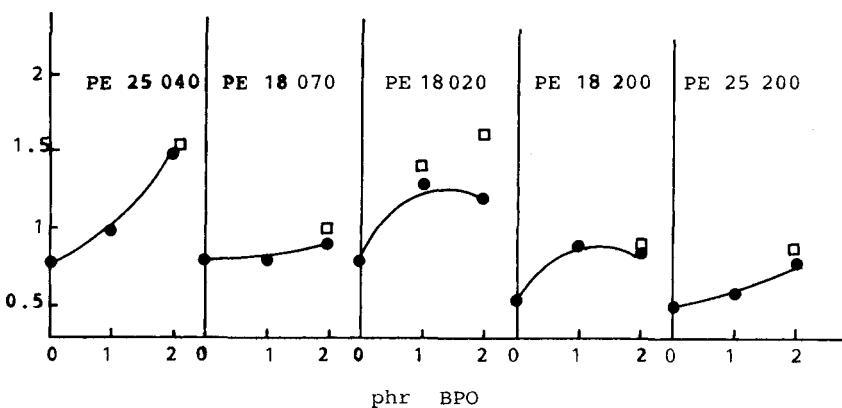
Fig. 5. The relation of melt flow index with torque changes for various PE types: (□) max torque; (●) torque at 10 min.

TABLE I
Time for Maximum Torque

PE grade	phr BPO	Time (min)
18 020	1	8.5
	2	5
18 200	1	—
	2	8.5
25 040	1	—
	2	8.5
18 070	1	—
	2	7.5
25 200	1	—
	2	12

—: No peak is observed.

criterion. The low diffusion rate of free radicals, which accompanies the low melt flow, is negligible in our case where mechanical mixing occurs during the reaction. On the other hand, low melt flow values are connected with high molecular weights, so that fewer crosslinks enable the formation of a three-dimensional network.

In addition, Table I confirms the following series of increasing peak time: 18 020 < 18 070 < 25 040 ~ 18 200 < 25 200. The above classification declares that reaction characteristics are not a sample function of melt flow but the density value must also be taken into account.

Analytical Determination of the Gel Content

The characterization of the samples prepared was carried out by the determination of gel content. The results for PE 18 020 at 120°C are plotted versus peroxide concentration in Figure 6. As the curves of Figure 6 indicate, there is a continuous increase in gel content for BPO concentration up to 4 phr, and thereafter an equilibrium effect is evident. When the processing time increases (25 min), the gel content is considerably reduced for the same
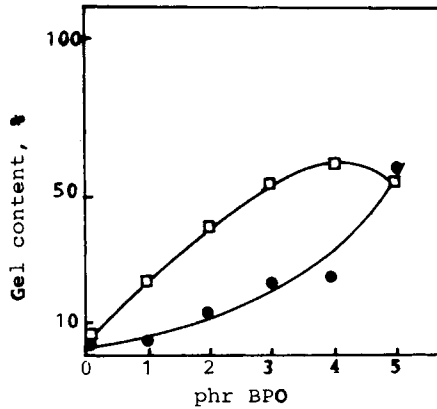
Fig. 6. The gel content as a function of BPO concentration for PE 18 020 processed at 120°C: (●) 25 min processing; (□) 10 min processing.

peroxide percentage and the limiting effect is not observed up to 5 phr BPO. This fact is possibly due to the mastication which occurs simultaneously with crosslinking reaction into the plasticorder mixing head. This process leads to chain scisions and subsequently lowers the gel content. For the same reason, higher peroxide concentrations are effective, since it propagates crosslinking reaction in a further stage, after the network destruction.

Mechanical Properties

The tensile strength of specimens, prepared from PE 18 020 with 2 phr BPO and processed for 10 min in the plasticorder, is plotted versus gel content in Figure 7. In the same figure the tensile characteristics of the specimens derived from the same material mixed for 3 min and cured at 100°C for 5 hours are also shown. Both curves indicate a decrease in tensile strength with gel content and a limiting effect is evident about 30%. On the other hand, the measurements presented in Figure 7 can lead to the conclusion that some inhomogeneity is present in the specimens prepared from the crosslinked
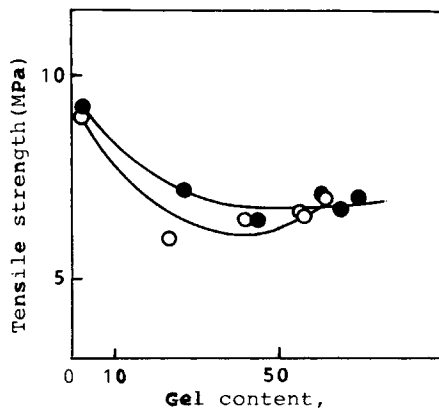

Fig. 7. The tensile strength versus gel content for various processing techniques: (●) 120°, 10 min; (○) 5 hr 100°.
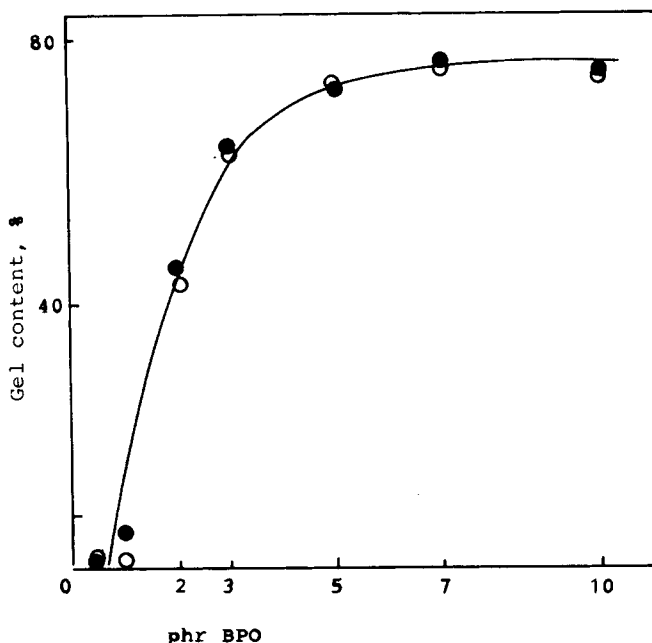
Fig. 8. The repeatability of gel content values for PE 18 020 in powder: (●) 1st run; (○) 2nd run.

samples. This can be attributed to the fast decomposition of BPO at 120°C and the resulting quick reaction, which produces crosslinked areas with more or less dense structure. In the rheological or analytical investigation such variations could not be observed, since the results in these cases, are an expression of the average behavior of a sample. In the case of mechanical testing, an inhomogeneity is a defect which affects decisively the overall behavior of a specimen and it is, therefore, obvious that it can be easily revealed.

Crosslinking of PE Powder

The repeatability of the gel content determinations, as a function of particle size, is shown in Figures 8 and 9. As the curves of Figure 8 indicate, there is a good repeatability when powdered material is used. On the contrary, the use of pellets leads to an inhomogeneous product, especially for BPO concentrations up to 5 phr. For higher concentrations this effect is restricted, since the peroxide is in excess and further consumption eliminates the differences, as Figure 9 demonstrates.

CONCLUSIONS

From the above results, the following conclusions can be drawn: (1) The use of BPO, as a crosslinking agent for low density PE, could be effective especially with powdered resin; (2) The preferred melt flow index values lie within the range 20–40 g/10 min; (3) Temperatures up to 120°C and peroxide
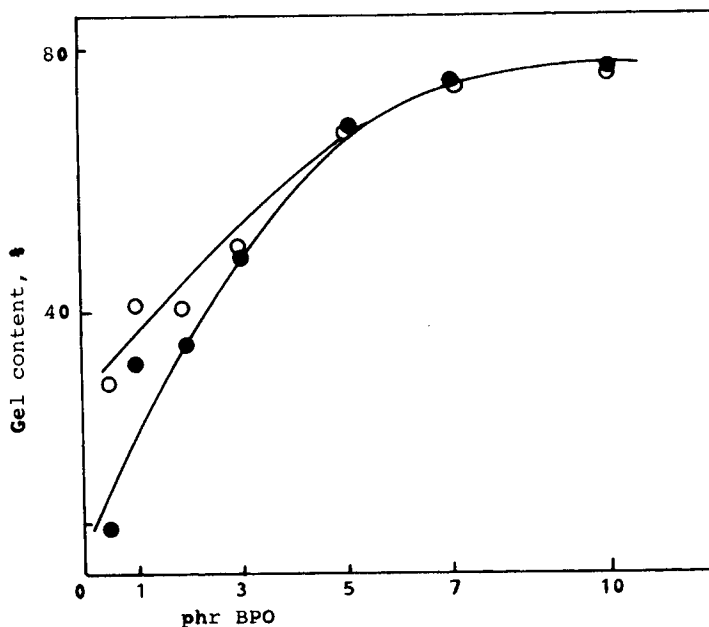
Fig. 9. The repeatability of gel content values for PE 18 020 in pellets: (●) 1st run; (○) 2nd run.

concentrations up to 2 phr are recommended; (4) The mechanical properties of the crosslinked polymer at room temperature, are lowered to some extent.

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