

Torsional Braid Analysis of Antioxidant Activity in Elastomer Systems. I. Initial Studies*

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Synopsis

The torsional braid apparatus as originally described by Lewis and Gillham has been explored as a means of providing a quantitative measure of antioxidant activity of selected compounds when formulated with certain elastomer systems prone to oxidative crosslinking on heat aging. With this technique the time dependence of the sharp torsional modulus increase, corresponding to a change from a rubbery to a highly cross-linked state, is determined. This time dependence is taken as a measure of the rate of oxidative crosslinking in heat-aged elastomer films coated on a fiber-glass braid. In this manner an assessment of the activity of antioxidants can be made. To illustrate the application of this technique, two initial studies will be cited. In one study the relative protective effect on a carboxylated styrene-butadiene latex system of a series of antioxidants was found to be in the following order: α, α' -2,6-bis(2-hydroxy-3-*tert*-butyl-5-methylphenyl)xylenol > the reaction product of nonylated paraethylphenol and formaldehyde > crude 2,2'-methylene bis(6-nonylparacresol). In another study, with *cis*-polybutadiene as the elastomer, the effectiveness of a series of antioxidants was found to be in the following order: 2,2'-methylene bis(6-*tert*-butyl paracresol) > 1,3,3,5-tetramethyl-1-*m*-tolylindane-4',6-diol > 4,4'-methylene bis(2,6-di-*tert*-butylphenol). In addition, the effect of concentration and temperature was studied with the most efficient antioxidant in this last series.

INTRODUCTION

The present work examines a new application of the torsional-braid analysis (TBA) technique¹ for assessing the effectiveness of antioxidants as stabilizers for elastomers prone to oxidative degradation. This technique is uniquely suited to problems of antioxidant activity assessment in which the elastomer in question is unvulcanized or in a form in which it cannot support its own weight. It consists of dip-coating fiber-glass braids with the elastomer containing given concentrations of candidate antioxidants. A coated braid prepared without antioxidants serves as a control. Heat-aging these coated braids at a constant elevated temperature induces oxidative reactions in the elastomer coatings. These reactions will be more or less inhibited or retarded in accordance with the concentration and

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activity of any antioxidants present. The oxidative changes are manifested by a progressive softening or embrittlement of the elastomer with time of heat-aging, depending upon whether chain scission or crosslinking processes dominate the degradative mechanism. Intermittent measurement of the torsional rigidity of the braids during the course of their heat-aging provides a convenient and sensitive measure of the rate of degradation of the elastomer. This is accomplished by vertically suspending a braid of fixed length in the TBA apparatus described by Lewis and Gillham.² An inertial mass of convenient size is hung on the lower end of the braid to form a torsional pendulum which, when operating in free oscillation, can be used to measure rigidity changes of the elastomer coated braid as a function of time. This is accomplished by determining the period of oscillation of the pendulum. The rigidity can be calculated through the utilization of the approximate relationship $G' \approx k (1/P^2)$, where G' is the rigidity (shear) modulus, P is the period of oscillation, and k is a constant that depends on the geometry and mass of the pendulum.^{3,4} The relative rigidity G'_t/G'_0 is defined as the ratio of the rigidity modulus G'_t obtained after some heat-aging time t to the rigidity modulus G'_0 obtained initially. In terms of experimentally determined quantities the relative rigidity is given by P_0^2/P_t^2 .

Since the rigidity modulus is temperature-dependent, it is essential that both P_0 and P_t be measured at the same temperature. One method of obtaining these measurements is to mount a braid specimen in the TBA apparatus, thermostated at the heat-aging temperature. In this case the heat aging is accomplished directly in the TBA apparatus, and both P_0 and P_t are measured at this temperature. With this method, however, heat-aging data in the form of a curve of G'_t/G'_0 versus heat-aging time can be obtained for only one braid specimen at a time. In antioxidant screening studies, in which such data are required on a series of stabilized braid specimens as well as on an unstabilized control, an alternative method of measurement can be used. With this method a fixed length of each coated braid is permanently fastened at either end to light spring-loaded clamps. These clamps are readily attached through simple set-screw couplings to the extension rods of the torsional braid apparatus. With this arrangement any braid can be readily and repeatedly inserted in, and removed from, the torsional braid apparatus without altering its dimensions or condition. It is then possible to measure P_0 for a series of braids at room temperature in the torsional braid apparatus and also heat-age the braids in an oven. During the heat-aging intermittent measurements of P_t can be made at room temperature by transferring the braids from the oven to the torsional braid apparatus. In this manner curves of G'_t/G'_0 versus heat-aging time can be obtained from the whole series of braids at one time. A comparison of rate curves thus obtained from braids containing antioxidants with that obtained from an unprotected control provides a convenient quantitative measure of antioxidant activity.

EXPERIMENTAL

Materials

Two specific elastomer systems were used in this study: carboxylated styrene-butadiene latex (Goodyear Pliolite 480 latex) and *cis*-polybutadiene (American Synthetic Rubber). The antioxidants studied in the respective elastomers were crude 2,2'-methylene bis(6-nonylparacresol), the reaction product of nonylated paraethylphenol and formaldehyde, α,α' -2,6-bis(2-hydroxy-3-*tert*-butyl-5-methylphenyl) xylenol, 4,4'-methylene bis(2,6-di-*tert*-butylphenol), 2,2'-methylene bis(6-*tert*-butyl paracresol), and 1,3,3,5-tetramethyl-1-*m*-tolylindane-4',6-diol. In the case of the carboxylated styrene-butadiene latex the antioxidants were first emulsified, and this emulsion was added to the latex. In the case of the *cis*-polybutadiene a toluene solution of the antioxidant was added to the toluene solution of the elastomer.

Braid Preparation

The composite elastomer-glass-fiber specimen is prepared by dip-coating a fiber-glass braid. This braid is obtained by loosely braiding multifilament glass strands (available in the form of heat-cleaned glass cloth, 181-112 of United Merchants and Manufacturers, Inc., New York). In the two elastomer systems studied in this paper the coating was accomplished either by dipping in a solution or an emulsion of the elastomer. The number of dips required depends upon the concentration of the elastomer. The important thing to achieve during the coating step is the formation of a continuous surface film in addition to a thorough impregnation of the braid interstices. The final coated braid should contain about 50% by weight polymer, which will produce at least a 1 mil of polymer coating on the braid. Under these conditions it was found that the precision of the visual determination of the period of oscillation of the composite system was at a maximum, thus providing optimum sensitivity. In the case of *cis*-polybutadiene, since the elastomer concentration was only 7% by weight, two coating dips were necessary. In the case of the carboxylated styrene-butadiene the elastomer concentration was 58% by weight, and thus only one coating dip was necessary. The length of the composite elastomer-glass-fiber specimen actually used in the measurement was 10 in.

Since torsional braid analysis is to be used as a quantitative method of investigation, the reproducibility of the coating technique requires special consideration. The coating procedure can be controlled to produce (on the glass support) the required elastomer deposition, which varies only by 2% of the weight of the elastomer. The solvent removal from the solution or emulsion-dipped systems is readily achieved by vacuum-drying; because essentially only thin films are being considered, a maximum drying time of 2 hr. is sufficient.

In order to study the effect of accelerated aging, the specimens were conditioned by three different methods: in a circulating air oven at 150°C., in a cell oven at 80°C., and in a thermoregulated fluidized-bed torsional braid apparatus.⁵

RESULTS AND DISCUSSION

In the two systems under investigation the effect of oxidative change was found to be one of embrittlement. That is, as a function of accelerated heat aging, the relative modulus of the composite elastomer-glass braid sample was found to increase. Thus, by plotting these parameters—relative modulus versus heat-aging time—on a log-log graph a characteristic curve could be obtained, such as shown in Figure 1. The profile of this

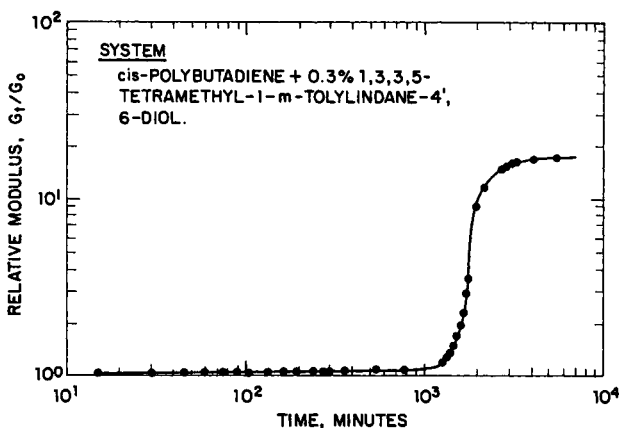


Fig. 1. Relative modulus (G_t/G_0) as a function of aging time in the torsional braid apparatus at 100°C. Actual measurements performed at the aging temperature.

curve was found to exhibit a certain pattern very similar to that of the absolute-modulus profile obtained when a polymer is cooled from a rubbery to a glassy state. In the latter instance the inflection point of the curve is used to determine the glass transition temperature T_g of the system. In a similar manner the inflection point of the profile obtained in this study of antioxidant-elastomer-glass composite systems is used to determine an embrittlement point. The dependence of this embrittlement point on the aging time is in turn taken as a measure of the ability of a particular antioxidant to inhibit the oxidative crosslinking of the system.

The reproducibility of this technique can readily be seen from the results shown in Figure 2. In this case the relative modulus as a function of aging time is plotted for three different coated braids prepared from the same elastomer-antioxidant system and a control containing no antioxidant. It can be seen that the systems containing the antioxidant produce a profile with an embrittlement point occurring after a longer period of aging time than that of the control. Furthermore, though the profiles

are not completely superimposable, particularly in the crosslinked plateau region, the reproducibility of the embrittlement point of each of these profiles is excellent. The inflection point of each of these curves occurs at 180 min. of accelerated aging time. The aforementioned variation in the magnitude of the relative modulus in the crosslinked plateau region most likely occurs from minor variations in the deposition of the elastomer on the braid.

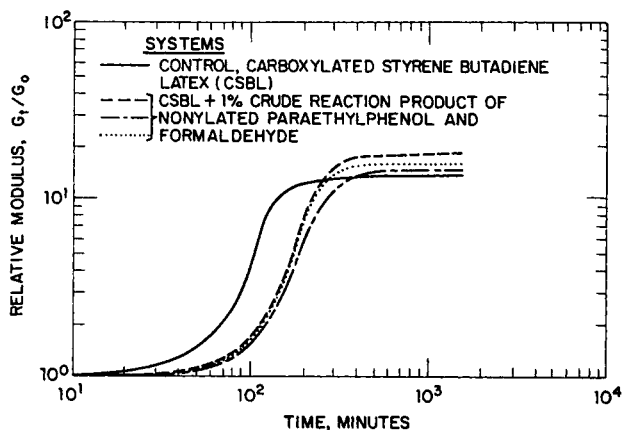


Fig. 2. Relative modulus as a function of aging time in a circulating air oven at 150°C. Actual measurements performed at 25°C.

Effect of Antioxidants in Carboxylated Styrene-Butadiene Latex Systems

The effectiveness of antioxidants in inhibiting embrittlement of carboxylated styrene-butadiene latex systems was studied as a function of aging

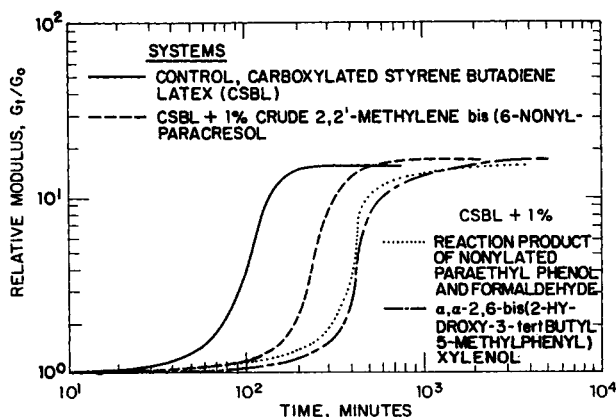


Fig. 3. Relative modulus as a function of aging time in a circulating air oven at 150°C. Actual measurements performed at 25°C.

time at 150°C. in a circulating air oven. By measuring the change in the period of oscillation of the elastomer-glass composite specimen over a period of aging time a profile of the change in relative modulus was obtained. The use of a thin film in the study of a carboxylated styrene-butadiene latex is of particular practical use, for one of the commercial applications of this latex is that of a coating on rug backings. Thus, the embrittlement of this coating as a function of the temperature history produced by the processing variables is of primary importance. The results obtained from a control and three samples containing different potential antioxidant compounds are shown as relative modulus-aging-time profiles in Figure 3. The aging time required to reach the embrittlement point, obtained from each of these curves, is tabulated in Table I. It can be seen from these results that each of the three additives improved the stability of the latex. Using the control sample as the standard, compound A increased the aging time stability by a factor of 2, and compounds B and C increased it by a factor of 4.

TABLE I
Time Required to Reach Embrittlement Point on the Relative-Modulus Profiles
Obtained for Carboxylated Styrene-Butadiene Latex Aged at 150°C.

Identification	System	Time, min.
O	Control	1.05×10^2
A	1% Crude 2,2'-methylene bis(6-nonylparacresol)	2.35×10^2
B	1% reaction product of nonylated paraethylphenol and formaldehyde	4.00×10^2
C	1% α,α' -2,6-bis(2-hydroxy-3-tert-butyl-5-methylphenyl) xyleneol	4.20×10^2

Effect of Antioxidants in *cis*-Polybutadiene

The effectiveness of antioxidants in another elastomer system, *cis*-polybutadiene, was also studied by means of torsional braid analysis. Moreover, in addition to a study of the comparative effectiveness of three antioxidants, a study of the effect of concentration and aging temperature on a particular antioxidant-based system was also made. The relative modulus-aging-time profiles obtained in the comparative study are shown in Figure 4. In this series the samples were obtained at the aging temperature. The aging time required to reach the embrittlement point for these systems is tabulated in Table II. These results indicate that each of the three additives improved the stability of the *cis*-polybutadiene elastomer toward oxidative embrittlement. The effectiveness of compounds D, E, and F were thus found to differ essentially by factors of 5, 6.5, and 7, respectively, from that of the unprotected control.

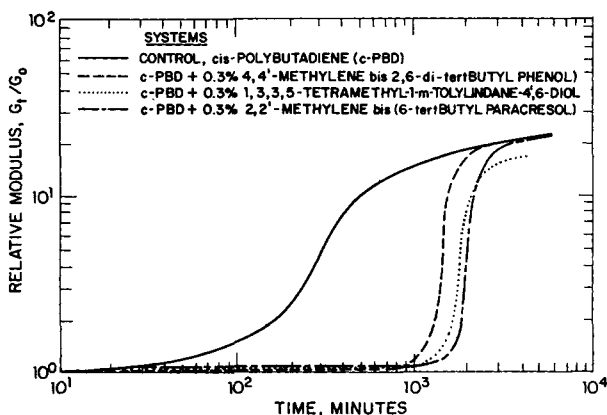


Fig. 4. Relative modulus as a function of aging time in the torsional braid apparatus at 100°C. Actual measurements performed at the aging temperature.

The effect of concentration as an experimental variable was also investigated. Compound F [2,2'-methylene bis(6-*tert*-butyl paracresol)] was selected for this study, and the relative modulus of the formulated samples was determined at room temperature as a function of cell oven aging at 80°C. The resulting profiles are shown in Figure 5. It can be seen that there is very little difference in the embrittlement points obtained from

TABLE II
Time Required to Reach Embrittlement Point on the Relative-Modulus Profiles
Obtained for *cis*-Polybutadiene Aged at 100°C.

Identification	System	Time, min.
P	Control	2.75×10^2
D	0.3% 4,4-methylene bis(2,6-di- <i>tert</i> -butyl phenol)	1.40×10^3
E	0.3% 1,3,3,5-tetramethyl-1- <i>m</i> -tolylindane-4',6-diol	1.80×10^3
F	0.3% 2,2'-methylene bis(6- <i>tert</i> -butyl paracresol)	1.95×10^3

TABLE III
Time Required to Reach Embrittlement Point on the Relative-Modulus Profiles
Obtained for *cis*-Polybutadiene as a Function of Aging Temperature

System	Concn., %	Time, min.	
		At 80°C.	At 100°C.
Control		6.5×10^2	2.75×10^2
2,2'-Methylene bis(6- <i>tert</i> -butylparacresol)	0.3	5.9×10^3	1.95×10^3
2,2'-Methylene bis(6- <i>tert</i> -butyl paracresol)	0.5	6.0×10^3	2.2×10^3

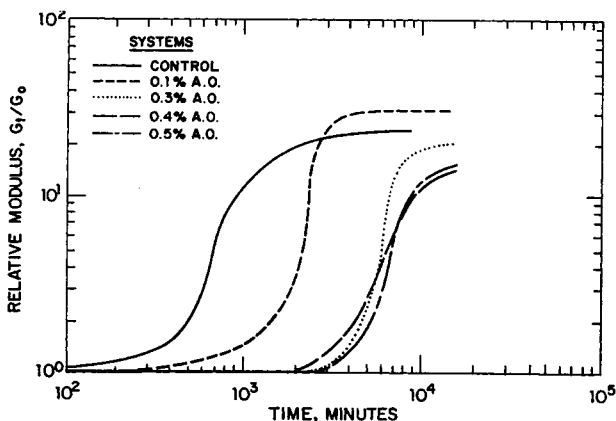


Fig. 5. Relative modulus as a function of aging time in a cell oven at 80°C. Actual measurements performed at 25°C. The effect of concentration of the antioxidant 2,2'-methylene bis(6-*tert*-butyl paracresol) on *cis*-polybutadiene.

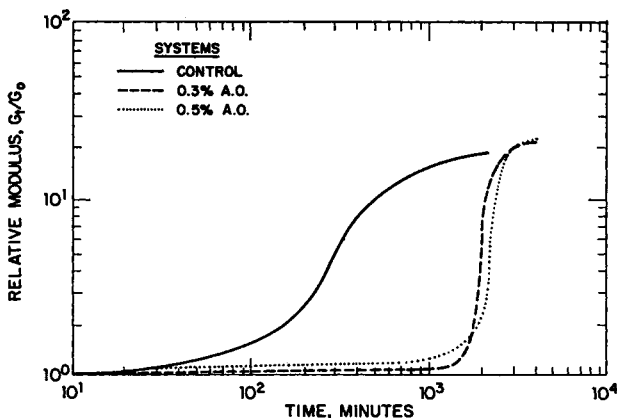


Fig. 6. Relative modulus as a function of aging time in the torsional braid apparatus at 100°C. Actual measurements performed at the aging temperature. The effect of concentration of the antioxidant 2,2'-methylene bis(6-*tert*-butyl paracresol) on *cis*-polybutadiene.

these profiles after a certain concentration level has been achieved. That is, between 0.3 and 0.5% the effectiveness of these levels is essentially the same, indicating some sort of threshold level between 0.1 and 0.3%. To determine whether this threshold behavior was temperature-dependent, two levels of concentration, 0.3 and 0.5%, were studied at 100°C. The samples were aged and run directly in the apparatus at this temperature. The profiles obtained are shown in Figure 6. Once again, there is no marked concentration effect. However, the higher aging temperature did exert an influence on all the systems in this study. In Table III are listed the various times required to reach the embrittlement point, compiled from the profiles generated from the data obtained at 80 and 100°C. It

may be seen that the unprotected control reached the embrittlement point in less than half the time from 80 to 100°C. The effective protection afforded this elastomer by the addition of the antioxidant, however, provided essentially a tenfold increase in time before the embrittlement points at both temperatures was reached.

CONCLUSION

The torsional braid apparatus has been successfully adapted for use in studying the effectiveness of antioxidant compounds in elastomer systems. This was accomplished by utilizing the concept of the embrittlement point on the generated relative-modulus-accelerated-aging-time profiles. The reproducibility of the torsional braid technique for such a study was shown for a particular antioxidant, the crude reaction product of nonylated paraethylphenol and formaldehyde, in a carboxylated styrene-butadiene latex. In this same elastomer system and in a *cis*-polybutadiene system the relative effectiveness of a series of antioxidant compounds was determined in a quantitative manner. In the latex the antioxidants, at a 1% level, were found to decrease in effectiveness as follows: α, α' -2,6-bis(2-hydroxy-3-*tert*-butyl-5-methylphenyl) xylenol > reaction product of nonylated paraethylphenol and formaldehyde > crude 2,2'-methylene bis(6-nonylparacresol). In the *cis*-polybutadiene the antioxidants, at a 0.3% level, were found to decrease in effectiveness as follows: 2,2'-methylene bis(6-*tert*-butyl paracresol) > 1,3,3,5-tetramethyl-1-*m*-tolylindane-4',6-diol > 4,4'-methylene bis(2,6-di-*tert*-butylphenyl). Moreover, in this latter system the effectiveness of 2,2'-methylene bis(6-*tert*-butyl paracresol) was found to be essentially independent of concentration between 0.3 and 0.5%. In addition, though the overall stability of this particular system was found to decrease as a function of increased aging temperature from 80 to 100°C., the approximate tenfold difference in stability of the antioxidant protected system was found to prevail over that of the control.

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