

Heat Stability of Chemically Crosslinked Polyethylene

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Synopsis

Heat stability in air of chemically crosslinked polyethylene loaded with medium thermal (MT) carbon black was studied as a function of temperature and carbon black content. Weight loss at 200° to 250°C is practically independent of the carbon black concentration. Modulus-temperature curves are changed with various heat treatment periods at 225°C. These curves show that the rubbery modulus (amorphous state) increases with increasing the heating period, while the modulus of the partially crystalline polymer goes through a minimum and then increases. Continuous stress-relaxation and intermittent stress curves show the existence of degradation and crosslinking reactions, the latter becoming more important at higher temperatures or longer times. The degradation reaction is practically independent of the carbon black content while the crosslinking reaction at 225°C is faster with increasing MT black concentrations. It is concluded that reasonable heat stability, in the crosslinked polyethylene compounds studied, can be obtained at temperatures lower than 150°C.

INTRODUCTION

In a recent publication¹ preliminary results on the heat stability of chemically crosslinked polyethylene were presented. The effect of medium thermal (MT) carbon black on heat stability was studied by measuring modulus-temperature curves at a constant heating rate in the temperature region of 140° to 320°C. These curves measured with the Gehman apparatus have shown that at a heating rate of approximately 2°C/min in air, degradation reactions begin at 210° to 220°C; but at slightly higher temperatures, namely 230° to 240°C, crosslinking reactions become more important. Stress relaxation studies in air at 250°C of samples containing 50 pphr MT carbon black have shown that the intermittent stress² increases rapidly from the very beginning of the experiment. The continuous stress-relaxation curve initially exhibits a rapid stress decrease and a minimum stress is achieved after about 30 min. The continuous stress then increases rapidly. The dependence of the continuous stress-relaxation curve on the crosslinking does not permit the use of the "continuous and intermittent stress-relaxation technique."

In the present work heat stability is studied as follows: (a) weight loss at 225°C in air as function of time for various concentrations of MT carbon black; (b) modulus-temperature curve as function of various heat treatment periods at 225°C in air; (c) continuous stress-relaxation and inter-

mittent stress curves at various temperatures and MT carbon black concentrations.

EXPERIMENTAL

One hundred parts of powdery low-density polyethylene with melt flow index of 2 g/10 min were dry blended with 3 parts Varox peroxide (50% active, Vanderbilt), 0.5 parts antioxidant (Agerite resin D, Vanderbilt), and various proportions of MT carbon black (Cabot). The formulations of the experimental samples are summarized in Table I. The dry blends were mixed on a roll mill and then press cured.³

TABLE I
Polyethylene-MT Black Formulations (Weight Units)

Polyethylene	Varox	Agerite resin D	MT black	Gel content
100	3	0.5	0	79.5
100	3	0.5	5	78.0
100	3	0.5	15	77.0
100	3	0.5	50	80.0
100	3	0.5	100	81.0

Samples of 1 in. \times 1 in. were cut from the press-cured sheets and used for determination of weight loss versus time at 225°C in air.

The effect of heat treatment was studied on the unloaded crosslinked polyethylene. Samples were kept at 225°C in air for various periods. After cooling, modulus-temperature curves were determined by using the Gehman apparatus.

Continuous stress-relaxation and intermittent stress curves were determined in air at various temperatures. The imposed tensile strain was 6%.

RESULTS AND DISCUSSION

In Figure 1, weight loss, calculated on the original sample weight, is plotted versus time for the various MT carbon black concentrations. At a given time the weight loss is higher for a lower concentration of carbon black. This result is expected since a lower MT black concentration means a higher concentration of the other components which are the sources for the production of volatile compounds. Figure 1, however, does not supply the answer as to whether MT carbon black has an effect on the mechanisms leading to the formation of volatile compounds. In order to analyze the role of MT black on weight loss, the latter quantity has to be calculated on a carbon black-free basis. One has also to consider the thickness of the samples because the rate of weight loss is a diffusion process. Figure 1 is accordingly replotted as shown in Figure 2 by recalculating the weight loss on a carbon black-free basis and multiplying this quan-

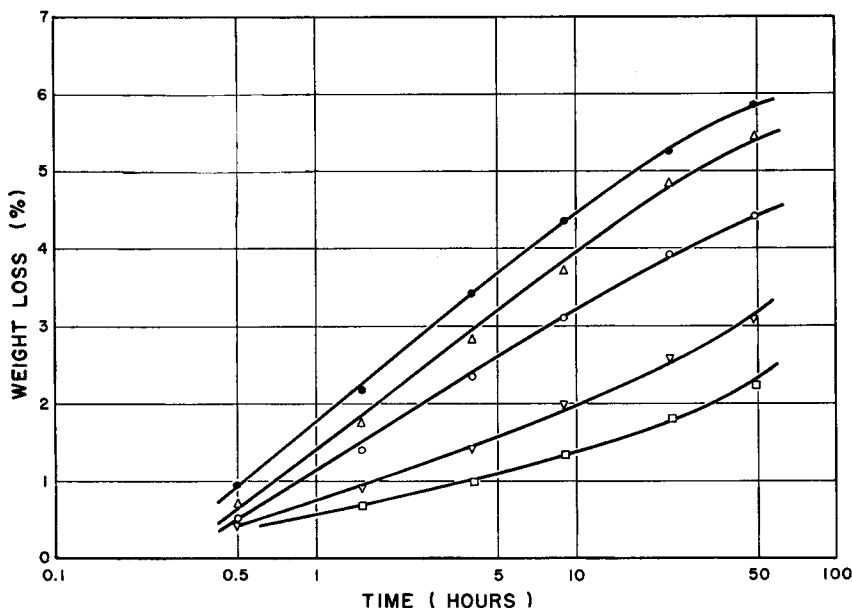


Fig. 1. Polyethylene weight loss versus time at 225°C. MT carbon black concentration: (●) unloaded; (Δ) 5 pphr; (○) 15 pphr; (∇) 50 pphr; (□) 100 pphr.

tity by the sample thickness. In the present work the thickness correction is important since the latter varied from 1.8 to 3 mm. Figure 2 shows that the weight loss is independent of MT black concentration at least up to about 15 hr at 225°C in air. Similar conclusions resulted from weight loss studies at 200° and 250°C.

In Figure 3 shear modulus, $G(10)$, is plotted versus temperature for the unloaded crosslinked polyethylene after various heating periods at 225°C in air. At this temperature the polymer undergoes both degradation and crosslinking reactions, where the latter reaction becomes more important. These reactions undoubtedly affect the crystallinity content of the polymer, and lower crystallinity content is expected with longer heat treatment periods. It has been shown that crystallinity content decreases with increasing the peroxide concentration in chemically crosslinked polyethylene,^{3,4} and the same tendency is expected if further crosslinking is achieved by heating the polymer at elevated temperatures in air. The modulus at temperatures below the crystalline melting point depends on both crystallinity content and concentration of crosslinks. Higher crystallinity content and crosslink density result in a higher modulus. In the present case the change in the modulus (at temperatures below the crystalline melting point) due to heating at high temperatures is governed by the relative importance of crosslink density increase and crystallinity content decrease. This behavior is clearly shown in Figure 3 if shear moduli after various heating periods are compared at a common temperature, say 90°C. After 1 hr of heating at 225°C the modulus is about 35% lower than the modulus

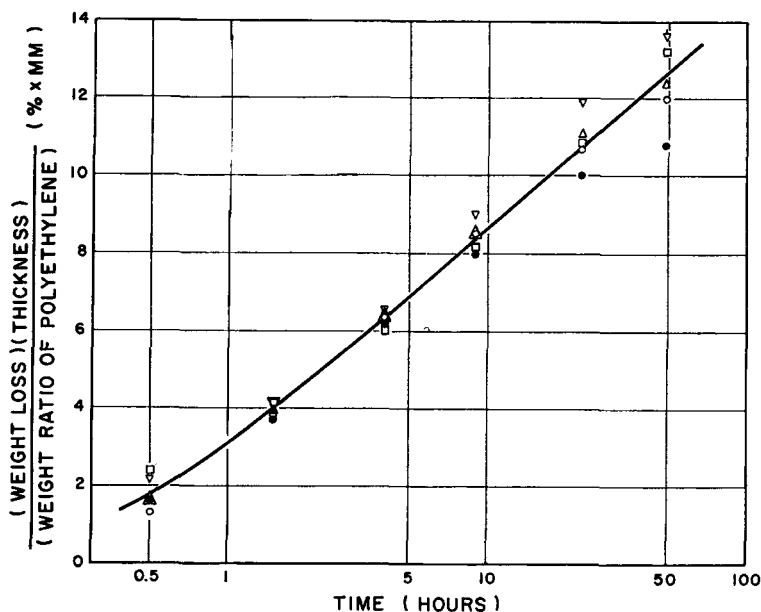


Figure 2. Polyethylene weight loss times thickness on a carbon black-free basis, 225°C. MT carbon black concentration: (●) unloaded; (Δ) 5 pphr; (○) 15 pphr; (▽) 50 pphr; (□) 100 pphr.

corresponding to the untreated sample, while after 3 hr of heating the modulus is only 24% lower than the latter. After 3 hr of heating the effect of increasing crosslink density becomes more important than the accompanied crystallinity decrease. After 10 and 47 hr of heating, the modulus at temperatures below the crystalline melting point is higher than the modulus of the untreated polymer due to the heavy crosslink density achieved. Above the melting region the rubbery modulus is a function of the number of crosslinks per unit volume, the change of which is governed by the relative importance of the degradation and crosslinking reactions. Figure 3 shows that the crosslinking reaction is the important one, since even under 1 hr of heating at 225°C a significant modulus rise is found. According to our previous results¹ it is believed that a modulus decrease exhibiting the presence of the degradation reaction can be found if samples are heat treated at 225°C for short periods, say a few minutes, but this has not been checked experimentally. The discussion of the modulus change below and above the crystalline melting region explains the intersection of the modulus-temperature curves for 0, 1, and 3 hr of heating periods shown in Fig. 3. It is also interesting to notice that a rather high proportion of the crystallinity content is retained even under 47 hr of heating as shown by the clear melting region in the corresponding modulus-temperature curve. Overly long heating periods resulted in small cracks and voids in the samples. The decrease of modulus with temperature within the rubbery region of the samples heated for 10 and 47 hr is apparently due to the

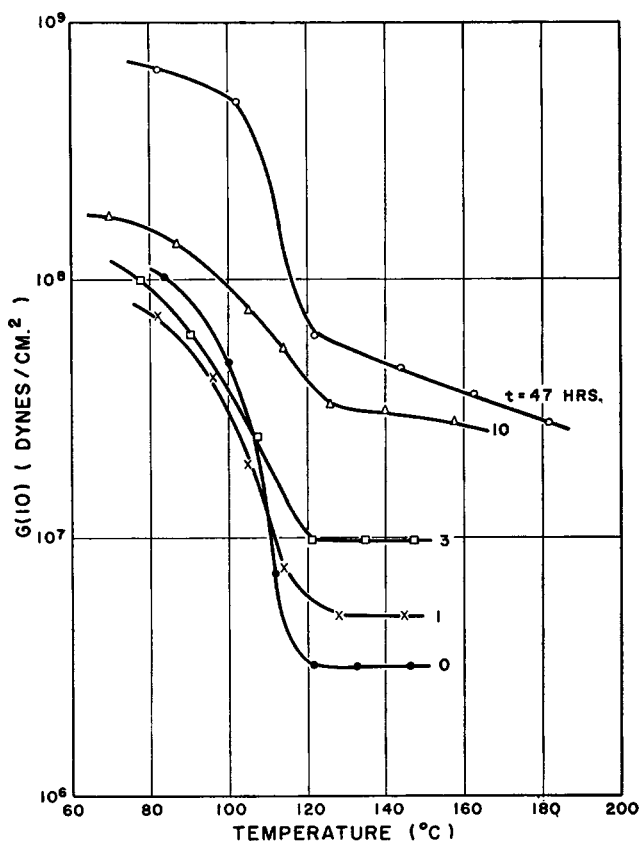


Figure 3. Polyethylene modulus-temperature curves after various periods of heating at 225°C in air.

presence of these cracks and voids, which keep growing under additional twisting of the samples during each reading. The heat treatment process at elevated temperatures in air should be further studied from a practical point of view. If the 3-hr heating period is taken as an example, one can see that the modulus below the crystalline melting point is practically unchanged while the rubbery modulus rises by a factor of about three.

Continuous stress-relaxation and intermittent stress curves at various temperatures are shown in Figures 4, 5, and 6 for unloaded, 15- and 50-pphr MT carbon black compounds, respectively.

Comparison of the short-time moduli at 200°C in Figures 4, 5, and 6 shows that similar values are obtained. Thus the influence of MT carbon black concentration on the rubbery modulus is practically insignificant. This conclusion is in agreement with our previous results¹ in which it has been shown that the rubbery shear modulus, $G(10)$, in practice does not depend on the carbon black concentration for 0 to 100 pphr black.

In our previous paper,¹ shear modulus-temperature curves determined at a heating rate of about 2°C/min were presented. These curves exhibit the

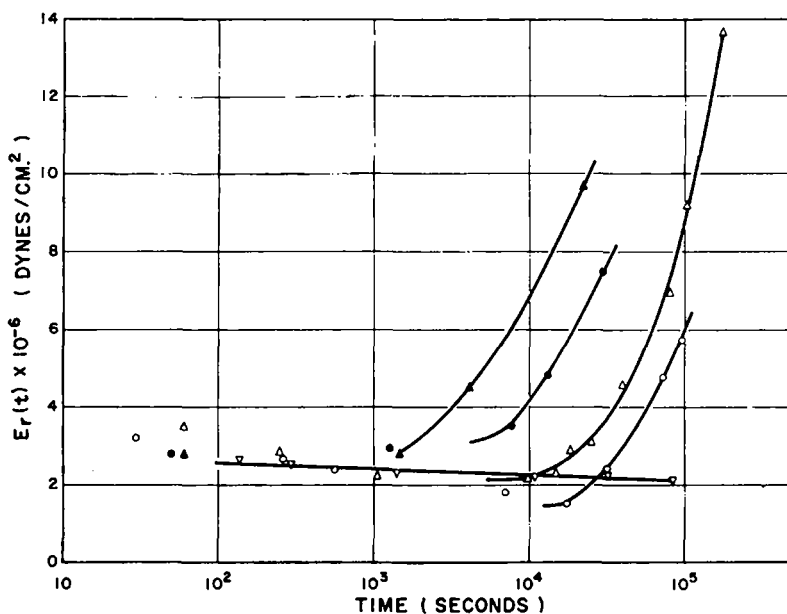


Figure 4. Stress-relaxation and intermittent stress curves for unloaded crosslinked polyethylene: (∇) 150°C., continuous; (O) 200°C, continuous; (\bullet) 200°C, intermittent; (Δ) 225°C, continuous; (\blacktriangle) 225°C, intermittent.

existence of both degradation and crosslinking reactions with the former predominating at first, while the latter becomes much more important at slightly higher temperatures. No chemical reactions occurred up to about 210° to 220°C at the above-mentioned heating rate. The time variable which was kept constant in the previous work is studied in the present article.

The "continuous and intermittent stress-relaxation" technique² was suggested as a tool for the separation of degradation and crosslinking reactions. This method is valid if the continuous stress-relaxation curve exhibits degradation processes to the first approximation while the intermittent stress reflects the combined effect of degradation and crosslinking. If these assumptions hold, then the difference between the intermittent and continuous curves at a certain time represents the contribution of the linking reaction. One should also assume that a crosslinked network in its rubbery state should exhibit little stress decay with time. In Figure 4, the behavior of unloaded crosslinked polyethylene in continuous stress-relaxation and intermittent stress is shown. Comparison of the continuous stress-relaxation curves at 150° and 200°C shows that at the higher temperature, a faster stress relaxation occurs up to about 10^4 sec. Thus at 200°C the stress decay is mainly due to the degradation reaction which is taking place. Comparison of the continuous and intermittent curves at a common temperature shows that the differences between the two curves are rather small for an initial time period whose length is temperature

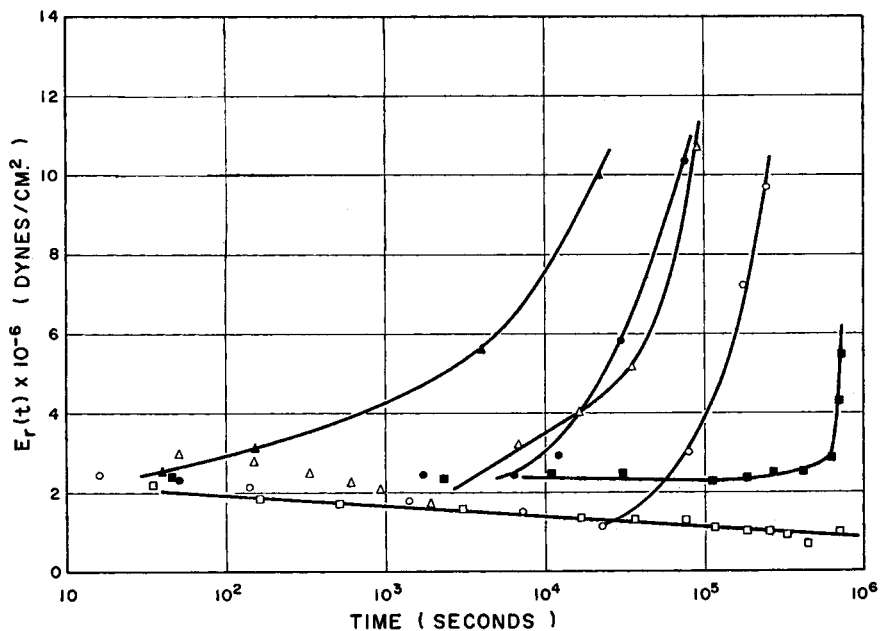


Figure 5. Stress-relaxation and intermittent stress curves for crosslinked polyethylene loaded with 15 pphr MT carbon black: (\square) 175°C, continuous; (\blacksquare) 175°C, intermittent; (\circ) 200°C, continuous; (\bullet) 200°C, intermittent; (\triangle) 225°C, continuous; (\blacktriangle) 225°C, intermittent.

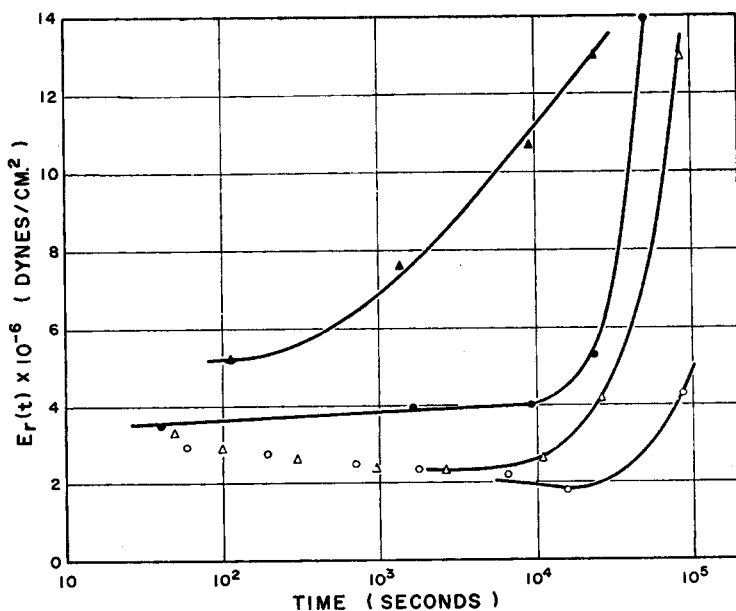


Figure 6. Stress-relaxation and intermittent stress curves for crosslinked polyethylene loaded with 50 pphr MT carbon black: (\circ) 200°C, continuous; (\bullet) 200°C, intermittent; (\triangle) 225°C, continuous; (\blacktriangle) 225°C, intermittent.

dependent and decreases with temperature increase. In this initial period, degradation therefore is the important reaction. When crosslinking commences, the intermittent stress curve rises while the continuous stress-relaxation curve decreases, reflecting mainly the degradation process. When a rather high crosslink density is achieved, the nondependency of the continuous stress-relaxation curve on crosslinking reaction does not hold any more and the continuous curve begins to rise, probably due to the sample contraction under the increasing crosslinking density. It is approximately the time interval between the beginning of the experiment and the minimum modulus in the continuous stress-relaxation curve that can be analyzed by the continuous and intermittent stress-relaxation technique. One of the main difficulties in the above-mentioned technique is concerned with the significance of the preheating stage until the experiment is begun. The length of this period is generally about 2 hr starting from room temperature. Such a time period cannot be neglected if studies at 225° and 200°C are made (see Fig. 4).

In Figures 5 and 6, continuous stress-relaxation and intermittent stress curves are presented for crosslinked polyethylene containing 15 and 50 pphr MT carbon black. Comparison of Figures 4 to 6 shows that the degradation reaction is practically independent of the carbon black content. The crosslinking reaction at 225°C as shown by the intermittent stress curves is faster with increasing carbon black content from 0 to 50 pphr. This result is in agreement with our previous data¹ found by modulus-temperature studies at high temperatures. At 175°C a high crosslinking rate occurs after about a week and at 200°C, after about 3 hr (Fig. 5). According to these results it seems that the compounds of crosslinked polyethylene studied in the present work can practically be used in air for reasonable time periods only at temperatures below 150°C.

The maximum temperature of use can be raised, however, by better stabilization systems. In addition, the effect of gel content on heat stability should be further studied.

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