

Chemically Crosslinked Polyethylene: Modulus-Temperature Relations and Heat Stability

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Synopsis

The influence of MT black concentration on the shear modulus of low-density crosslinked polyethylene can be approximated by the Guth-Gold equation, at temperatures below the crystalline melting zone. Above the melting zone shear modulus does not depend practically on the carbon black level. At high temperatures both degradation and crosslinking reactions are taking place. The variation of the shear modulus with temperature due to these reactions is shown for various carbon black loadings. A preliminary chemical stress-relaxation study at 250°C is presented.

INTRODUCTION

Carbon black is a useful filler for polyethylene compounds; however, only low black concentrations can be added to the thermoplastic polymer since higher loadings result in inferior properties. Crosslinking of the polyethylene-black compound by irradiation or chemical means permits the incorporation of higher black concentrations. The black is tightly bound in the polymeric network and cannot be removed by refluxing samples in good polyethylene solvents. Only in the case of insufficient crosslinking does the solution become black due to partial carbon black separation.

The properties of unloaded crosslinked low-density polyethylene do not differ appreciably from the properties of the original polyethylene at room temperature.^{1,2} This phenomenon is due to the rather low degree of crosslinking actually achieved and to the relatively small decrease in crystallinity content as a result of crosslinking. The main differences between the thermoplastic and crosslinked polyethylene are found at temperatures above the crystalline melting point where the crosslinked polymer behaves as a soft rubber, while the thermoplastic polyethylene has no significant strength above the melting temperature.

The incorporation of carbon black alters the properties over the whole temperature range. The brittle point and yield stress increase with the black concentration.³ Carlson⁴ has shown from stress-strain measurements at room temperature that the modulus increases and elongation decreases with increasing black content. The tensile strength at 302°F was found to increase with the black concentration, while at room temperature tensile strength was practically unaffected.⁵ These results show that the role of

carbon black in crosslinked polyethylene should be studied separately below and above the crystalline melting point since one cannot carry any conclusions from one temperature region to the other.

Crosslinked polyethylene has interesting properties above its melting point, and it is therefore important to study the heat stability of these compounds. It is well known that hydrocarbon rubber networks might undergo both degradation and crosslinking⁶ and the existence of these processes limits the highest use temperature.

EXPERIMENTAL

One hundred parts of powdery low-density polyethylene with melt flow index of 2.0 were dry blended with three parts Varox peroxide (50% active, Vanderbilt), 0.5 parts antioxidant (Agerite resin D, Vanderbilt), and various proportions of carbon black (MT black, Cabot). These mixtures were further mixed on a two roll mill for short periods and at temperatures only slightly above the polymer melting point. The crude thermoplastic sheets were then press cured in an ASTM mold at 200°C for 30 min. Gel content was determined in boiling toluene.⁷ Shear modulus G as a function of temperature was measured by using the Gehman and Clash Berg instruments. Deflection readings were taken in all cases after 10 sec.

RESULTS AND DISCUSSION

Table I summarizes the compounds prepared in the present work and their gel content. In previous studies it was shown that the gel content in crosslinked polyethylene depends on the peroxide concentration and specific polymer.⁸ According to Table I, MT black has practically no influence on the crosslinking process in agreement with the other authors.³

In Figure 1 shear modulus is plotted against temperature. At temperatures lower than the crystalline melting point a clear picture is obtained: namely higher modulus is associated with higher black concentrations at the same temperature. In the melting zone these curves practically coincide; thus the black level has no significant influence on this zone. Above the melting zone the polymers behave as true elastomers. In this temperature region the differences between the modulus values for the various compounds are smaller than those found in the region below the melting zone.

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%

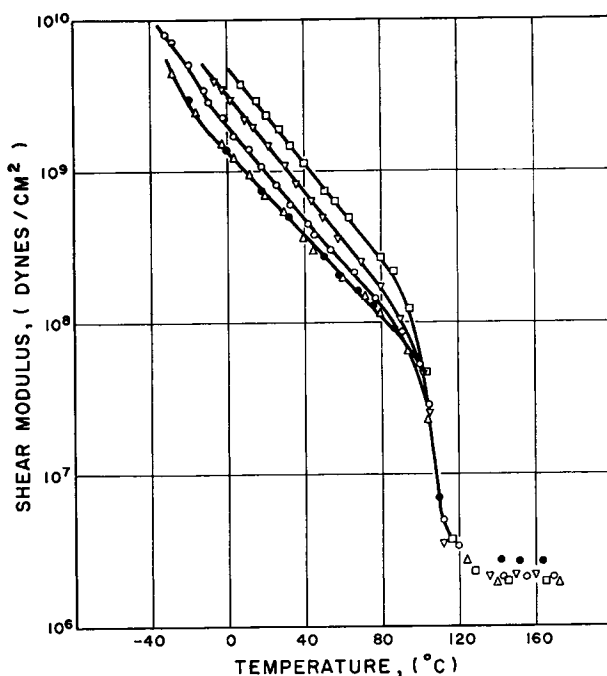


Fig. 1. Modulus vs. temperature for crosslinked polyethylene containing various concentrations of MT black. MT carbon black: \square) 100 PPHR; ∇) 50 PPHR; \circ) 15 PPHR; Δ) 5 PPHR; \bullet) unlocked.

In addition, the curves are not positioned systematically according to the black level. It seems, therefore that the MT black concentration has only a minor influence on the rubbery shear modulus of these compounds. Previous stress-strain measurements² at 135°C have shown that the initial tensile modulus (at zero stress) increases very slightly with the black level at low strain rates (0.13%/sec). Higher modulus increase with increasing the black concentration was found at higher rates of straining (3.3%/sec).

The incorporation of a rigid filler which does not interact with the polymer is often described by the Guth-Gold equation:⁹

$$M = M_0 (1 + 2.5C + 14.1C^2) \quad (1)$$

where C is the volume fraction of filler and M is the modulus. The volume fraction C was calculated assuming a density of 1.86 for the MT black. In Figure 2 experimental modulus-temperature data are compared with calculated curves according to eq. (1) in the temperature range of -20 to 100°C . The calculated curves in Figure 2 were obtained using eq. (1) and the modulus-temperature curve for the unloaded polyethylene. The good agreement between eq. (1) and experimental modulus values shows that practically MT black behaves as a filler which does not interact appreciably with the polymer, at least under the testing conditions in the present work.

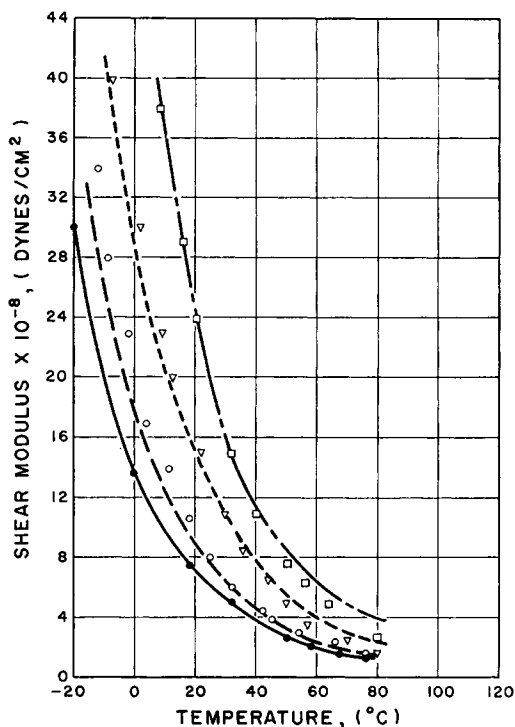


Fig. 2. Comparison of experimental modulus-temperature data with calculated modulus temperature curves according to eq. (1). MT carbon black: 100 PPHR, exp. \square , calc. —; 50 PPHR, exp. ∇ , calc. - - - -; 15 PPHR, exp. \circ , calc. — · — ·; unloaded, exp. \bullet .

One should expect lower interaction degree at temperatures above the crystalline melting point since this transition is accompanied by a rather high volumetric expansion. This expectation is actually confirmed experimentally in Figure 1 and as was previously mentioned in the discussion of the stress-strain measurement at a low rate of straining.

The heat stability in air of crosslinked polyethylene loaded with various amounts of carbon black was measured using a high temperature Gehman apparatus. Modulus measurements were begun at 140°C and the heating rate was about 2°C/min. Any sharp deviation from the rubbery modulus is a result of chemical reactions which change the material structure. The main processes which may take place are degradation and/or crosslinking and both influence the value of the modulus. Carbon black may influence these processes and it is also possible that it takes part in the reactions. More elaborate techniques such as continuous and intermittent stress-relaxation are needed to permit the distinction between crosslinking and degradation.⁶ In Figure 3 the ratio of a modulus G' at a given temperature to the rubbery modulus G in the temperature region where no chemical reactions take place is plotted against temperature. This ratio (G'/G)

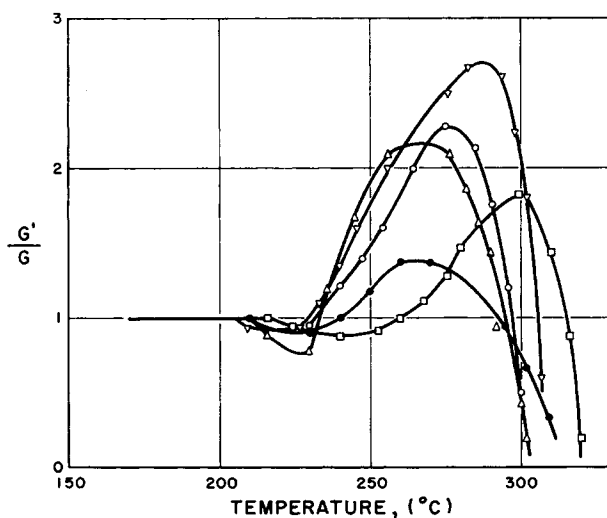


Fig. 3. (G'/G) vs. temperature for crosslinked polyethylene containing various concentrations of MT black at the high temperature region. MT carbon black: \square) 100 PPHR; ∇) 50 PPHR; \circ) 15 PPHR; Δ) 5 PPHR; \bullet) unloaded.

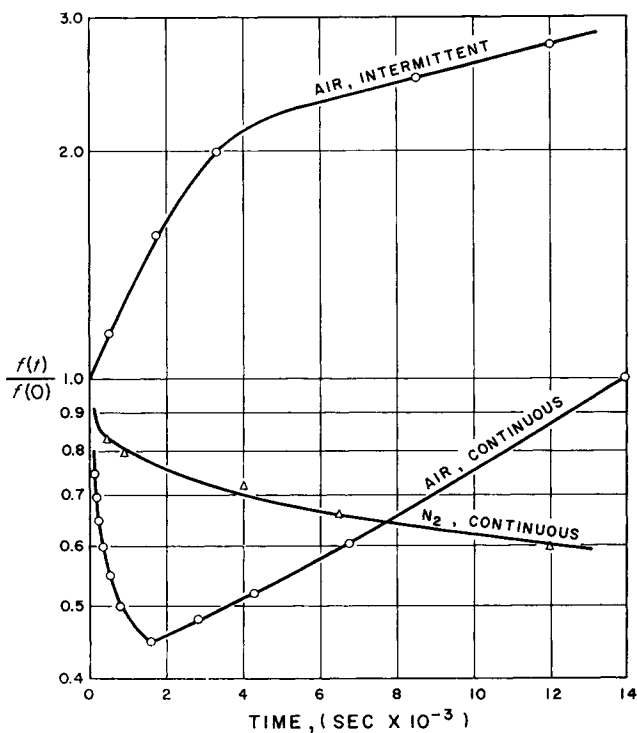


Fig. 4. Continuous stress-relaxation and intermittent-stress measurements at 250°C and 4% elongation for crosslinked polyethylene containing 50 pphr MT black.

begins to decrease at the temperature range of 210 to 220°C and then a sharp increase occurs at the temperature range of 230 to 240°C. It can be seen that degradation is effective initially but at slightly higher temperatures the crosslinking reaction becomes more important. The regions for significant initiation of degradation and crosslinking are rather narrow and are therefore practically independent of the MT black concentration. The black content has a significant influence after the ratio (G'/G) begins to rise. Here the slope $d(G'/G)/dT$, the value of $(G'/G)_{\max}$, and the temperature corresponding to $(G'/G)_{\max}$ all depend on the carbon black concentration.

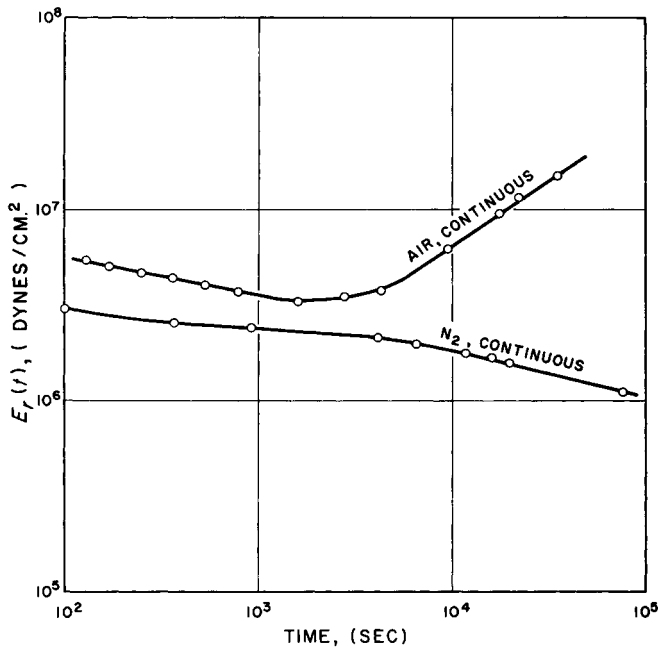


Fig. 5. $E_r(t)$ vs. time at 250°C and 4% elongation for crosslinked polyethylene containing 50 pphr MT black.

The slope $d(G'/G)/dt$, in the rising modulus region, increases with the black concentration and then decreases. The curve for 5 pphr black is an exception in this case. The temperature corresponding to $(G'/G)_{\max}$ increases with the black concentration, and the highest value of $(G'/G)_{\max}$ is obtained at about 50 pphr black.

It should be pointed out that the molding conditions of the samples examined in this work were such that the molding period was many times more than the peroxide half lifetime; thus all the peroxide is assumed to be decomposed. The present data are not sufficient to conclude whether the MT black takes place in the chemical reactions which occur at high temperatures and this point will be further studied by comparing chemical stress-relaxation curves of unloaded and loaded crosslinked polyethylene.

A preliminary stress-relaxation study was carried out on the crosslinked polyethylene containing 50 pphr MT black. Continuous stress relaxation was measured under air and nitrogen, and intermittent stress was measured under air. All measurements were carried out at 250°C, a temperature which is well within the region of fast chemical reactions. In Figure 4 the ratio of the time-dependent force $f(t)$ to the initial force $f(0)$ is plotted against time. Under nitrogen the stress decays continuously, while under air the continuous stress-relaxation curve is composed of an initial part of sharp stress decay followed by a steady stress increase which should be attributed to the sample contraction due to the rapidly increasing crosslinking density. The intermittent-stress curve under air is shown to increase from the very beginning of the experiment, manifesting the rapid crosslinking process taking place in agreement with Figure 3. Separation of the degradation and crosslinking processes by the "continuous and intermittent stress-relaxation" technique is not possible in this case since the assumption of the dependency of the continuous curve on degradation only is not valid here. Another interpretation of the continuous stress-relaxation data for longer times is shown in Figure 5 by plotting $\log E_r(t)$ against $\log t$. The relaxation curve under air can be approximately described by two straight lines separated by a rather narrow "transition zone." $E_r(t)$ under air is always higher than $E_r(t)$ under nitrogen, and this is due to the new crosslinked junctions which were formed in the preheating stage before the experiment was begun. It is expected that at lower temperatures, say 225°C, the relaxation region in which the crosslinking reaction has only a minor effect would be much wider, thus enabling the use of the "continuous and intermittent stress-relaxation" technique.

The partial support of the Office of Naval Research is gratefully acknowledged.

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Received January 22, 1969