Chemical Degradation and Mechanical Testing of Polyethylenes*

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INTRODUCTION

Plastics are generally not subject to the corrosion problems that afflict metals, but they have degradation problems of their own. Since degradation of a plastic article can gradually lead to its failure in the uses for which it was intended, it is of practical concern to predict the service life in a given application, or to select from alternative materials the ones likely to last longer in use. Ultimately, the only sure test is actual service in the intended application. This procedure is often so slow as to be impracticable. Therefore, accelerated tests must be used in order to select from an array of materials the potentially useful ones, even without validation by parallel tests in actual service. The usual practice in these tests is to accelerate the degradation by raising the concentration of the corrosive reagent or the temperature, or both.

At elevated temperatures oxygen and oxidizing agents attack polyethylenes. The chemical degradation results in physical changes and ultimately in the destruction of the useful properties. We have investigated the correlation of oxidative exposure with physical decay of polyethylenes as measured by mechanical testing.

EXPERIMENTAL PROCEDURE

A series of commercially available polyethylenes in various thicknesses from 2 mils to 125 mils, extruded or molded, was obtained from various suppliers. All stocks were cut with steel dies into tensile bar specimens which conformed in all essential dimensions to Die C, ASTM D412-51T. As the

samples were cut, they were given code numbers from a table of random numbers so that random sampling could be used to select the test specimens.

In air aging, specimens were exposed during measured intervals of time in a mechanical convection oven (Precision Scientific Company 645–501, catalogue number 31060). The temperature was maintained at $100 \pm 0.5°C$.

The oxygen absorption apparatus has been described in the literature.[1] Specimens were hung vertically on glass prongs in a static oxygen atmosphere at 100°C. By periodic manual adjustments, the pressure was maintained nearly constant at one atmosphere. Volume changes due to consumption of oxygen by the samples were recorded at suitable intervals.

The reagent which was chosen to study the effect of an aqueous oxidant on polyethylene was nitric acid; concentrations employed were 69, 50, 25, and 10 wt.-%. Sample containers were 32 × 200 mm. Pyrex test tubes. Only one sample was immersed in each tube. The sample tubes were supported in water baths controlled at $50 \pm 1°C.$ and $70 \pm 1°C.$

Each series of weight measurements was made with an analytical balance to the nearest 0.1 mg. Samples were first conditioned in a standard atmosphere at $23 \pm 1°C.$ and approximately 50% R.H., weighed, and then oxidized. After exposure, samples were dried, weighed and conditioned in the above standard atmosphere for at least one week before tensile tests were performed.

In the study on degradation in the forced-air oven, tensile testing was done at a cross-head separation speed of two inches per minute on the Tate-Emery universal testing machine, with the use of the automatic recording device described by M. Nakamura.[2] The data were recorded in the form of a graph in which load was plotted versus time, with a supplementary trace which related time versus elongation as measured by the operator. In the aqueous oxidation study the cross-head separation speed was maintained at three inches
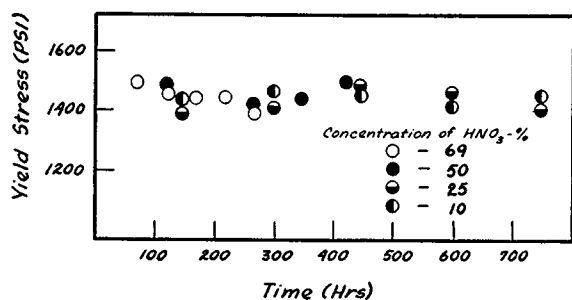
Fig. 1. Variation of average yield stress with exposure time in various concentrations of nitric acid at 50°C. Each point represents the average from four samples which were cut from 125-mil sheets of DYNH-3 polyethylene.
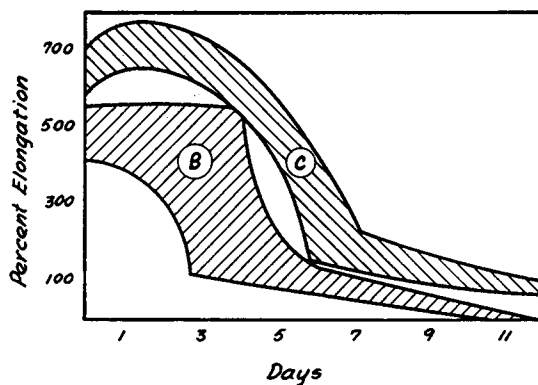

Fig. 2. Variation of ultimate elongation with exposure to forced air at 100°C. Specimens B were cut from 50-mil molded sheets of Alathon 34, an intermediate-type polyethylene; Specimens C, from 50-mil extruded sheet DYNH-3, a branched type. The bands enclose data from six samples at each day or two days of aging.

per minute. Values recorded (manually) were the force and elongation at the yield point and the maximum force and elongation just prior to break.

DISCUSSION

When polyethylene, linear or branched, is exposed to oxygen, air, or aqueous solutions of oxidizing reagents such as nitric acid and potassium permanganate, the plastic discolors, embrittles, and loses strength. In short, the polymer is degraded or corroded.

This does not necessarily mean that the plastic begins to lose its usefulness with the slightest degree of oxidation. If a practical application requires that the material not yield, i.e., that any tensile distortion must be small and elastic, then it may be that polyethylene is cushioned against failure in such applications. The plastic degrades with exposure to gaseous oxygen and aqueous oxidants, but the damage is not at first reflected in its yield properties, as shown, for example, in Figure 1. After long exposure times in air at 100°C., the polyethylenes were found to break at stresses below the normal yield stress, but after exposure for less than eight days, the original yield stress and yield elongation were retained. Although other properties revealed that the plastic was deteriorating, the yield properties remained those of the unaged materials.

On the other hand, even a slight amount of oxidation can decrease the toughness and flexibility of a polyethylene. Tensile properties which measure toughness are the area under the stress–strain curve, and, indirectly, the ultimate elongation, which is simpler to obtain. In accelerated aging in air or oxygen, we found that the decline of ultimate elongation with time of aging (Fig. 2) was the clearest aspect of deterioration which we could measure. Therefore, if the practical application demands
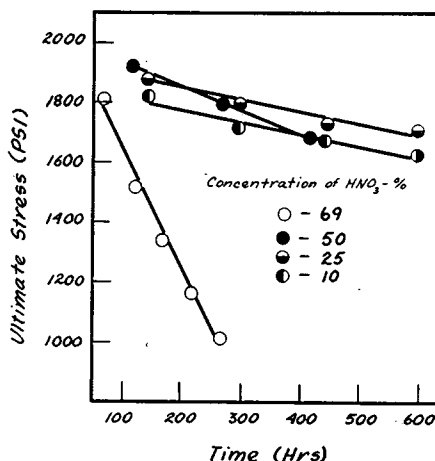

Fig. 3. Variation of average ultimate stress with exposure time in various concentrations of nitric acid at 50°C. Samples were cut from 125-mil DYNH-3 polyethylene.

toughness beyond the yield point, then even slight oxidation at elevated temperatures can be dangerous.

When polyethylene is exposed to aqueous solutions of oxidizing reagents it is probably not the absorption of oxygen which causes the degradation of the plastic but rather the reaction of the chemical reagent with reactive sites in the polymer chains. The exact nature of the reactions occurring with aqueous oxidants was not investigated. In the case of aqueous oxidation, ultimate elongation did not vary in a sufficiently regular way so as to indicate the extent of corrosion. The tensile property which provided the only satisfactory index of the degree of degradation was the ultimate tensile
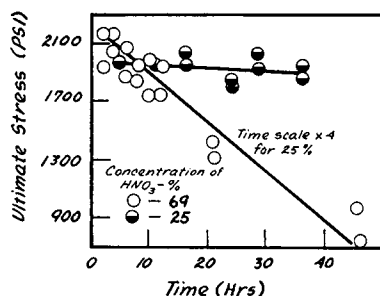
Fig. 4. Variation of average ultimate stress with exposure time in two concentrations of nitric acid at 70°C. Samples were cut from 50- and 90-mil sheets of DYNH-3.

strength (Fig. 3). The effect of reagent concentration and temperature were investigated with a view to establishing the optimum conditions for comparing degradation rates of different polyethylenes. The effects of changing concentration were small for concentrations in the range of 10 to 50-wt.-% nitric acid. The concentrated reagent, 69% nitric acid, gave degradation rates which were about 10-fold greater than 50% acid. Therefore, for the purpose of defining a test method for comparing degradation rates of different polyethylenes in nitric acid, it would be sufficient if only two concentrations of acid were used, one representing the dilute range and the other the concentrated range. As expected, the effect of increasing temperature was to increase the rate of degradation (Fig. 4). The limits of standard deviation calculated for the ultimate stress showed that, with reference to reproducibility, one temperature was not more favorable than another. However, where it is desired to speed up the testing procedure, higher temperatures should be employed.

It is the tensile test that gives us all the properties which we have so far discussed. The tensile test can give still more information about the physical structure of the polyethylene and its decay. With a little experience, in fact, one can examine a few sample stress-strain curves and with reasonable assurance identify the polyethylene, estimate the oxidative exposure it has received at a given temperature, and summarize its state of structural usefulness, provided that all the tensile testing is done under identical conditions.

One can learn something about degradation by measuring the rate of volumetric oxygen absorption at constant pressure. For any given plastic, the volume of oxygen absorbed can be a very good indication of the degree of physical degradation, once the correlation has been established. For poly-

ethylenes, the rate of oxygen absorption at 100°C. shows a characteristic induction period[3] which may be lengthened by the incorporation of antioxidants in the plastic. At 100°C., this is not a true induction period but rather a period of slow oxidation. Consequently, physical damage does occur during this period. Indeed, once the absorption goes into the rapid stage which follows, it may safely be assumed that the polyethylene is physically worthless. Therefore, the so-called induction period might be taken as a crude indicator of the useful life of the plastic under oxygen attack, as compared to that of others under the same test conditions. This method is particularly useful in comparing oxidation inhibitors or in detecting impurities (such as catalyst residues) which promote oxidation.

Unfortunately, one cannot assume that the same amount of oxygen absorbed means the same degree of physical decay for different polyethylenes. In fact, it seems that from oxygen-absorption rates alone one cannot even predict which of two polyethylenes will be more resistant to physical degradation by oxygen. We supposed, for example, that polyethylenes A and B (linear and intermediate types, respectively) were to be preferred over C (a branched polyethylene) for resistance to degradation, because of their comparative oxygen uptake rates at 100°C., shown in Figure 5. Yet when the same polyethylenes were oven-aged at 100°C., and deterioration measured by tensile testing, it was found that C was slightly superior in retaining useful properties the longest (Fig. 2).

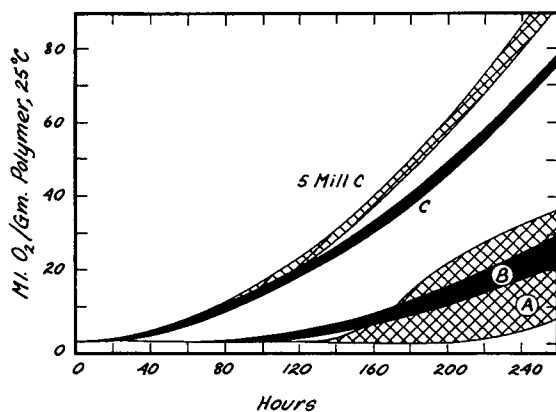Even less reliable as an indicator of degradation

Fig. 5. Oxygen uptake of polyethylenes in oxygen at 100°C. Specimens A were cut from molded Superdylan, a linear, Ziegler type polyethylene; Specimens B were Alathon 34, intermediate; Specimens C were DYNH-3, branched. Thicknesses were 50 mils with the exception indicated.
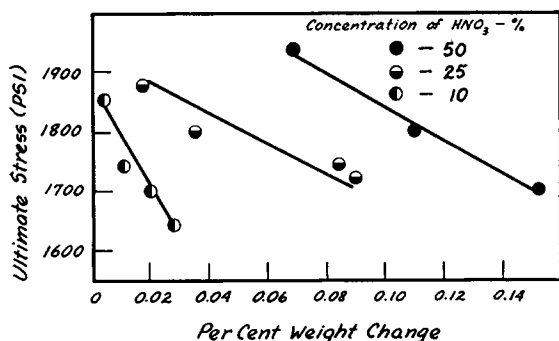
Fig. 6. Average ultimate stress vs. average per cent weight change for samples from 125-mil sheet DYNH-3. Samples were aged in various concentrations of nitric acid at 50°C.

is the weight gain. After degradation with aqueous oxidants it was found that there was a very poor correlation between the weight gain and the degree of degradation as measured by ultimate tensile strength.

It is not possible to measure the per cent weight change experienced by a test specimen and predict its ultimate stress. As shown by Figure 6, the variation of ultimate stress with per cent weight change is different for each concentration. Therefore, there is no justification for substituting easier and faster weight measurements for the tedious proce-
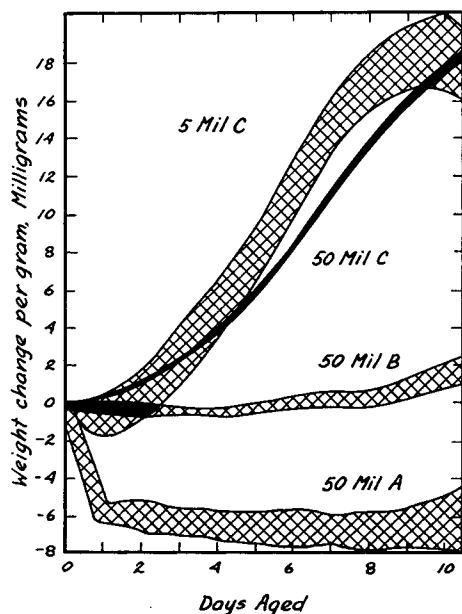

Fig. 7. Weight variation of polyethylenes in forced air at 100°C.: Samples A were Superdylan, a linear type; Samples B were Alathon 34, intermediate; Samples C were DYNH-3, branched.

dure of tensile testing. After oxidation in air or oxygen, the weight change was a function of exposure time, but the dependence on exposure time was very different for different polyethylenes and for various thicknesses of the same polyethylene. From Figure 7 it is apparent that some polyethylenes gained weight while others lost weight during the same treatment.

These results strongly suggest that it is unsafe to rely on indirect methods of gauging degradation in accelerated tests, unless such methods have been validated by comparison with more direct methods such as tensile testing. For particular applications, of course, it would be more convenient to use a more specific and still more direct mode of testing for failure of the plastic in that application. For example, the burst strength of plastic pipe might best be tested by bursting the pipe with a measured internal pressure. In general, the tensile test (including stress–strain data) is versatile and can be used to discriminate various types of physical failure simultaneously.

CONCLUSION

There is a peculiarity about the course of polyethylene oxidative degradation which is both useful and perplexing. We have discussed the fact that polyethylenes are more useful, at least for some purposes, because they can undergo a large amount of oxidation without significant change in resistance to tensile distortion. Should one not expect the yield properties to change gradually under the progressive attack of oxygen or oxidizing agents? The fact that for a long time they do not invites speculation.

Possibly the key to the problem lies in the heterogeneous nature of polyethylene. It is partly crystalline, partly amorphous. All of the plastic consists of very long, hydrocarbon-chainlike molecules, but in the crystalline regions the molecules are very regularly and tightly packed, held together by their forces of attraction for each other at close range, the van der Waal's forces. In the gross structure there is an enormous number of microscopic, highly crystalline regions or "spherulites," multifariously linked together by loosely arranged molecular chains. Presumably the spherulites are denser and therefore less readily penetrated by oxygen or other invading molecules than is the amorphous portion.

Polyethylene's tensile behavior is attributed to its partial crystallinity. There is good evidence[4] that for this type of plastic the yield point does

not depend primarily on ruptures or slippages in the amorphous regions. What actually may be more crucial is a massive reorientation of the crystalline regions. This is more readily understood if one concedes that the weakest structural forces in the solid plastic are those keeping the spherulites intact. It follows that, when increasing tension is applied, the deformation will be essentially elastic until the force acting throughout the plastic exceeds the strength of the spherulites. Then the spherulites will deform, unravel, or slip open, producing an irreversible elongation of the specimen. The stretched polyethylene may still be as crystalline,[5] but it will be reoriented.

In this view, the amorphous content can be regarded as a cushion against degradation. It may succumb to oxygen or to similar reagents while the spherulites tend to be by-passed, being difficult for foreign molecules to penetrate. The partially-degraded plastic yields under tensile stress in some ways as though it were undegraded because its yield-determining crystalline structure is intact. The actual degradation still shows its effect, however, because the plastic loses toughness, breaking at lower elongation or lower ultimate stress, or both.

If the amorphous content offers protection against degradation by preferentially using up the attacking reagent, it follows that the more crystalline polyethylenes are the more vulnerable. Their greater density should help them repel the corrosive reagents, but the penetration that does occur should result in greater damage. Our experiments suggested that the physical destruction of the linear (more crystalline) polyethylene was greater, even though the oxygen absorbed in a given time was less than for the branched polyethylene. Because the amorphous content confers flexibility and to some extent toughness, it may need more protection in linear polyethylenes, which have so little of it. Perhaps these plastics need to be unusually free of oxidation promoters or need better inhibitors of oxidation.

Kavafian[6] independently has likewise suggested that in air oxidation of linear polyethylenes at 100°C. oxygen preferentially attacks outside the spherulites. He measured degradation by the tensile impact test, which is a measure primarily of toughness and not a measure of yield behavior. Other workers[7] have recently confirmed the selective oxidation of the noncrystalline regions, and still others[8] have assumed this effect. (Also, very recently, Meltzer, Dermody, and Goldey[9] have

compared methods of testing the oxidizability of polyethylenes).

In viewing the problem of polyethylene degradation from a practical perspective, several aspects should be remembered. For one thing, we have little assurance that the behavior observed at the high temperatures used in accelerated tests can be projected into the lower temperature region which is more often of practical concern. Since results of physical tests depend on the tests, the appropriateness of the test method for the material's intended use must always be kept in mind. For a polyethylene with no visible defects, oxidative damage can be serious or negligible depending on what use is intended for the plastic. In either case, the damage can be measured by an appropriate physical test.

References

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Synopsis

Polyethylene films and sheets were oxidized in oxygen, air, or aqueous nitric acid at temperatures up to 100°C., and the decay of physical properties was measured by mechanical testing. In some instances, weight change and volume of oxygen absorbed were reliable indexes of the physical degradation as measured by a particular property such as ultimate stress or ultimate elongation, but they were unreliable in comparing the degradation of different types of polyethylene. Although the more crystalline polyethylenes absorbed less oxygen than branched polyethylenes, the former

degraded more rapidly in air at 100°C. In degradation by air or oxygen, exposure time affected the ultimate elongation more than it did ultimate tensile strength. In nitric acid the reverse was true. The yield elongation and the yield stress were virtually unaffected by any of the degradation methods unless the exposure was very long. A preferential oxidation of the noncrystalline regions is proposed to account for this result. The appropriateness of any tensile property as a measure of degradation is concluded to depend on the intended use of the plastic.

Résumé

Des films et des feuilles de polyéthylène ont été oxydés dans l'oxygène, l'air, ou l'acide nitrique en solution aqueuse à des températures supérieures à 100°C et la diminution des propriétés physiques a été mesurée par test mécanique. Dans certains cas le changement de poids et le volume d'oxygène absorbé sont des indices certains de la dégradation physique lorsqu'ils sont mesurés par une propriété particulière comme la tension limite ou l'étirement limite, mais ils ne sont pas concordants si on compare entre eux la dégradation de différents types de polyéthylène. Bien que les polyéthylènes les plus cristallins absorbent moins d'oxygène que les polyéthylènes branchés, les premiers dégradent plus rapidement à l'air à 100°C. Dans la dégradation par l'air ou l'oxygène, la durée d'exposition agit plus sur l'étirement limite que sur la tension limite. Dans l'acide nitrique c'est l'inverse qui est vrai. Les rendements d'élongation et de tension ne sont virtuellement pas affectés par n'importe quelle méthode de dégradation à moins que l'exposition ne soit très longue. On se propose de faire une oxydation préférentielle des régions non cristallines pour prouver ce résultat. L'utilisation de n'importe quelle propriété de tension comme mesure de la dégradation dépend de l'emploi que l'on veut faire du plastique.

Zusammenfassung

Filme und Platten aus Polyäthylen wurden in Sauerstoff, Luft oder wässriger Salpetersäure bei Temperaturen bis zu 100°C oxydiert und der Abfall der physikalischen Eigenschaften wurde durch mechanische Prüfung gemessen. In manchen Fällen bildeten die Gewichtsänderung und das Volumen des aufgenommenen Sauerstoffs ein verlässliches Mass für den physikalischen Abbau, wie er an einer besonderen Eigenschaft wie Spannungs- oder Dehnungsgrenze gemessen wurde, sie waren aber unbrachbar zum Vergleich des Abbaus verschiedener Typen von Polyäthylen. Obwohl die stärker kristallinen Polyäthylene weniger Sauerstoff absorbierten als verzweigte Polyäthylene, wurden die ersteren bei 100°C unter Luft rascher abgebaut. Beim Abbau durch Luft oder Sauerstoff hatte die Reaktionsdauer einen grösseren Einfluss auf die Dehnungsgrenze als auf die Zugfestigkeitsgrenze. In Salpetersäure lagen die Verhältnisse umgekehrt. Dehnung und Spannung bei fer Fliessgrenze blieben praktisch von allen angewendeten Abbaumethoden unbeeinflusst, ausser für den Fall einer sehr langen Reaktionsdauer. Um dieses Ergebnis erklären zu können, wird die Annahme einer bevorzugten Oxydation der nicht-kristallinen Bereiche vorgeschlagen. Man kommt zu dem Schluss, dass die Eignung irgendeiner Zugeigenschaft als ein Mass für den Abbau von der geplanten Verwendung des Kunststoffes abhängt.