

## High Speed Tensile Testing as an Index of the Oxidative Degradation of Polyethylene Resins

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### Synopsis

A study was made of the tensile properties of two polyethylene resins incrementally oxidized on a two roll mill at 160°C. Changes in tensile parameters were related on a theoretical basis to the net effect of crosslinking and chain scission, and compared with solution viscosity measurements for the same materials. It was shown that polymeric oxidative degradation was affected by molecular weight distribution and by crystallinity. In addition, measurement of properties over 5 decades of time revealed a "critical velocity," reflecting a relatively sensitive measure of degradation. High speed tensile tests provided a useful diagnostic tool for detecting early evidence of molecular decomposition in the materials studied.

### Introduction

Tensile properties obtained under the conventional static speeds of testing (0.2-10 in./min.) were shown in a previous study<sup>1</sup> to have a greater diagnostic value than solution viscosity, melt index and zero strength temperature measurements in following the relative degree of cross linking and chain scission occurring in polyethylene while being incrementally oxidized on a 2-roll mill. Two resins, Alathon 10 (having a broad molecular weight distribution) and Alathon 20 (having a narrow molecular weight distribution) were studied. Specimens were molded from both materials subjected to various periods of time on a mill, by (1) quenching and (2) cooling slowly, in order to separate out the effects of crystallinity.

Some interesting results as a function of testing speed were noted, even within the narrow range reported. It is the object of this paper, to present tensile data on these same materials at rates of loading up to 10,000 in./min. and to discuss the criterion of rate sensitivity as it may be used to evaluate the oxidative degradation of polymeric substances, with particular emphasis on the effects of molecular weight distribution and crystallinity.

### Tensile Measurements

Tensile tests were conducted at 0.2 and 10 in./min. on an Instron Model TTC† and at 100, 1000, and 10,000 in./min. on a Plastechon Model 581.‡

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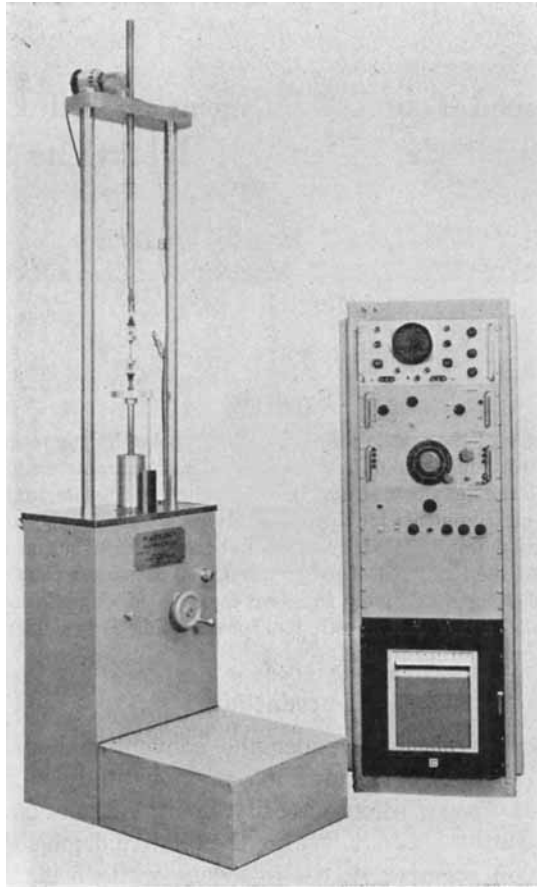


Fig. 1. Plastechon, 581, a universal tester capable of measuring tensile, flexural, and compressive properties at rates of loading from 50 to 15,000 in./min.

The Plastechon 581 is a universal tester capable of measuring tensile, flexural, and compressive properties at rates of loading from 50 to 15,000 in./min. It is pictured in Figure 1. Basically it consists of a double-acting air cylinder whose piston is attached to the moving specimen grip. The fixed grip is attached to a load-sensing device. During the test, gas is instantaneously released into the top of the cylinder, moving the piston and the attached grip downward, thus loading the specimen. The speed of test is controlled by the gas pressure and the setting of a continuously adjustable exhaust orifice. Load information (measured by a strain gage type load cell) is fed into the  $y$  axis of the oscilloscope, while displacement information (measured by a linear potentiometer attached to the piston) is fed into the  $x$  axis. An oscillator is introduced, modulating the  $z$  axis, to provide a measure of time superimposed on the load-elongation curve obtained. A permanent record of the oscilloscope trace is obtained with a Polaroid Land Camera.

Tensile properties to yield were obtained in all instances, while tensile properties to fail were measured to check certain effects on ultimate properties. Specimens were all 3 in. strips  $\frac{1}{2}$  in. wide  $\times$   $\frac{1}{8}$  in. thick. The cross-sectional area was measured, and a 2-in. gauge length was used for all specimens.

### Tensile Strength and Molecular Weight Distribution

In Figure 2, tensile strength at a loading rate of 10 in./min. is plotted against milling time for Alathon 10 and Alathon 20 quenched. The values are lower for Alathon 10 for all degrees of oxidation. This is generally attributable to the broader molecular weight distribution of Alathon 10 with the attendant plasticizing effect of the low molecular weight chains.

The Alathon 10 with its broad molecular weight distribution increases in tensile values as a function of the initial milling. Perhaps this is due to the predominant effect of crosslinking, or tying together of the lower molecular weight chains before the gross effects of chain scission begin to

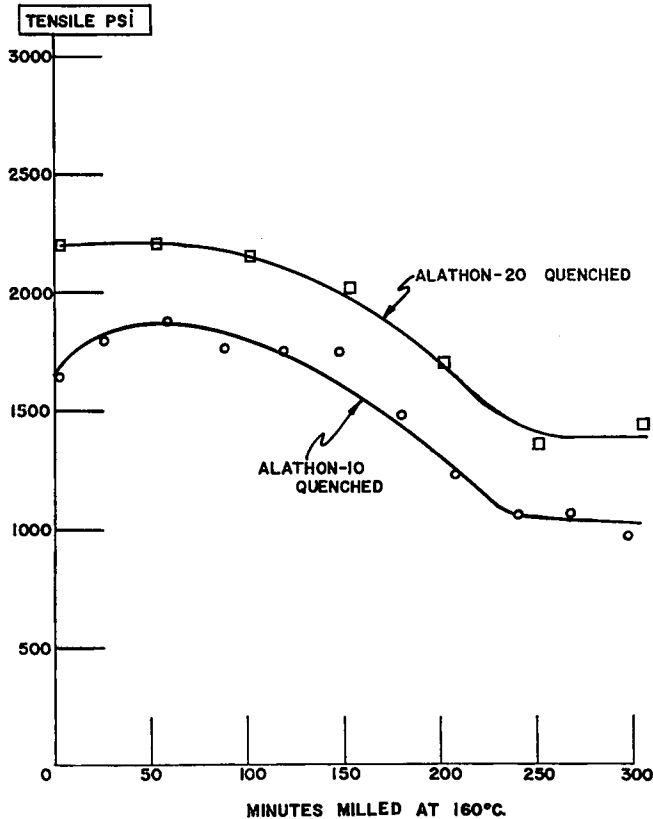


Fig. 2. Tensile strength versus milling time for Alathon-10 and Alathon-20 quenched at rate of loading 10 in./min.

be felt. It is interesting to note that beyond 50 min. the curves are grossly similar for both materials, gradually decreasing as time on the mill increases, until at 250 min. they begin to level off. This indicates that from 0 to 50 min., crosslinking is the major effect; from 50 to 250 min. chain scission is predominating; and after 250 min., the effects of crosslinking equals that of chain scission and no further decrease in strength is noted.

### Yield Stress and Critical Velocity

Figure 3 shows stress at yield plotted against time on the mill for Alathon 20 in the amorphous state. This property was measured at 0.2, 100, 1000, and 10,000 in./min., as well as at 10 in./min. reported above. It can be seen that at rates of loading up to and including 100 in./min., yield stress increases very slightly as time on the mill increases. At 1000 in./min. yield stress increases gradually at milling times to 200 min., then increases rapidly to 250 min. before levelling off. The slope of the curve obtained at 10,000 in./min., however, is negative and intersects the curve obtained at 1000 in./min. at 210 min. on the mill. Thus a "critical

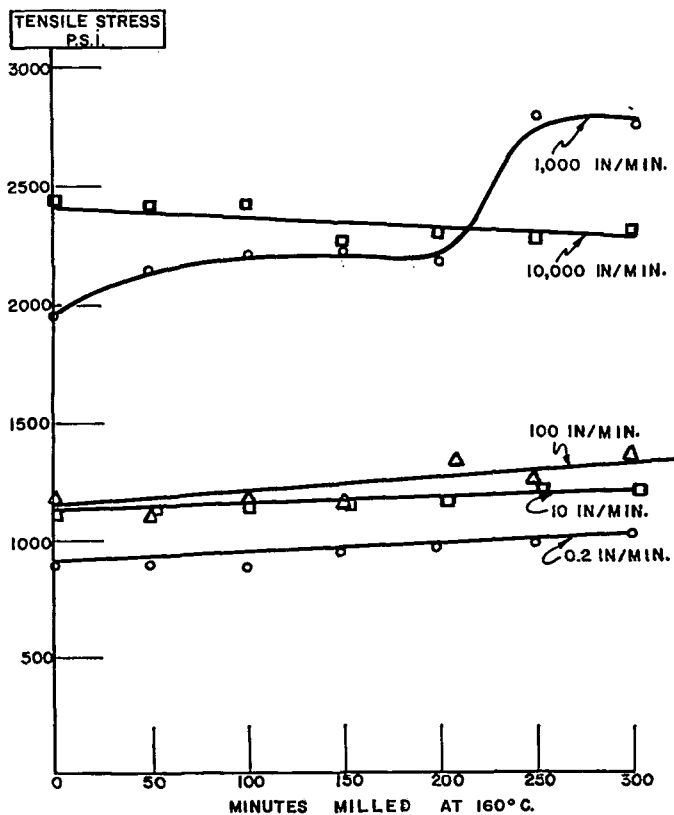


Fig. 3. Tensile stress at yield versus milling time for Alathon-20 quenched at various rates of loading.

velocity," (critical velocity being defined as the speed of test at which some parameter (e.g., yield stress) changes abruptly<sup>2</sup>), is observed between 1000 and 10,000 in./min. for materials milled for 210 min. and more.

This is presented more clearly by Figure 4 where yield stress is plotted against rate of loading for two levels of oxidation. It can be seen that material on the mill for 250 min. passes through a maximum at a rate of 1000 in./min., whereas material on the mill only 50 min. continues to increase as rate of loading increases. Perhaps a critical velocity also exists for the less oxidized material, but at a rate of loading greater than 10,000 in./min. Thus, the longer the milling time (or the greater the degradation), the lower is the critical velocity.

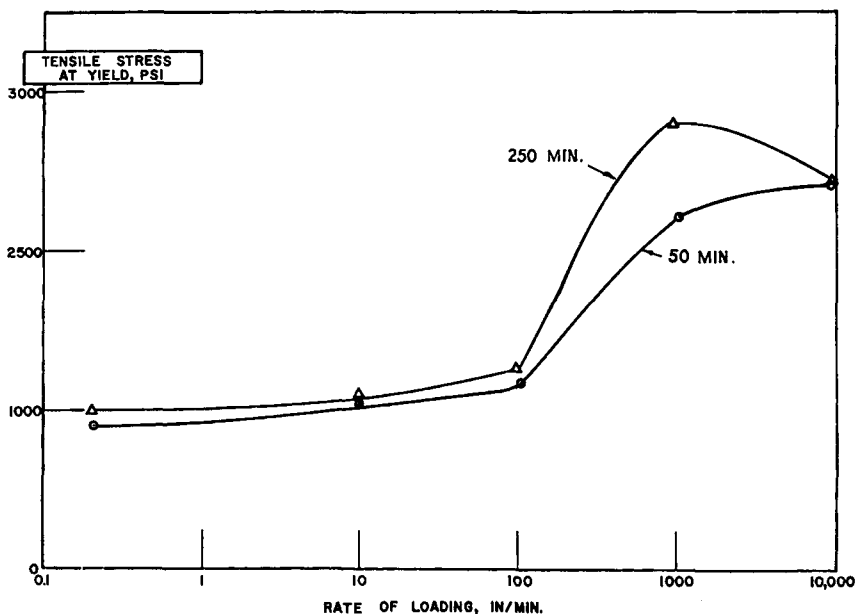


Fig. 4. Yield stress versus rate of loading for Alathon-20 quenched milled at 160°C. for 50 and 250 min.

If this is true, then perhaps the technique can be utilized to follow the net effects of degradation more quantitatively than can be done by other techniques. Polymers are ideally represented as a suitable combination of springs and dashpots, the initial oxidative alteration, crosslinking, ostensibly affecting primarily the backbone of the polymer chain, the spring component of the system. In slow speed measurements this small amount of crosslinking is masked by the action of the dashpot, the viscous component in the polymer. As the rate of loading increases, however, the dashpot has less and less effect until finally a rate is reached at which the dashpot does not have time to react at all. The greater the degree of crosslinking, the less the viscous component, the narrower the distribution

of relaxation times, and the lower the speed of test at which the viscous component ceases to respond.

### Elongation and Degree of Crosslinking

In Figure 5 percent elongation at yield measured at 10 in./min., is compared for quenched Alathons 10 and 20 after various times on the mill. The elongation of Alathon 20 increases rapidly from 22% at 0 time, to 35% at 150 min., and then decreases just as rapidly to 13% at 300 min. on the mill. It is interesting to compare this curve with the plot of solution viscosity versus milling time shown in Figure 1. Here a peak is observed at 250 min.—similar to the elongation curve but displaced somewhat to

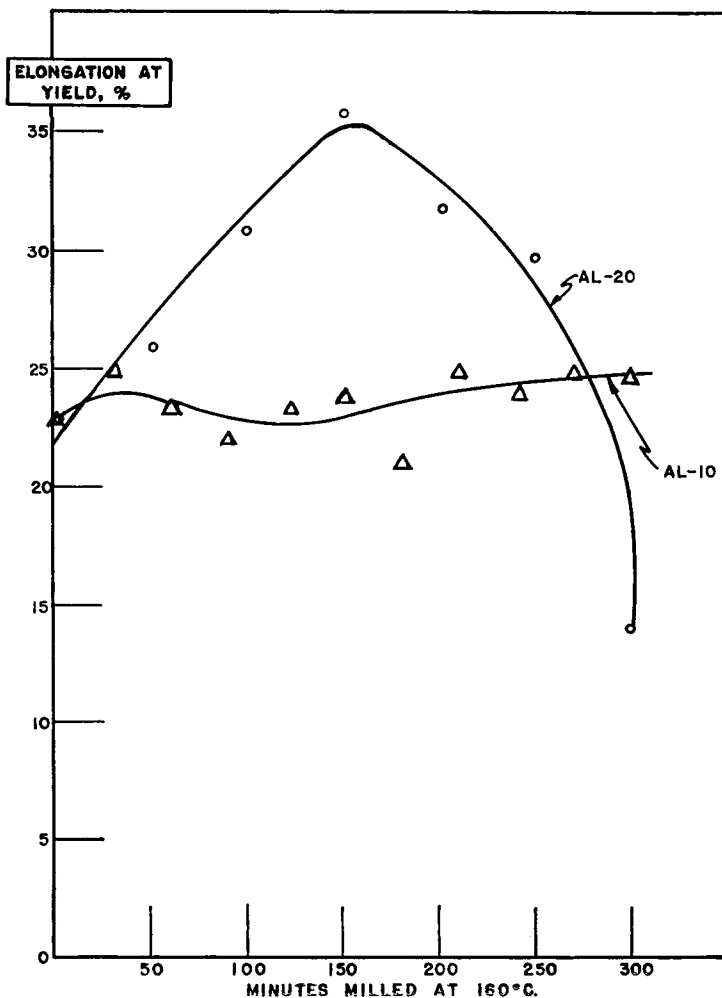


Fig. 5. Elongation at yield milling time for Alathon-10 and Alathon-20 quenched at rate of loading 10 in./min.

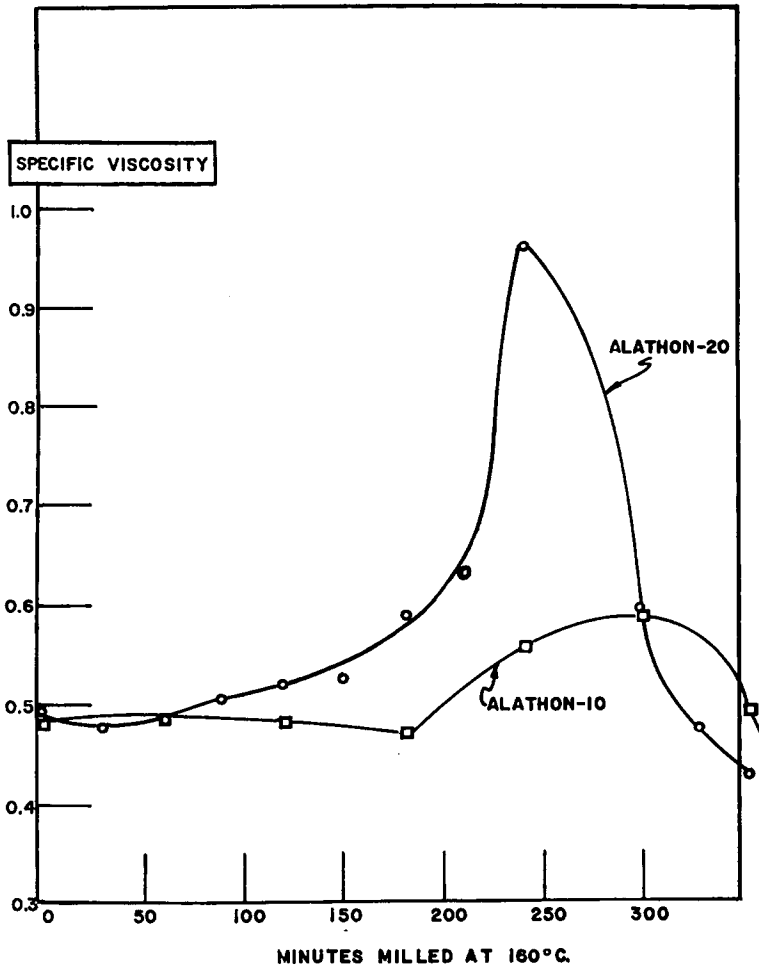


Fig. 6. Specific viscosity versus milling time.

the right. Now the solution viscosity peak value is interpreted as corresponding to that time interval at which the greatest preponderance of crosslinking occurs. The lower value of this peak (at 150 min.) as shown by the elongation value at yield can be explained to some extent by the kinetic theory of rubber elasticity. It is known from tensile studies on vulcanized rubber, for example, that there is an optimum degree of crosslinking which, presumably by creating a network lattice of polymer chains, so serves to distribute imposed loads on the polymer as to allow high tensile strengths and elongation values to be reached. Too few crosslinks do not achieve this effect. An excess serves to decrease stress tolerances by interfering with the optimum network needed for evenly dispersing imposed stresses. Thus, the extent of elongation is strongly influenced by the type and degree of crosslinking. Solution viscosity, however, con-

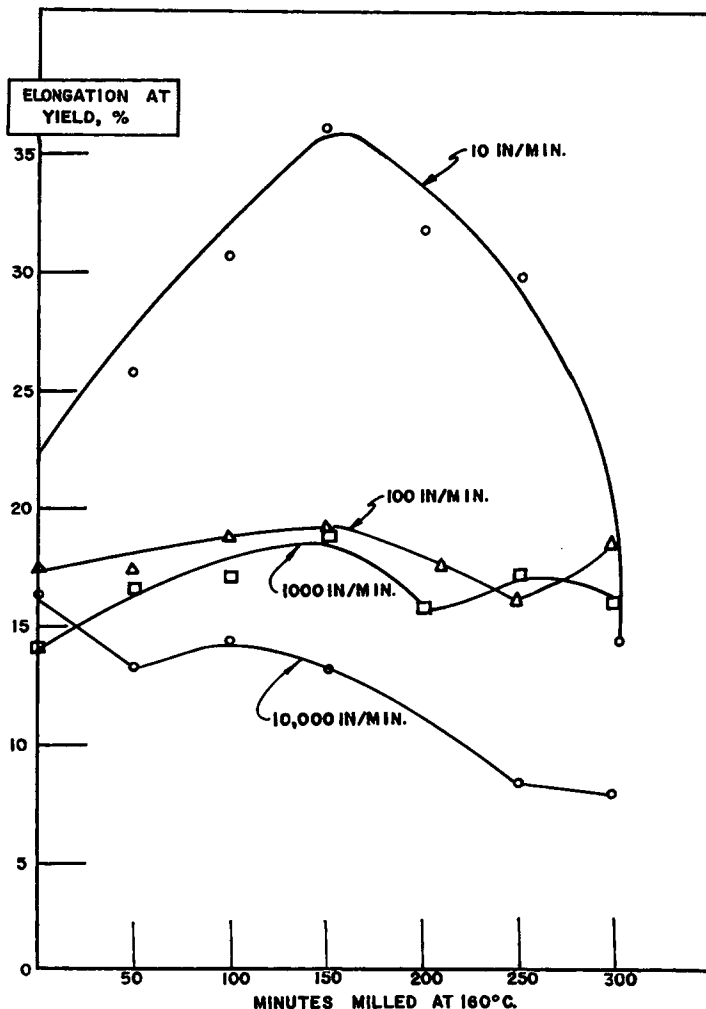


Fig. 7. Elongation at yield versus milling time for Alathon-20 quenched at various rates of loading.

tinues to increase with increasing amounts of crosslinking regardless of how suitable the crosslinking is for stress distribution. See Figure 6.<sup>1</sup>

According to this conceivable hypothesis, which seeks at least grossly to relate the peak of the Alathon 20 specific viscosity curve with that of the Alathon 20 elongation at 10 in./min., extent of elongation is strongly influenced by crosslinking. Moreover, from the relative areas under these curves it must be concluded that crosslinking has a more potent effect on elongation than does chain fragmentation. For in the specific viscosity measurement, the values and the curve derived from them set forth merely the predominance of crosslinking or chain-cutting over one another. When crosslinking has only a sparse edge or is overcome in the



competition with chain scission, its extent of occurrence is concealed by this measurement. Nevertheless its effect (presumed by this hypothesis) on elongation is even then profound. The fact, therefore, that chain scission masks the existence of crosslinking in the case of specific viscosity measurements, but not in the case of elongation, may be taken to indicate its relatively subordinate influence on the latter property.

Substantiation of this hypothesis is afforded by the data in Figure 5 wherein the elongations at yield are compared for the quenched Alathons 10 and 20 at the 10 in./min. rate of loading. It is seen that the far less pronounced specific viscosity maximum of Alathon 10 (Fig. 6), is consonant, albeit roughly, with the more moderate elongation expression for this resin. Despite the apparent causality, too much is left to be desired for any correlation of tensile values with solution viscosity to be made at this time.

At 10,000 in./min. the yield elongation values of Alathon 20 quenched generally decrease as time on the mill increases. This is illustrated in Figure 7. At this speed of test, the complicating effects of the viscous component are not introduced, and the elongation observed is attributed directly to the elastic component, i.e., to the direct degradative effects on the polymer backbone. This suggests that static data alone may not be adequate to follow properly oxidative degradation in polymeric systems, but that their implementation by high speed data offers a useful diagnostic tool.

#### Effect of Crystallinity on Elongation

Both static and dynamic elongation at yield for quenched and conditioned Alathon 20 is plotted against time on the mill in Figure 8. Elongation is substantially higher for amorphous material than crystalline resin for times on the mill under 250 min. This is expected since in polymers having higher crystallinity the chains are bound more tightly together in the crystallites by the secondary valence bonds. Moreover, when subjected to tensile loading, the crystallites themselves tend to line up to provide greater stiffness, higher yield strength, and lower yield elongation than do the amorphous portions of resin. Crystallinity, in tying together segments of different polymer chains, and/or of different segments of the same polymer chain within a given crystal site, serves as a crosslinking agent.<sup>3</sup> In this view, the optimum amount of crosslinking, previously mentioned, is exceeded by the plenitude of crystallinity. As a sequel, the conditioned samples are restrained in their ability to apportion evenly the imposed stresses among the polymeric bonds. The result is a lower elongation value for the conditioned than for the quenched samples. Elongation values at 10,000 in./min. are significantly lower than at 0.2 in./min. for both quenched and conditioned material. This is in accord with the known effect of high rates of loading in denying the polymer chains ample time in which to unravel themselves. At 0.2 in./min. the elongation at yield of conditioned resin decreases over milling time up to 50 min., then

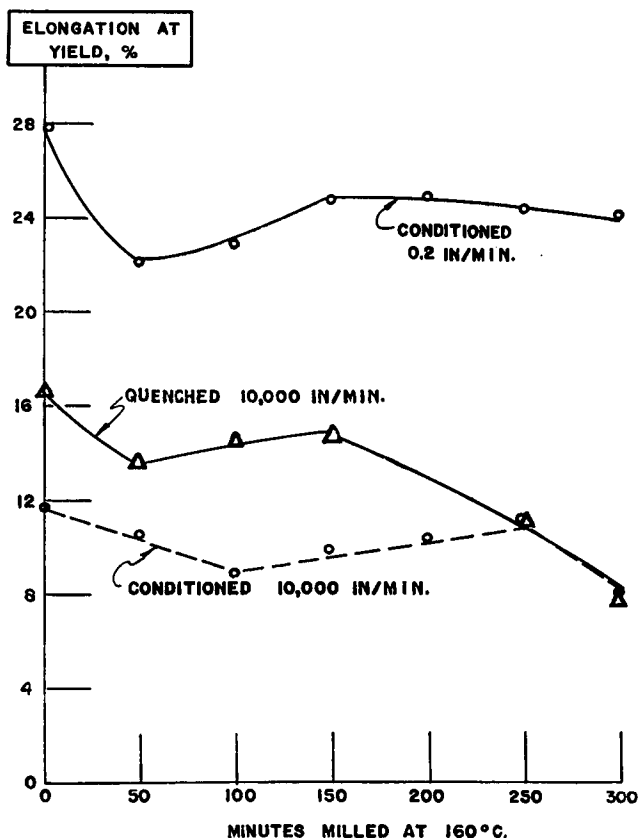


Fig. 8. Elongation at yield versus milling time for Alathon-20 quenched and conditioned.

increases to 150 min. of milling time, and then decreases again as oxidation proceeds. Once again the presence of increased elongation values can be ascribed to the chain-size aggrandizement of crosslinking. When this is overcome by chain scission, the values fall.

#### Effect of Crystallinity on Tensile Strength

Figure 9 illustrates a comparison for oxidized Alathon 20 quenched and conditioned samples in terms of tensile stress at yield measured at loading rates of 0.2 and 10,000 in./min. It is seen that as a consequence of crystallinity, the conditioned samples exhibit higher values than do their quenched counterparts. It is also evident that higher values are obtained for higher rates of loading. This is rationalized as being a consequence of the minimization of the effects of molecular weight limitations caused by high rate of loading. For a given molecular weight distribution, a low rate of loading will yield a tensile value that reflects the ability of short polymeric chains to unravel themselves as the sample is stressed (dash pot effect). Chain-unravelling is equivalent to local specimen

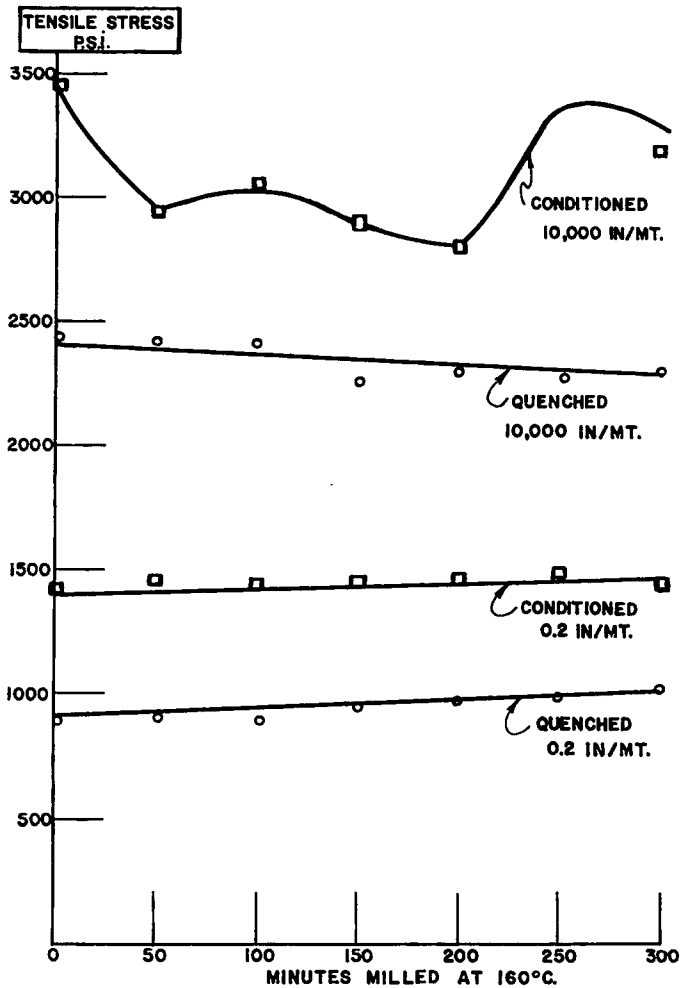


Fig. 9. Tensile stress at yield rate of loading versus conditioned-quenched Alathon-20.

failure and contributes poor values. At high rates of loading, however, there is less time for chain untangling to occur. The many entangled small chains, therefore, act as a few large ones. Consequently, the tensile values at high rates of loading exhibit a pseudo-high molecular weight effect.

#### Attenuation of Oxidative Damage

Of even greater significance is the influence crystallinity exerts in minimizing the effects of polymeric oxidative degradation. This has been reported by Hawkins et al.<sup>4</sup> In this study, Figure 9 reveals that while the elongation of quenched Alathon 20 determined at 10,000 in./min. essentially decreases with progressive oxidation, the value for that property

as exhibited by the conditioned resin remains rather constant. Since at this high rate of loading, elongation is more apt to be decreased by significant polymer chain cleavage rather than by excessive crosslinking, the results obtained for the quenched resins are explained on this very basis. In the conditioned resin, however, crystallinity serves to connect polymer segments that would otherwise have become independent low molecular weight entities. The result is that chain cutting, in the case of crystalline polyethylenes, does not necessarily result in chain fragmentation with its concomitant loss of elongation.

There is utilitarian significance to the above discussion. As judged from the effects of crystallinity on elongation values, the proper conditioning of polyethylene resins should be a matter of concern in applications wherein constancy of properties is of importance. For in the case of the crystalline polymer, accelerated ageing did not cause a decrease in the elongation value with time.

### References

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### Résumé

Une étude a été effectuée sur les propriétés d'élongation de deux résines de polyéthylène oxydées d'une façon progressive à 160°C sur une machine à deux rouleaux. Les changements dans les paramètres d'élongation sont reliés en se basant du point de vue théorique, à l'effet de réseau du pontage et à une scission de la chaîne. Ces résultats sont comparés avec des mesures de viscosité en solution pour les mêmes matériaux. On a montré que la dégradation polymérique oxydante est influencée par la distribution du poids moléculaire et par la cristallinité. De plus, une mesure des propriétés sur 5 décades du temps révèle une "vitesse critique" ce qui reflète une mesure relativement sensible de la dégradation. Des essais d'élongation à vitesse élevée fournissent un mode de diagnostic utile pour la détection précoce de la décomposition moléculaire dans les matériaux étudiés.

### Zusammenfassung

Eine Untersuchung des Zugverhaltens von zwei Polyäthylenharzen wurde bei schrittweiser Oxydation auf einem Kalandrier bei 160°C ausgeführt. Die Änderungen der Zugparameter wurden auf theoretischer Grundlage zum Einfluss der Vernetzung und Kettenspaltung in Beziehung gesetzt und mit Lösungsviskositätsmessungen an den gleichen Stoffen verglichen. Es wurde gezeigt, dass ein Einfluss der Molekulargewichtsverteilung und der Kristallinität auf den oxydativen Abbau des Polymeren besteht. Ausserdem ergab eine Messung der Eigenschaften über 5 Zeitdekaden das Vorhandensein einer "kritischen Geschwindigkeit," die ein verhältnismässig empfindliches Mass für den Abbau liefert. Hochgeschwindigkeit-Zugtests lieferten ein brauchbares diagnostisches Werkzeug zum frühen Nachweis einer Molekülzerersetzung in den untersuchten Materialien.