Prediction of Mechanical Behavior of Plastics Undergoing Decomposition from the Combined Effects of Environmental Exposure and Stress

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Synopsis

A study was made to determine whether the behavior of plastics undergoing break-down from the effects of stress, elevated temperatures, and chemical attack could be predicted by means of a mechanical-chemical equation of state. Five systems were studied, the first four of which were tested for retention of strength at room temperature after environmental exposure: (a) glass-reinforced polyester laminate exposed to an alkaline medium at elevated temperatures; (b) cellulose laminate exposed to elevated temperatures, resulting in oxidative degradation; (c) paper–phenolic laminate exposed to elevated temperatures, resulting in further crosslinking followed by oxidative degradation; (d) heat-resistant glass fiber polyester resin laminate exposed to very high degradative temperatures; and (e) same material and treatment as (d) except that the specimens were under stress during the exposure (stress rupture). It is concluded that the effects of the various environments on the mechanical properties of the plastics under study can be predicted accurately by use of a parameter of the equation of state representing a second-order chemical reaction.

INTRODUCTION

The object of this study was to determine whether the behavior of plastics undergoing breakdown from the effects of stress, elevated temperatures, and chemical attack could be predicted by means of a mechanical-chemical equation of state.

Background and Previous Investigation

Prediction of properties of plastics under a variety of conditions of time and temperature but short of chemical decomposition has been accomplished with high accuracy in the past by using rate theory.[1–8] Unlike results which have been obtained from viscoelastic studies, there were no limitations to the use of rate theory, such as level of stress or strain, type and structure of polymer, temperature restrictions based on glass temperature, duration of stress, and limited accuracy.[8,9] Properties of plastics and metals, such as tensile, compressive, and flexural strengths, stress rupture, creep, and high rate of loading, have been computed for time periods from milliseconds to thousands of hours and temperatures to almost 1000°C. The method was subsequently extended to cover chemical

activity in metal while under stress and while subjected to elevated temperatures for extended periods of time, and the basic formula was designated a mechanical-chemical equation of state.[10,11]   In this investigation, a similar study was made with plastic materials so as to include chemical activity in addition to the other variables described.

DERIVATION OF MECHANICAL-CHEMICAL EQUATION OF STATE

The equation of state was derived from the Arrhenius expression.

$$d \ln k/dt = E/RT^2 \tag{1}$$

where k is the reaction rate constant, T the absolute temperature, E the activation energy of the process, and R the gas constant.   If the process of rupture or creep in a material is defined as the separation and/or breaking apart of molecules, then it may be viewed as a chemical reaction.   By integration:

$$\ln (k_0/k) = (E/R)[(1/T) - (1/T_0)] \tag{2}$$

is obtained where k_0 and T_0 are the upper limits.   If T_0 is interpreted as the zero-strength temperature or highest temperature at which the material can exist as an entity, k_0 becomes the corresponding rupture rate at that temperature.   The activation energy, E, although not a constant, does not vary appreciably with temperature.   If E is assumed to be constant in the temperature ranges to be investigated, eq. (2) may be rearranged with all the constants incorporated in the parameter K as follows:

$$K = [TT_0/(T_0 - T)](\log k_0 - \log k) \tag{3}$$

Since there are 6.02×10^{23} atoms in a mole, the maximum possible rupture rate will be 6.02×10^{23} atoms per unit time.   The value of $\log k_0$ is 22.78, and eq. (3) assumes the form of the mechanical-chemical equation of state:

$$K = [TT_0/(T_0 - T)](22.78 - \log k) \tag{4}$$

Since what has been considered in the past to be a purely mechanical phenomenon is now being handled as a chemical reaction, the reaction rate k may be expressed in terms of the time t by using kinetic relationships.

Three orders of chemical reactions will be considered: zero order, where

$$k = x/t \tag{5}$$

and where x is the concentration of the material under stress in time t, first order, where

$$k = \ln 2/(t/2) \tag{6}$$

and second order, where

$$k = 1/(at/2) \tag{7}$$

and where a is the product of the concentration of the reactants or the square of the concentration of one reactant.

Equation (4) may now be written in terms of t by combining it with eqs. (5), (6), or (7). This will give

$$K = [TT_0/(T_0 - T)](22.78 + \log t - \log x) \qquad (8)$$

in the case of a zero-order reaction. The value of $\log x$ may be evaluated in the following manner. In the case of an iron alloy, the highest concentration of the material undergoing stress will be approximately 140 mole/l. of the iron. The logarithm of $140 = 2.146$. Thus, 22.78 will be reduced to 20.53 when consolidated with the value of $\log x$.

In the case of plastics, a polymer with a molecular weight of 50,000 and a density of 1.3 will have 0.026 mole/l., the logarithm of which is -1.59. This would be an approximation of $\log x$. The value of $\log k_0$ should also be adjusted. If it is assumed that the plastic has a hydrocarbon structure, there will be approximately 3,500 atoms in the chain. The effective number of molecules per mole would then be $6.02 \times 10^{23}/3.5 \times 10^3 = 1.7 \times 10^{20}$, the log of which would be 19.2. The value of $\log k_0 - \log x$ would then be $19.2 + 1.59 = 20.79$.

Equation (8) can be used where the rupture strength is independent of the concentration of an ingredient in the material and T_0 and T are relatively close as in all thermoplastic and thermosetting resins with or without filler or fibrous reinforcement. This equation has been useful in predicting the strength of thermoplastics where the constant 22.78 was rounded off to 20.[4] When T_0 is very high with respect to T, the fraction $[T_0/(T_0 - T)]$ reduces almost to unity and eq. (8) reduces to

$$K = T(22.78 + \log t) \qquad (9)$$

When 22.78 is rounded off to 20, eq. (9) will be recognized as the empirically derived Larson-Miller parameter which has been useful in predicting stress rupture and creep in glass-reinforced plastics and some metals at elevated temperatures.[1−6,10,11]

If a first-order reaction occurs, eq. (8) becomes

$$K = [TT_0/(T_0 - T)][22.94 + \log (t/2)] \qquad (10)$$

and must be used where T and T_0 are relatively close but may be used in all other cases.

When eq. (10) is reduced to

$$K = T[22.94 + \log (t/2)] \qquad (11)$$

a number of alloys such as 2Cr–Mo and DM (chrome-moly high temperature steel) are characterized by eq. (11).[10] In the case of a second-order chemical reaction, the equation becomes

$$K = [TT_0/(T_0 - T)][22.78 + \log (at/2)] \qquad (12)$$

and in its reduced form,

$$K = T [22.78 + \log (at/2)] \qquad (13)$$

Equations (12) and (13) should be useful where chemical reactions in the

usually accepted sense occur simultaneously with or prior to an applied mechanical stress.

APPLICATION OF PARAMETERS

The parameters may be used in several ways. Master rupture curves may be drawn with stress-rupture properties as the ordinate and the parameter as the abscissa. Or they may be made with such static strength properties as tensile strength as the ordinate and the parameter as the abscissa.

Since t in eqs. (8)–(13) represents the time during which the material is under a constant stress rather than a gradually increasing one, the time to ultimate failure measured during the static test cannot be used in the parameter without excessive error. A steady-load-time equivalent (SLTE) is needed, i.e, the time to failure if the ultimate stress determined in the static test were applied instantaneously to the specimen.

Empirical studies have indicated that the SLTE is approximately 10^{-4}–10^{-5} hr. When a master curve is being drawn based on static tests, this value can be introduced for t in eqs. (8)–(13) for all values of T and a. Once the curve is drawn, however, any combination of values of T, t, and a can be used to determine creep-rupture stress or creep. Creep may be simply calculated from static properties by dividing the stress by the tangent modulus at a specified stress level, using a master curve drawn with the modulus as the ordinate.[3,4]

It is not necessary to draw a complete master curve if only isolated data are required. For example, suppose a simple case requires the use of a zero-order reaction parameter [eq. (2)], i.e.,

$$K = T (22.78 + \log t)$$

The question is how long the plastic will last while under a specified constant stress and temperature.

A strength–temperature curve may be available from the manufacturer's commercial literature, so that the strength at any temperature within the experimental limits of the data provided is known.

The parameter K at any given stress represents a spectrum of variations of time and temperature:

$$K = T_1(22.78 + \log t_1) = T_2(22.78 + \log t_2) = T_3 \text{ (etc.)}$$

The absolute temperature T_0 at the specified stress may be obtained from the strength–temperature curve. The time t_0 (the SLTE) will be 10^{-4} hr. If the long-time temperature is T_2, then the time t_2, the length of time the material will last, can be calculated readily since it is the only unknown.

Similarly, if it were known that the same plastic would stand up at a given stress level for 10 hr. at 250°F., then it would be a simple matter to calculate how long the plastic would last at 73°F., by equating the two conditions and solving for the unknown t; e.g.,

$$(250 + 460)(22.78 + \log 10) = (73 + 460)(22.78 + \log t)$$

GENERAL PLAN

A selection of conditions was chosen from the literature which included, according to the authors, exposure to high temperatures and an alkaline medium, oxidative degradation, crosslinking followed by thermal degradation, and thermal degradation comprising an aftercure followed by chain scission and oxidation. In previous investigations, master rupture curves were drawn from either long-term stress-rupture data or static strength data at elevated temperatures by using an SLTE. In this study, there was one case of the former type (compression stress-rupture) and a new type of condition consisting of treating the specimens for various periods of time and ranges of temperatures and exposure to a special environment, cooling them to room temperature, and then giving them a static strength test. It was not known if the data gathered under the latter conditions would be amenable to solution by the techniques described or if an SLTE would be required. It was found by a preliminary exploratory inspection that the data would not fit a zero- or first-order equation [eqs. (8)–(11)] and, hence, would require study to determine their compliance with a second-order reaction equation [eqs. (12)–(13)]. Since the values of a were unknown, it was necessary to find them by empirical means. The procedure used was first to calculate the values of the parameters by using the experimental data for t and T and combinations of assumed estimated values of T_0 and a. It is possible to obtain the T_0 by drawing temperature versus strength curves and then approximating its value at zero strength by extrapolation. In past work,[4] the manufacturers' lowest recommended injection molding temperature was found to give a good approximation of T_0. In the absence of information of either type, as was the situation with several cases studied here, the value of T_0 had to be estimated or found empirically. A computer was used to make the calculations. Master rupture curves of per cent retention of strength versus the value of the parameter were drawn on a Dataplotter by use of punched card input. The best curve from each group was selected and replotted. The degree of congruency of stress or stress-rupture parametric isothermals at various temperature levels indicated the exactness of the parameters. Perfection existed when the isothermals coalesced into one curve with no scattering of data.

Scattering of data and noncongruency of isothermals with the main curve were not to be blamed wholly on the inadequacy of the parameter to portray what was occurring inside the materials as conditions changed. The data were very often at fault. This would be discovered by a study of the internal consistency of the data. For example, Clauss,[12] in a study of stress-rupture curves, found that when isothermals were plotted on log–log paper and the temperature difference between them was constant, they fell into four classes of behavior: class 1: a family of parallel straight lines equidistant from each other along the ordinate axis; class 2: a family of parallel curved lines equidistant from each other along the ordinate axis; class 3: lines straight as in class 1 but fanning out so that the slopes of the

isothermals increase as the temperatures increase; class 4: lines curved as in class 2, the curvature being downward and increasing as the temperatures increase.

EXPOSURE TESTS

The tests to which the materials were exposed were as follows.

Exposure to High Alkalinity

An alkaline solution (consisting of a mixture of NaOH, H_3BO_4, KCl, and water) with a pH of 10 in combination with elevated temperatures constituted a simulated soil exposure accelerated test.[13] The test material, a glass-reinforced plastic, contained a resin of the isophthalic polyester type. Flexural strength test specimens, $3/16$ in. thick and $1/8$, $1/4$, and $3/8$ in. wide were placed in closed beakers for 70°C. and 100°C. exposures and in an autoclave for a 130°C. exposure. After removal at various intervals, the specimens were soaked in water for 24 hr. prior to testing at room temperature.

Oxidative Degradation

A laminate (containing unmodified cotton cellulose fibers bonded with a phenolic resin and butadiene acrylonitrile elastomer stabilized with an amine-type acid acceptor) was exposed to various temperatures for extended periods of time, cooled to room temperature, and tested. Oxidative degradation was reported as the chemical reaction which occurred during the process.

Crosslinking and Oxidation

A paper–phenolic laminate which was at an optimum cure for the application but was not fully crosslinked was heated to temperatures of 125, 150, 175, and 200°C. for periods of time up to 4000 hr.[14] The cure was advanced by the treatment, resulting in further crosslinking, finally followed by oxidative degradation.

Thermal Degradation

A heat-resistant polyester laminate molded by the Naugatuck Chemical Company of Vibrin 135 resin and 181 type glass fabric with Garan finish was heated for periods of time up to 1000 hr. and at various temperatures up to 538°C. (1000°F.)[15] At intermediate temperature levels [260°C. (500°F.)–306°C. (600°F.)], there was an increase in strength followed by a precipitous decline indicating further crosslinking followed by chain scission and oxidation. Loss of weight also indicated volatile decomposition products were being formed. Tests were run by two methods: (1) after exposure to elevated temperatures at no stress, and (2) combined stress and exposure to elevated temperatures at the test temperatures (stress-rupture).

RESULTS

The results of the calculations are shown in Figures 1–7 and Table I. All the materials studied appeared to be undergoing a second-order reaction as was indicated by the excellent congruency of most of the parametric isothermals in the master rupture curves drawn by using eqs. (12)
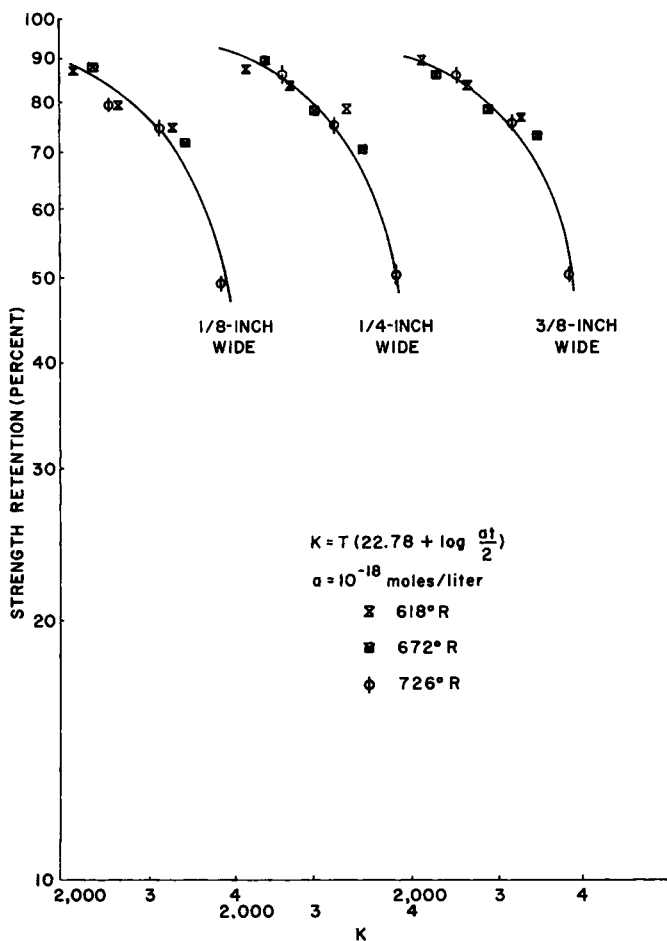

Fig. 1. Master rupture curves for polyester resin glass fiber-reinforced plastics exposed to combination of elevated temperatures and high alkalinity.[13]

and (13) the second-order reaction parameters. Moreover, the plastics which were studied and which had no glass fiber reinforcement (cellulose laminate and paper–phenolic laminate) and, consequently, whose T and T_0 were close, conformed to eq. (12), whereas the glass fiber-reinforced plastics conformed to eq. (13) as predicted.
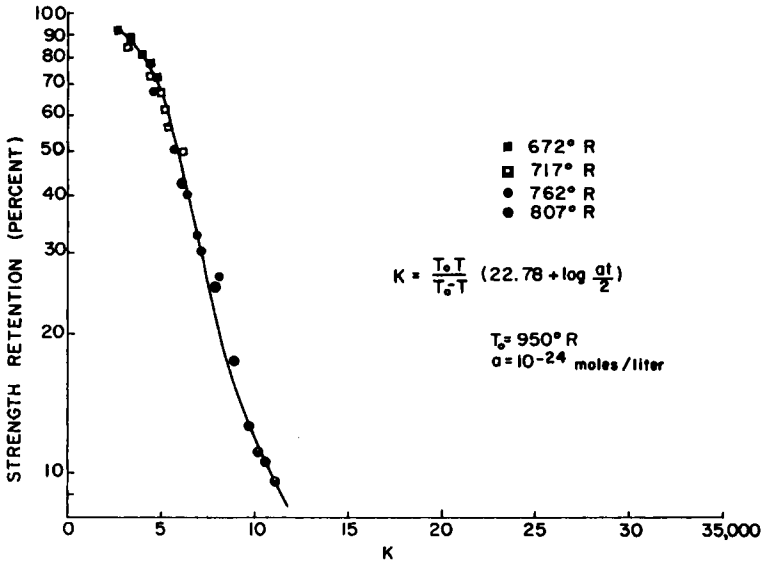
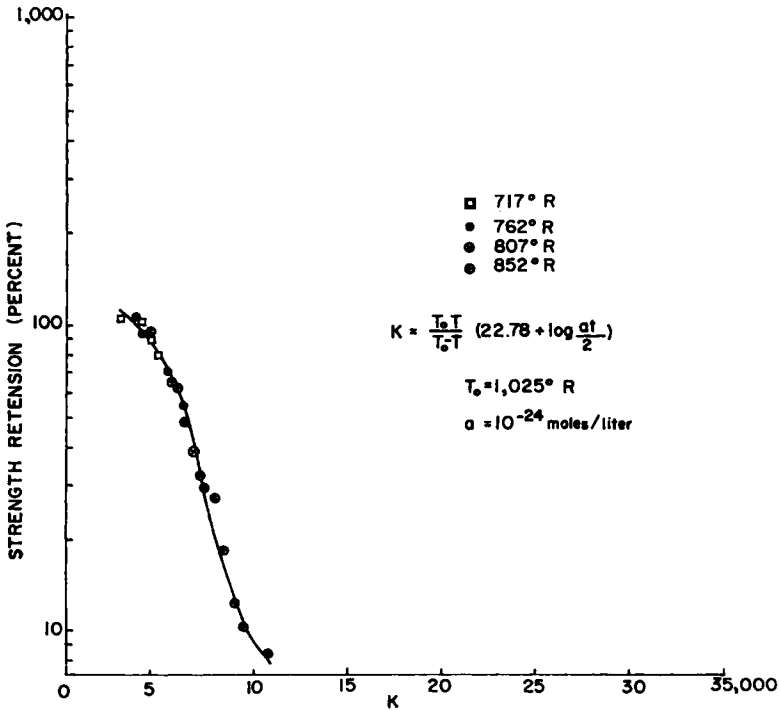Fig. 2. Master rupture curve for cellulose laminate stabilized with amine acid acceptor undergoing oxidative degradation.[14]

Fig. 3. Master rupture curve for paper–phenolic resin laminate reported to be undergoing crosslinking and thermal degradation.[14]
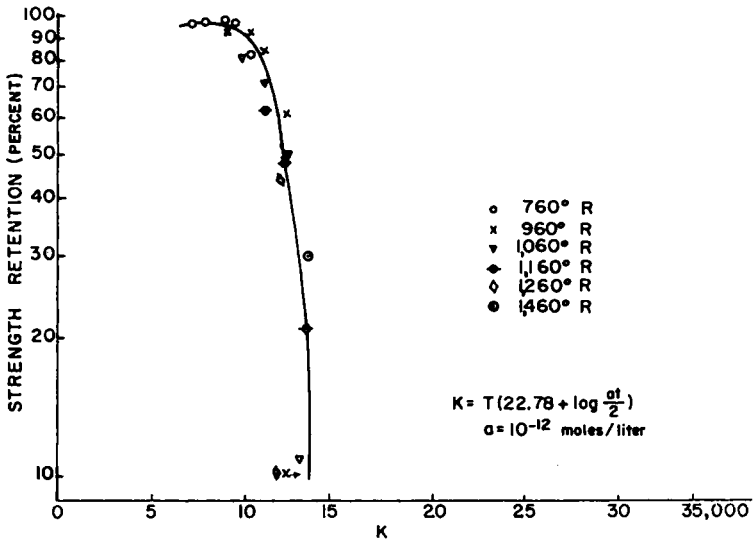
Fig. 4. Master rupture curve for thermal degradation of polyester resin Vibrin 135 glass cloth laminate as shown by tensile strength tests.[15]
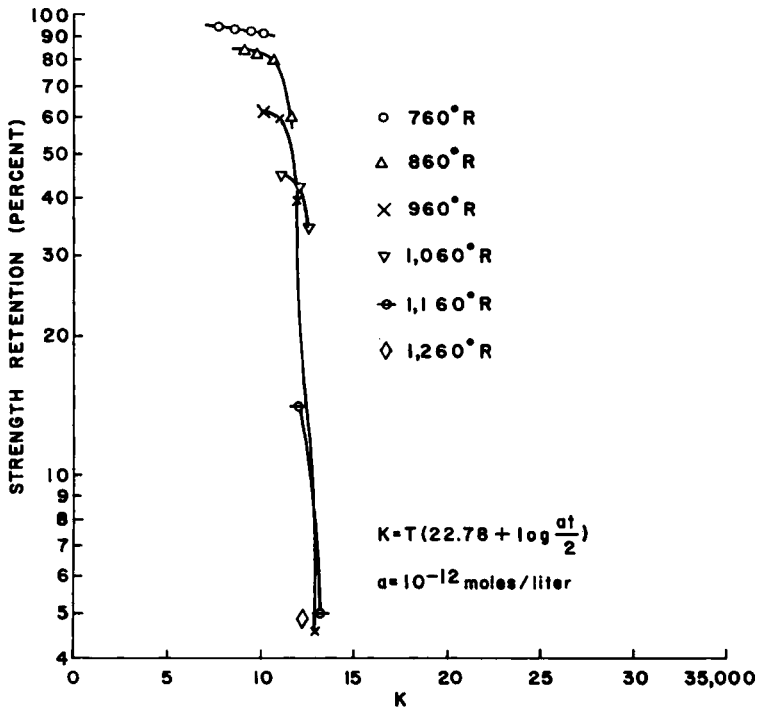

Fig. 5. Master rupture curve for thermal degradation of polyester resin Vibrin 135 glass cloth laminate as shown by flexural strength tests.[15]
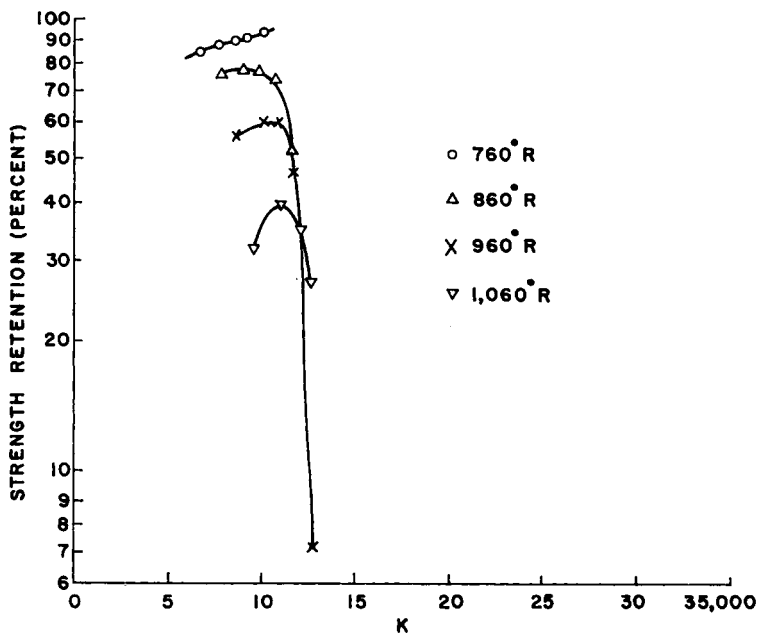
Fig. 6. Master rupture curve for thermal degradation of polyester resin Vibrin 135 glass cloth laminate as shown by compressive strength tests.[15]
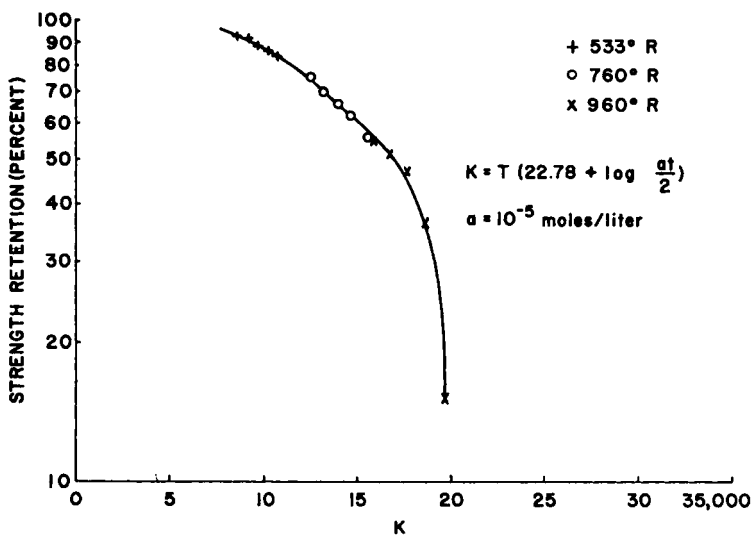

Fig. 7. Master rupture curve for thermal degradation of polyester resin Vibrin 135 glass cloth laminate as shown by compressive stress-rupture tests.[15]

DISCUSSION

Stress–time curves for the Vibrin 135 glass fiber cloth laminate indicated anomalous behavior, in that at higher temperatures some of the curves

TABLE I
Summary of Results of Study

Figure	Material	Environment, treatment	a, mole/l.
1	Polyester resin glass-reinforced laminate	Alkaline, pH 10	10^{-18}
2	Cellulose plastic, amine stabilized	Oxidative degradation	10^{-24}
3	Paper–phenolic laminate	Crosslinking, thermal degradation	10^{-24}
4	Heat-resistant polyester glass-reinforced laminate	Thermal degradation (tensile)	10^{-12}
5	Heat-resistant polyester glass-reinforced laminate	Thermal degradation (flexural)	10^{-12}
6	Heat-resistant polyester glass-reinforced laminate	Thermal degradation (compressive)	10^{-12}
7	Heat-resistant polyester glass-reinforced laminate	Thermal degradation, constant compressive stress	10^{-5}

first increased in slope and then finally decreased as the temperature and time increased. This was interpreted by Boller[15] as resulting from strengthening due to further crosslinking and possibly polymerization followed by oxidative degradation. Figures 4–6 show how the master rupture curves reflect this situation. The individual isothermals, all starting from different locations outside the backbone of the curve, meet the latter after first going through changes reflecting further curing and degradation of the resin. Since it is known that the glass fibers also go through an irreversible structural change starting at about 400°F., this would have a further degrading effect on the laminate as a whole as the polymer degrades. The
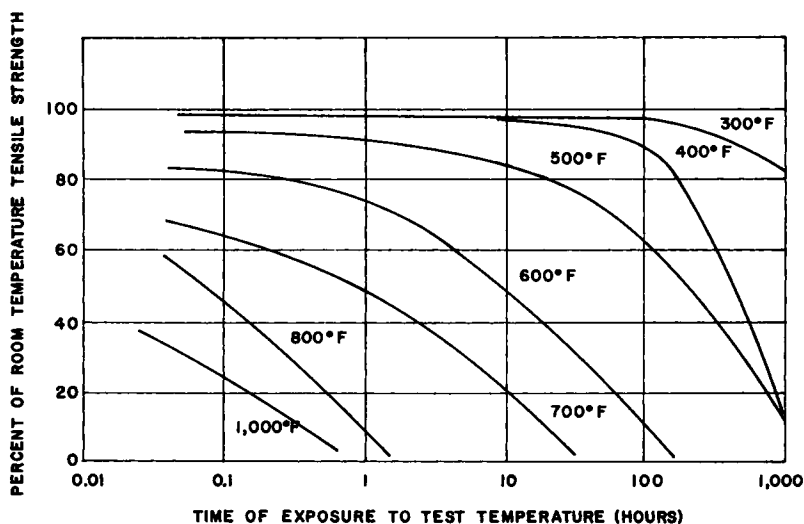

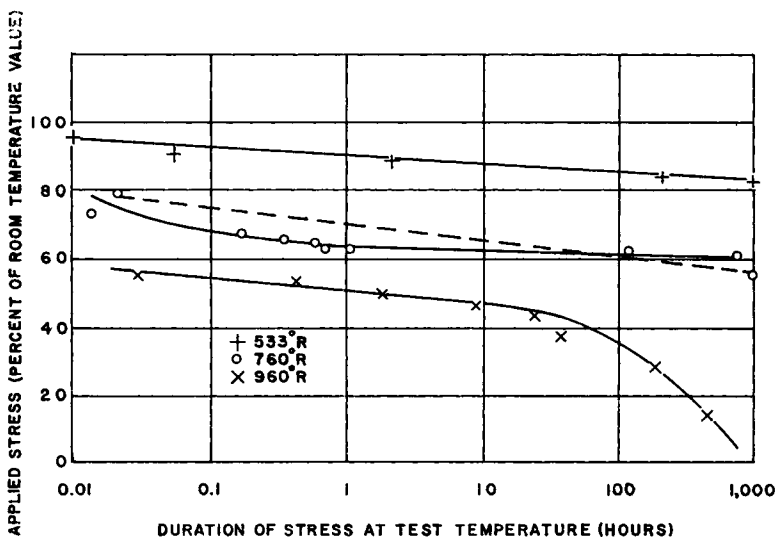Fig. 8. Curves of per cent retention of strength vs. time of exposure.

Fig. 9. Compressive stress-rupture curves of polyester laminates molded with Vibrin 135 and 181 glass cloth fabric.

master rupture curve shown in Figure 4 presented a special problem. The parametric isothermals, although close to each other and headed in the same general direction, never coalesced into one fine curve. A study of all the curves which were drawn with values of a varying in decade intervals indicated that this one had the minimum divergence of the isothermals. Values of a lower and higher than 10^{-12} mole/l. produced poorer results not only for the tensile strength but also for the flexural and compressive strengths (Figs. 5 and 6) representing properties of the same material exposed to the same environment. A study of the strength–time isothermals (Fig. 8) showed where the fault lay. The set of curves were either class 2 or 4 type as described by Clauss, but the isothermals were so irregularly spaced that it was impossible to tell to which group they belonged. This irregularity had the effect of spreading out the master rupture curve.

The compressive master rupture curve shown in Figure 7 also presented a problem. Data representing only three isothermals were available, and none of them overlapped with regard to stress levels. As a result, there was a large number of possibilities for the value of a which could not be checked in any manner. Recourse had to be made to a study of the stress-rupture curves as shown in Figure 9. If data were taken from the center isothermal representing 760°R. as shown by the solid-line curve, then a value of a of 100–1000 mole/l. would be obtained, a wholly unrealistic quantity. If the set of curves is examined from the standpoint of the four classes of behavior described by Clauss, then it is recognized immediately that the 760°R. curve should be redrawn as shown in the dashed-line curve, parallel to the 533°R. curve as a straight line and about midway between the 533°R. and 960°R. curves. Further evidence supporting the use of

this procedure was found by studying the 760°R. time–stress curves[15] and the parametric isothermals for 760°R. shown in Figures 4–6, which were all straight lines at this relatively low temperature. The new value of 10^{-5} mole/l. liter for a was realistic and, moreover, produced a smooth-flowing curve similar to the others.

It was found that the use of the SLTE was not necessary in drawing the master rupture curves shown in Figures 1–6, in spite of the fact that they were drawn with static strength data. The reason for this is not understood.

Table I gives a summary of the results of the study. The extremely small values of the initial concentration of the reactant a are of great interest and support the theory that a chain reaction can be initiated by one free radical within the polymer by energy from one of several sources; e.g., heat.[16] This would result in the gradual destruction of the polymer. In the case of the polyester resin laminate in the alkaline medium, it is probable that the resin was hydrolyzed with the alkaline material acting as a catalyst. The degradation of the heat-resistant polyester resin Vibrin 135 is also of much interest. Figures 4–6 reflect the results of, first, exposure to high temperatures and, second, effects of static testing at room temperature after the exposure. The value of a was 10^{-12} moles per liter. Figure 7 reflects the results of the simultaneous effect of high temperatures and constant compressive stress. The value of a was 10^{-5} mole/l. The difference between the two values of a (i.e., 10^{-12} and 10^{-5}) must represent the mechanical factor of creep. The latter may also have had an accelerating effect on the thermal degradation taking place.

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Résumé

On a effectué une étude en vue de déterminer si l'on pouvait prévoir au moyen d'une équation d'état mécanochimique le comportement de plastiques qui se dégradent par suite d'une tension, de températures élevées ou d'une attaque chimique.   Cinq systèmes ont été étudiés; les quatre premiers ont été examinés du point de vue de la rétention de leur force à température ordinaire après des traitements divers auxquels ils ont été soumis: (a) les laminés en polyester renforcé au verre, exposés à un milieu alcalin à températures élevées, (b) les laminés de cellulose exposés à températures élevées, résultant d'une dégradation oxydante, (c) les papiers laminés phénoliques exposés à températures élevées, avec comme conséquence un pontage progressif suivi de dégradation oxydante, (d) une résine laminée thermorésistante à base de polyester et fibre de verre, exposé à des températures de dégradation très élevées, et [(e) certain matériel comme (d) sauf que les échantillons étaient sous étirement au cours de leur exposition (rupture à l'étirement)]. On en conclut que les effets des divers traitements sur les propriétés mécaniques des plastiques étudiés peuvent être prédits avec précision, en utilisant un paramètre de l'équation d'état, qui représente une réaction chimique du second ordre.

Zusammenfassung

Es wurde untersucht, ob sich das Bruchverhalten von Plastomeren unter dem Einfluss von äusserer Spannung, erhöhter Temperatur und chemischem Angriff auf Grund einer mechanochemischen Zustandsgleichung voraussagen lässt.   Fünf Systeme wurden untersucht, von denen die ersten vier auf die Beibehaltung ihrer Festigkeit bei Raumtemperatur nach der entsprechenden Einwirkung getestet wurden: (a) glasverstärkte Polyesterlaminate nach Einwirkung eines alkalischen Mediums bei erhöhter Temperatur; (b) ein Celluloselaminat nach Einwirkung erhöhter Temperatur, welche zum oxydativen Abbau führte; (c) Papier-Phenolharzlaminate nach Einwirkung erhöhter Temperatur und dadurch bedingte weitere Vernetzung mit darauffolgendem oxydativem Abbau; (d) hitzebeständiges Glasfaser-Polyesterlaminat nach Einwirkung sehr hoher Abbautemperaturen und (e) gleiches Material und Behandlung wie (d), nur dass die Proben während der Einwirkung unter Spannung standen (Spannungsbruch).   Man kommt zu dem Schluss, dass der Einfluss der verschiedenen Beanspruchungen auf die mechanischen Eigenschaften der untersuchten Plastomeren mittels eines Parameters der eine chemische Reaktion zweiter Ordnung darstellenden Zustandsgleichung genau vorausgesagt werden kann.