

## Brabender Plasticorder Studies of the Process of Crosslinking Polyethylene

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### Synopsis

The process of crosslinking unfilled thermoplastic polyethylene has been followed with the aid of the Brabender Plasticorder. It is shown that extrusion conditions without any significant scorching can be obtained with this instrument. The maximum torque in the plastograms is discussed and shown not to be a correct criterion of crosslinking efficiency, since its value is influenced by a process of shear grinding of the crosslinked polymer. The crosslinking is further continued after the maximum torque is reached. The dependence of gel content on peroxide concentration is given.

### Introduction

Thermoplastic polyethylene can be converted to a thermoset resin by heating a mixture of polyethylene and suitable peroxides. Crosslinked polyethylene has several advantages over the conventional thermoplastic polymer. Its stress cracking resistance, resistance to chemicals, and thermal stability are all improved. Significant strength is observed at temperatures above the crystalline melting point of the crosslinked polymer.

Commercial extrusion processes for production of filled crosslinked polyethylene as an insulator have been developed by the wire and cable industry. These extrusion processes are characterized by two important stages: (1) extrusion of mixtures of polyethylene-peroxide, with such conditions that no premature crosslinking occurs in the extruder, and (2) the passing of the thermoplastic product through a crosslinking unit maintained at an elevated temperature. The residence time in this unit is such that at the prevailing temperature most of the peroxide is decomposed. Design of crosslinking units is based on peroxide half-life data. Extrusion conditions are so chosen that not more than 1-3% gel is formed in the extruder. Although half-life data and extrusion conditions are fairly well known, laboratory experiments have to be carried out on a new polyethylene, since extrusion and crosslinking processes are influenced by the various additives present in the polymer, its molecular weight, and molecular weight distribution.

Gregorian and Bafford<sup>1</sup> showed that the Brabender Plastograph is a useful tool for the prediction of peroxide crosslinking efficiency and measure-

ment of peroxide stability. According to their results, for complete cure to be obtained the crosslinking time should be about 10 times the half-life of the peroxide. Two peroxides are used today for crosslinking of low-density polyethylene: dicumyl peroxide (Di-Cup) and 2,5-dimethyl-2,5-di-(*tert*-butylperoxy)hexane (DMDBH, or Varox). Benning<sup>2</sup> used a platen press for the determination of crosslinking efficiency (gel percentage) as a function of temperature at various peroxide concentrations. Dannenberg et al.<sup>3</sup> followed the kinetics of dicumyl peroxide decomposition and determined the physical properties of crosslinked polyethylene loaded with carbon black. Benning et al.<sup>4</sup> recently described a system for the production of unsupported crosslinked polyethylene tubes. They assume that 60% gel formation is necessary to produce a crosslinked tube of optimum properties. Carlson<sup>5</sup> followed the change of physical properties of low-density polyethylene crosslinked with Varox as a function of the crosslinking propagation by means of the Williams plastometer. The Brabender Plasticorder proved to be a useful tool for studying carbon black-polymer interaction,<sup>6</sup> and an approximate calibration of shear rates in this instrument was recently reported.<sup>7</sup>

### Experimental

Low-density polyethylene, having a melt flow index of 2 g. per 10 min., a density of 0.922, and a low content of additives, was ground to a powdery form. This powder was thoroughly mixed at room temperature with known amounts of Varox peroxide (50% active), and 30 g. of this mixture were introduced to the roller measuring head of a Brabender Plasticorder, Model PL 3S. The temperature of the measuring head was kept at 75°C. during the feeding stage; then the measuring head was closed, and mixing at a rate of 20 rpm and a circulation of hot oil were started. The temperature of the sheared polymer and torque were recorded as a function of time. These experiments were carried out with different oil-bath temperatures and peroxide concentrations.

At the end of the experiment the crosslinked polymer was removed from the measuring head and reground to a powdery form. A known weight of this powder, kept in a closed-100-mesh pouch, was extracted in boiling toluene, containing 0.5% antioxidant, for 24 hr.<sup>8</sup> The per cent gel was calculated from this test. It was later found that a 12 hr. period of extraction sufficed for a complete extraction.

### Results and Discussion

In Table I experimental details and important results are summarized. The crosslinking time equals the time interval from the beginning of the experiment, as stated in the experimental part of this paper, until the machine was shut down. The torque difference  $\Delta M_{\max}$  equals the difference between the maximum torque obtained in the crosslinking zone and the minimum torque (or plateau torque) in the melting zone before crosslinking sets in. The time before crosslinking sets in equals the time

TABLE I  
 Brabender Plasticorder and Gel Content Results

No.	Bath temp., °C.	Varox, pphr	Crosslinking time, min.	Gel cont., %	$\Delta M_{\max}$ , m.-g.	$t_c^a$ , min.
1	150	1	74	0.3	0	>74
2	160	1	74	0.8	125	13
3	170	1	56	16.5	650	13
4	180	1	26	45.6	650	8.5
5	150	2	100	32.1	550	16
6	160	2	76	56	675	15
7	170	2	26	51.2	700	8
8	140	3	41	—	0	>41
9	145	3	73	—	100	46
10	150	3	81	—	650	17
11	155	3	60	—	650	17
12	160	3	51	55.7	750	9
13	165	3	36	58.4	725	10
14	170	3	32	58.8	675	10
15	180	3	19	59.4	590	7
16	140	5	40	0	0	>40
17	150	5	45	54.3	725	15
18	160	5	24	53.5	675	10
19	170	5	15	48	625	8
20	160	10	24	80.2	600	5
21	170	3	13	16.2	350	8.5
22	170	3	17.5	46.0	650	8
23	170	3	19	52.4	650	8
24	170	3	37	64.9	650	8.5
25	170	0.5	56	0.6	75	22
26	170	2	56	64.1	675	11
27	170	3	56	73	700	8
28	170	5	56	74.6	625	8

<sup>a</sup> Time until crosslinking sets in.

interval from the beginning of the experiment to the point of torque increases owing to crosslinking.

Although the bath temperature was practically constant, it should be noted that the polymer undergoes heating from 75°C. up to a level 10–20°C. higher than the bath temperature. This situation complicates the analysis of the plastograms obtained, from a scientific point of view, since true activation energies and other physical parameters cannot be calculated. However, this system reflects better the extrusion process, in which the polymer is processed from room temperature up to temperatures 20–30°C. higher than its melting point, without any significant scorching. As mentioned, the production of crosslinked polyethylene consists of two main subprocesses, namely extrusion at low temperatures and crosslinking by short exposure to high temperatures. The role of shear is very important in the extrusion part, while the crosslinking part is dependent only on heat transfer, since no shear exists.

Shear rates in the Brabender measuring head<sup>7</sup> resembles average shear rates in extruders (approximated by  $\pi DN \cos \theta/H$ ) operating at velocities suitable for processing polyethylene-peroxide mixtures. It is the authors'

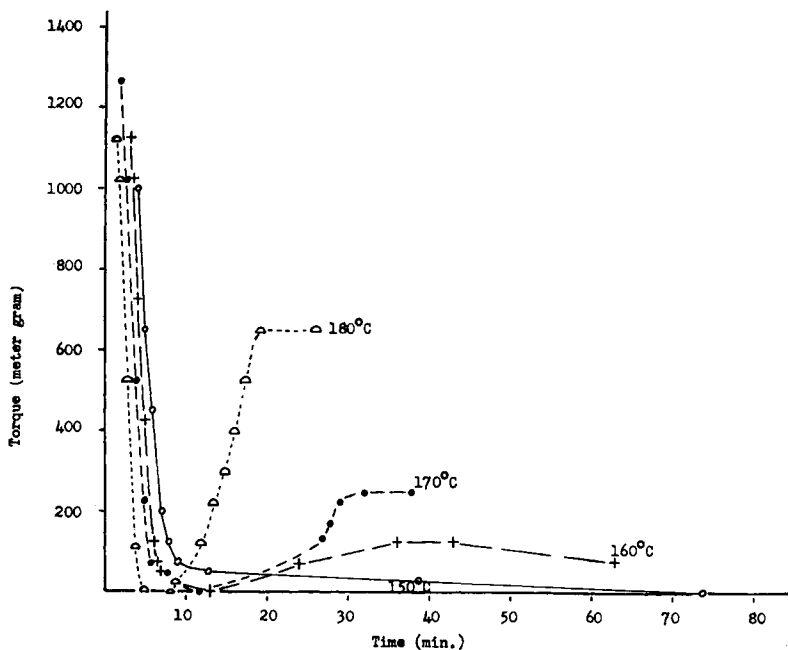


Fig. 1. Plastograms of polyethylene containing 1 pphr Varox, at various bath temperatures.

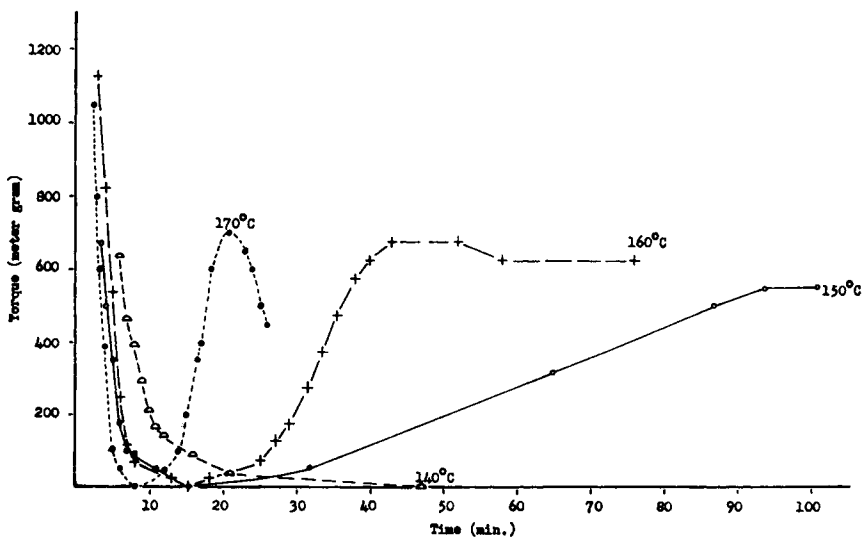


Fig. 2. Plastograms of polyethylene containing 2 pphr Varox, at various bath temperatures.

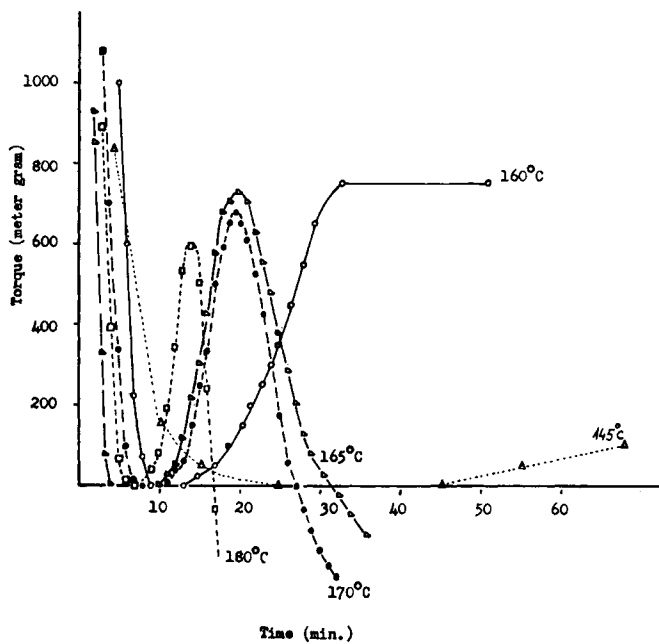


Fig. 3. Plastograms of polyethylene containing 3 pphr Varox, at various bath temperatures.

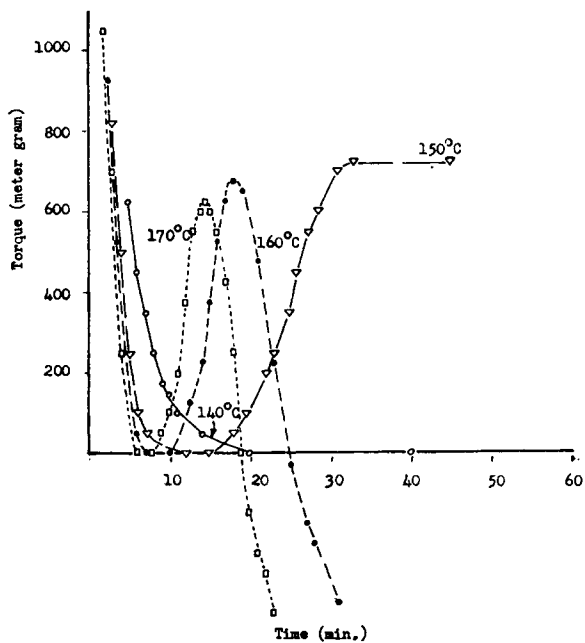


Fig. 4. Plastograms of polyethylene containing 5 pphr Varox, at various bath temperatures.

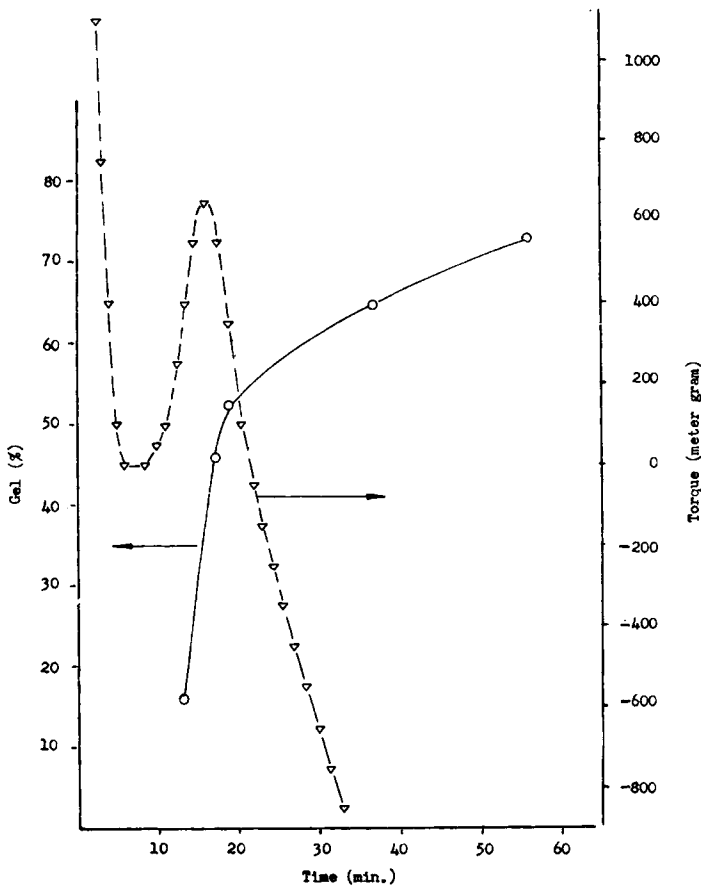


Fig. 5. Crosslinking propagation during plastogram determination; 3 pphr Varox at 170°C.

opinion that the Brabender Plasticorder is a useful tool for the prediction of safe processing conditions in extruders, but crosslinking conditions are better described at present by compression-molding. It is believed, however, that suitable measuring heads operated at lower rotation velocities (in order to minimize shear) can yield significant results concerning the crosslinking part.

In Figure 1 plastograms of polyethylene containing 1 pphr Varox are shown at several bath temperatures (torque in all figures indicates torque difference defined as the minimum torque in the melting zone subtracted from any point torque). At 150°C. no significant crosslinking occurs, whereas at 160°C. a clear torque increase is observed, although only 0.8% gel is obtained after 63 min.

At 170 and 180°C. bath temperature a sharp torque increase is observed. It should be noted that torque increase results in temperature increase, which partially compensates the former by lowering polymer viscosity.

Analysis of the plastograms given in Figure 1 with the aid of polymer temperature profiles (not given), while it is borne in mind that the average residence time of the polymer in the extruder is of the order of 3 min., shows that this mixture can be safely extruded at temperatures up to 155°C.

In Figure 2 plastograms of polyethylene containing 2 pphr Varox are shown. At a temperature of 150°C. significant crosslinking is observed, and comparison with Figure 1 leads to the conclusion that safe extrusion conditions not only are temperature-dependent but also are a function of

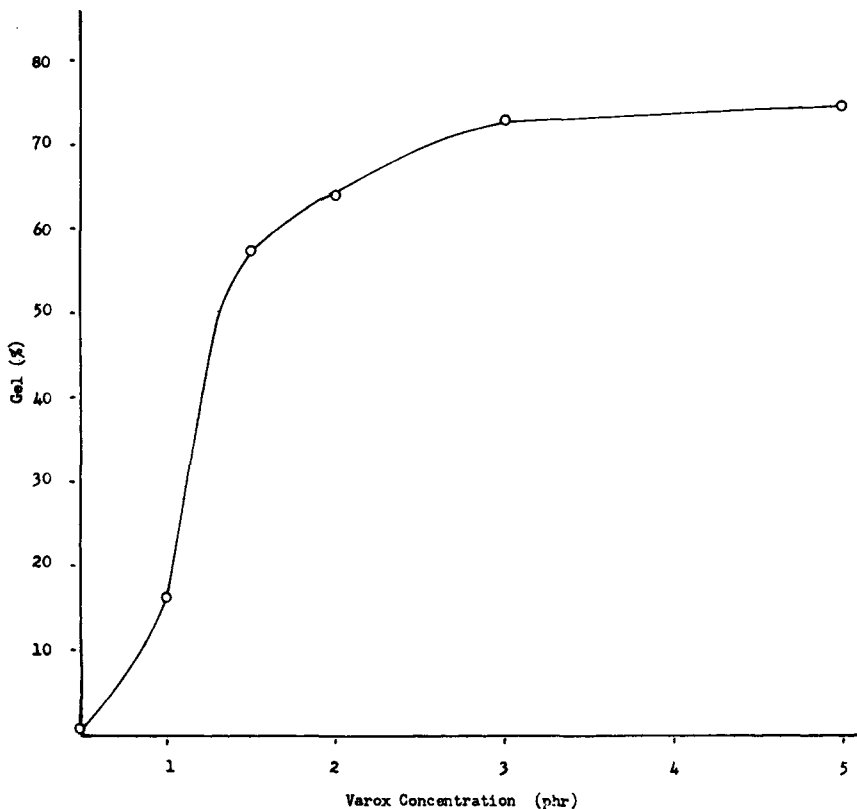


Fig. 6. Dependence of gel content on Varox concentration. Experiments ended beyond the maximum torque at an equal time; 56 min. (crosslinking time) at 170°C.

peroxide content. Again, analysis shows that this mixture containing 2 pphr Varox can be safely extruded at temperatures up to 145°C. At 160 and, better, at 170°C. the plastograms reach a maximum and then decrease; a sharp decrease is observed at 170°C. The polymer removed from the measuring head after 26 min. at 170°C. appears as a nonsticky powder containing 51.2% gel. If the experiment is continued beyond the 26 min. shown at 170°C., the torque might drop to zero. This phenomenon is a result of "shear grinding" of the polymeric mass, the elastic part of

which becomes more important with crosslinking propagation. The phenomenon of shear grinding is one of the main reasons which lead the authors to believe that the Brabender Plasticorder in its present form cannot give correct information related to the crosslinking process. At 160 and 170°C. the gel contents (see Table I) are 56 and 51.2%, respectively. This discrepancy is a result of different mixing periods in the measuring head. The mixing time at 160°C. is much longer, and a higher gel content is obtained at the lower temperature.

Figures 3 and 4 are plastograms made at higher peroxide content. The importance of shear grinding becomes greater as the peroxide content increases; that is, at a higher peroxide concentration the sharp torque decrease is obtained faster. It is clearly seen that the maximum torque before shear grinding decreases as the bath temperature increases. There are indications that the grinding action becomes significant above a certain gel content, and it is clear that this gel content is reached faster when higher temperatures are used. Again, analysis shows that these mixtures, containing 3 and 5 pphr Varox, can be safely extruded at 145 and 140°C., respectively. In conclusion, with low peroxide concentrations the maximum safe extrusion temperature is rather markedly changed, whereas with higher peroxide concentrations the maximum extrusion temperature is changed only slightly.

Gregorian and Bafford<sup>1</sup> used the torque difference  $\Delta M_{\max}$  as a criterion of crosslinking efficiency. It is the authors' opinion that, owing to the grinding action,  $\Delta M_{\max}$  is not a suitable criterion of crosslinking. At the maximum torque the gel content is still rather low and, although beyond this point there is a torque and temperature decrease, the crosslinking process continues further. This situation is confirmed in Figure 5, which is a result of five experiments identical except for duration. Figure 5 shows that about 40% gel is formed when the torque reaches its maximum value, and beyond the maximum torque the gel content increases up to 73% or more. Thus, the decrease of the maximum torque with bath temperature increase (see Figs. 3 and 4) cannot be attributed to crosslinking efficiency decrease, since the final value of  $\Delta M_{\max}$  is a result of competing processes of crosslinking and grinding.

According to Figure 5, in order to determine the dependence of the gel content obtained, as function of peroxide concentration, one should recall that time is a very important factor, even when the experiments are carried out beyond the maximum torque.

In Figure 6 the dependence of gel content on peroxide concentration is shown. The clear picture is due to the fact that all experiments were discontinued at the same time, namely 56 min. Actually a common time basis alone does not provide a complete definition, since the time should also be long enough to reach the region of slow crosslinking rate but not too long for thermal degradation to set in. The longest permissible time is easily obtained by running an experiment with the pure polymer and determining the heat stability period.



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