Study of a Heat-Resistant Plastic Laminate from the Standpoint of a Mechanical–Chemical Equation of State

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Synopsis

The object of this study was to analyze the complex degradation history of a heat-resistant epoxy resin laminate using the mechanical–chemical equation of state. A further object was to determine if weight-loss measurements at elevated temperatures could be used to predict long-term rupture strength. Master rupture curves drawn by using a second-order parametric form of the equation of state largely clarified the anomalous behavior of the laminate. It was not found possible to predict the long-term mechanical properties from weight-loss data although there was evidence of some correlation.

INTRODUCTION

The object of this study was to analyze the complex degradation history of a heat-resistant epoxy resin laminate by using the mechanical–chemical equation of state. A further object was to determine if weight-loss measurements at elevated temperatures could be used to predict long-term rupture strength. It has been found that it is possible to predict the mechanical properties of plastics and metals under a variety of conditions of varying time and temperature as well as chemical activity by using a mechanical–chemical equation of state.[1,2]

$$K + [TT_0/(T_0 - T)] (\log k_0 - \log k) \tag{1}$$

where T is the absolute temperature, T_0 is the zero-strength temperature, and k_0 is the upper limit of integration of the reaction rate constant k. For a glass fiber-reinforced plastic, the equation of state takes the parametric form

$$K + T[23.78 + \log (at/2)] \tag{2}$$

where a is the product of the concentration of the reactants or the square of the concentration of one reactant and t is the time. The value of $\log k_0$ was erroneously reported as 22.78, but it may range from 20 to 24 without significantly affecting the accuracy of the results. In the latter study,[2] analyses included studies of a glass fiber-reinforced polyester laminate

exposed to an alkaline medium at elevated temperatures and a heat-resistant glass fiber polyester resin laminate exposed to high degradative temperatures. The successful results of these studies prompted this investigation.

INVESTIGATION

The tensile and compressive properties as well as the weight loss at elevated temperatures of a heat-resistant epoxy laminate was investigated as a function of the parameter K, a value of 22.78 for log k_0 being used. Master rupture curves were drawn by using experimental data supplied by the Forest Products Laboratory[3] under contract with the U. S. Air Force at the Wright-Patterson Air Force Base. An analysis was then made of the curves.

Materials Used

Laminated panels of epoxy resin reinforced with glass fabric were furnished by the Union Carbide Plastics Company, Bound Brook, New Jersey. Information supplied with the material was as follows: resin, ERSB-0111 (a product of Union Carbide); catalyst $1^1/_2\%$ BF$_3$ monoethylene on resin solids; fabric, S 994 glass, 181 weave and HTS finish; number of plies, 12; fabric orientation, not nested but parallel laminated; resin content, 37% impregnated from solution, precure, none; cauls, polished steel with silicone release agent; cure, 1 hr. at 160°C. (320°F.) and 200 psi, then 2 hr. at 190°C. (374°F.), cool and discharge from press; postcure, 6 hr. at 205°C. (401°F.); panels, $1/_8 \times 22 \times 2$ in.; laminating pressure, 200 psi; barcol hardness, 75; specific gravity, 1.80; average resin content, 35% after burnoff.

Test Methods

The properties were determined in accordance with the methods presented in Table I.

TABLE I
Test Methods

Mechanical test	Federal test method standard no. 406	ASTM method
Tension	1011	D 638-60T
Compression	1021	D 695-63T
Weight loss	7041	None

The strength properties were determined for each specific temperature and are based on tests of specimens that were both soaked and tested at that temperature.

The procedure used was to first calculate the values of the parameters by using the experimental data for time t and temperature T and the as-

sumed estimated values of a. Although it was known from previous work that a value of a of 10^{-12} moles per liter gave the best results for chemical breakdown due to exposure at elevated temperatures, computation of K for values of a from 10^{-25} to 10 were made.[2] A computer was used to make the calculations. Master rupture curves of per cent retention of strength and weight versus the value of the parameter were drawn on a Dataplotter using punched card input. The best curve from each group was selected and replotted.

RESULTS AND DISCUSSION

Figures 1, 2, and 3 present the results of the tests in graphical form. Of particular interest are the curves representing the results of the tests after exposure of the laminate at elevated temperatures (Figs. 2 and 3). The retention of tensile strength test curves appear to be the most complex.

It was found that a value of 10^{-12} mole/l. for a gave the best set of master rupture curves. The results of the calculations are shown in Figures 1–3.

The value of 10^{-12} mole/l. for a was the same quantity which was found in a previous study for the thermal degradation of a heat-resistant polyester resin glass-reinforced laminate.[2] If future studies on materials in similar environments and treatments produce the same value for a, the necessity for checking all possible values of a for the best master rupture curve would be eliminated.

The anomalous behavior of the tensile and compressive strength as exemplified by the unusual set of curves in Figures 1 and 2 was clarified to a certain extent by the shapes of the master rupture curves shown in Figures 4 and 5. The isothermal parametric curves never did coalesce into
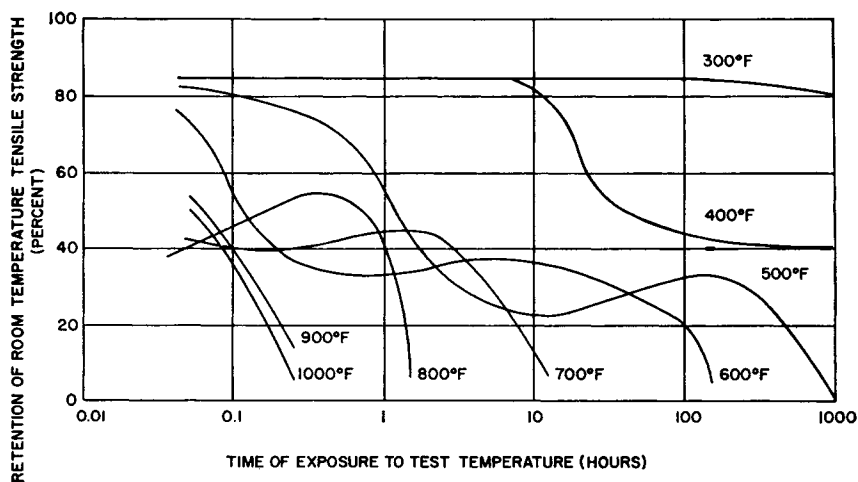

Fig. 1. Curves of tensile strength retention after elevated temperature exposure vs. time of exposure.
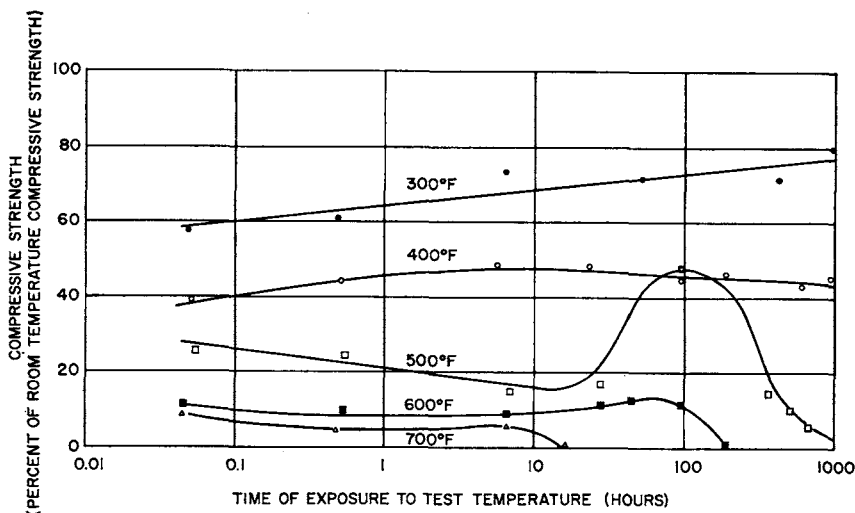
Fig. 2. Curves of compressive strength retention after elevated temperature exposure vs. time of exposure.
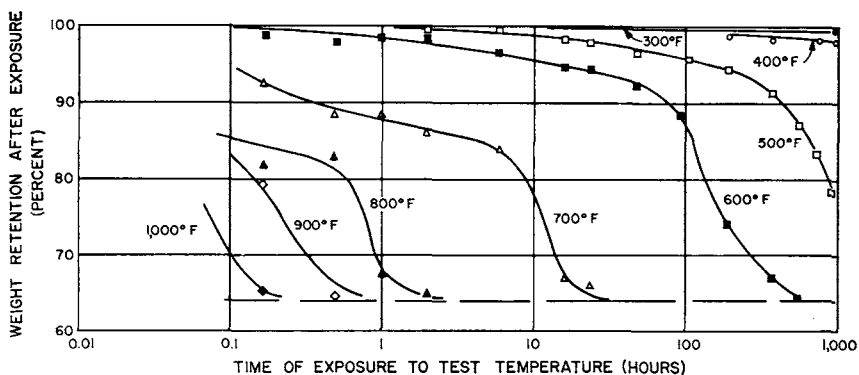

Fig. 3. Curves of weight retention after elevated temperature exposure vs. time of exposure.

one master curve. This was probably due to the fact that the resin itself was not fully crosslinked, and the rate of crosslinking and degradation were different at different temperatures. Figure 5 which represents the compressive strength and, hence, more directly the plastic component of the laminate is easier to follow. Treatment at either 300 or 400°F. produced further crosslinking immediately offsetting any reduction in strength caused by viscoelastic effects. On the other hand, at 500–700°F., viscoelastic effects at first predominated, resulting in a net reduction of strength masking the simultaneous crosslinking which must have been occurring. When the extra strength supplied by the crosslinking finally outweighed the drop caused by viscoelastic conditions, the strength rose precipitously until viscoelastic effects and chemical structural degradation again predominated
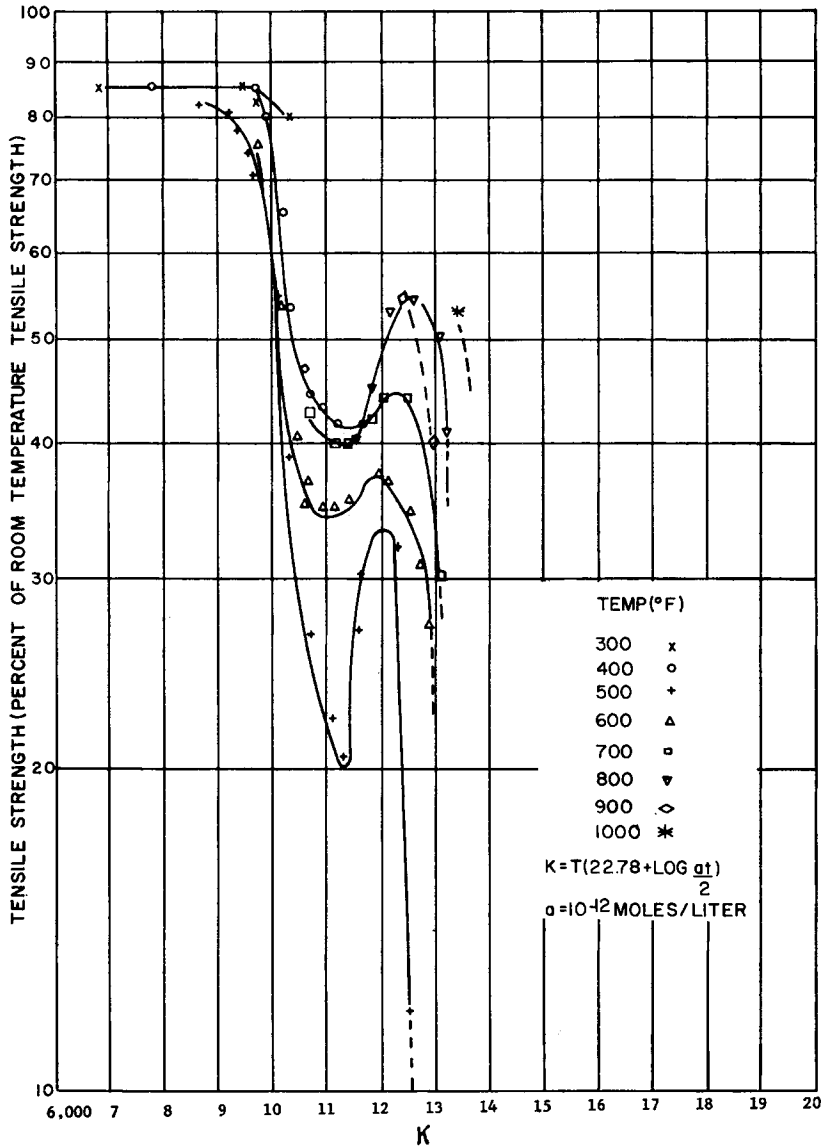
Fig. 4. Master rupture curve for tensile strength retention after exposure of laminate to elevated temperatures.

and took their irreversible toll, and the curve fell downward to new depths. The material could not be said to have behaved as a uniform material except perhaps at the very end of its life where its strength was so small as to be immaterial.

The tensile strength master rupture curve (Fig. 4) like the compressive one had a similar shape in outline only. However, whereas the higher
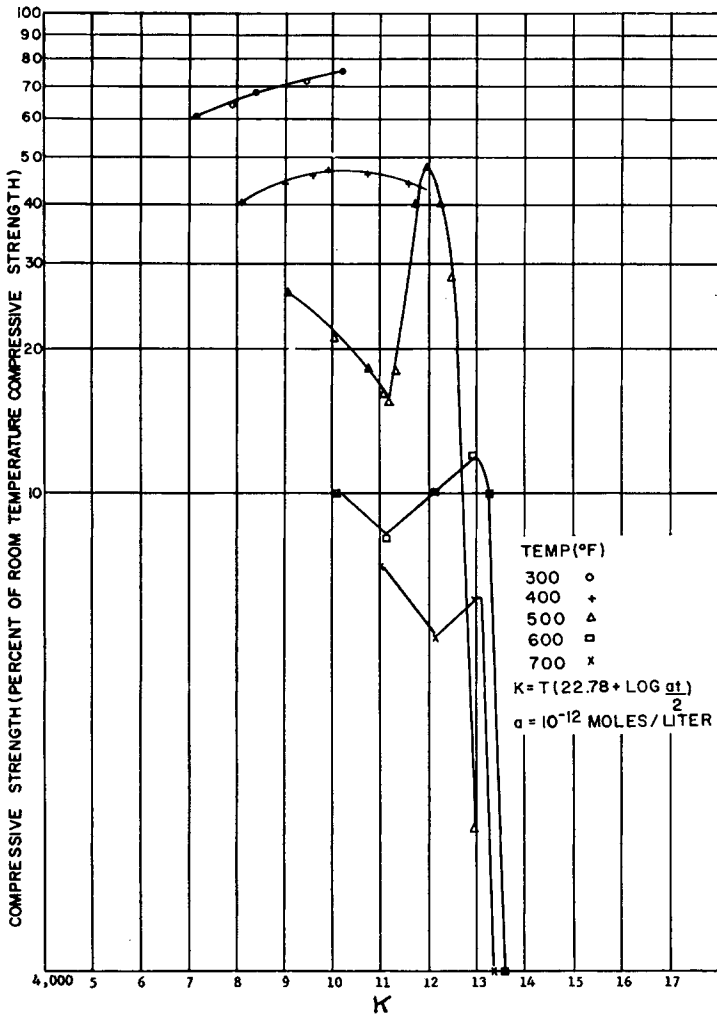
Fig. 5. Master rupture curve for compressive strength retention after exposure of laminate to elevated temperatures.
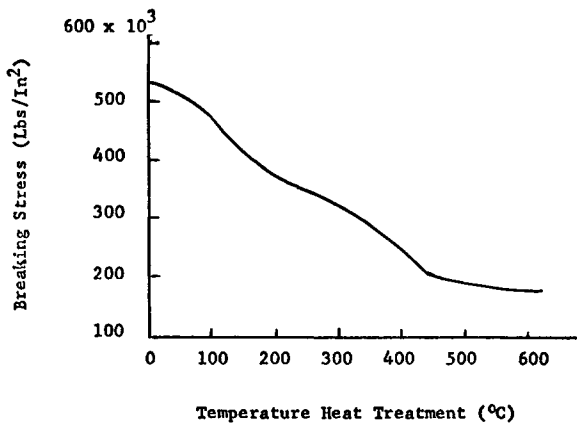

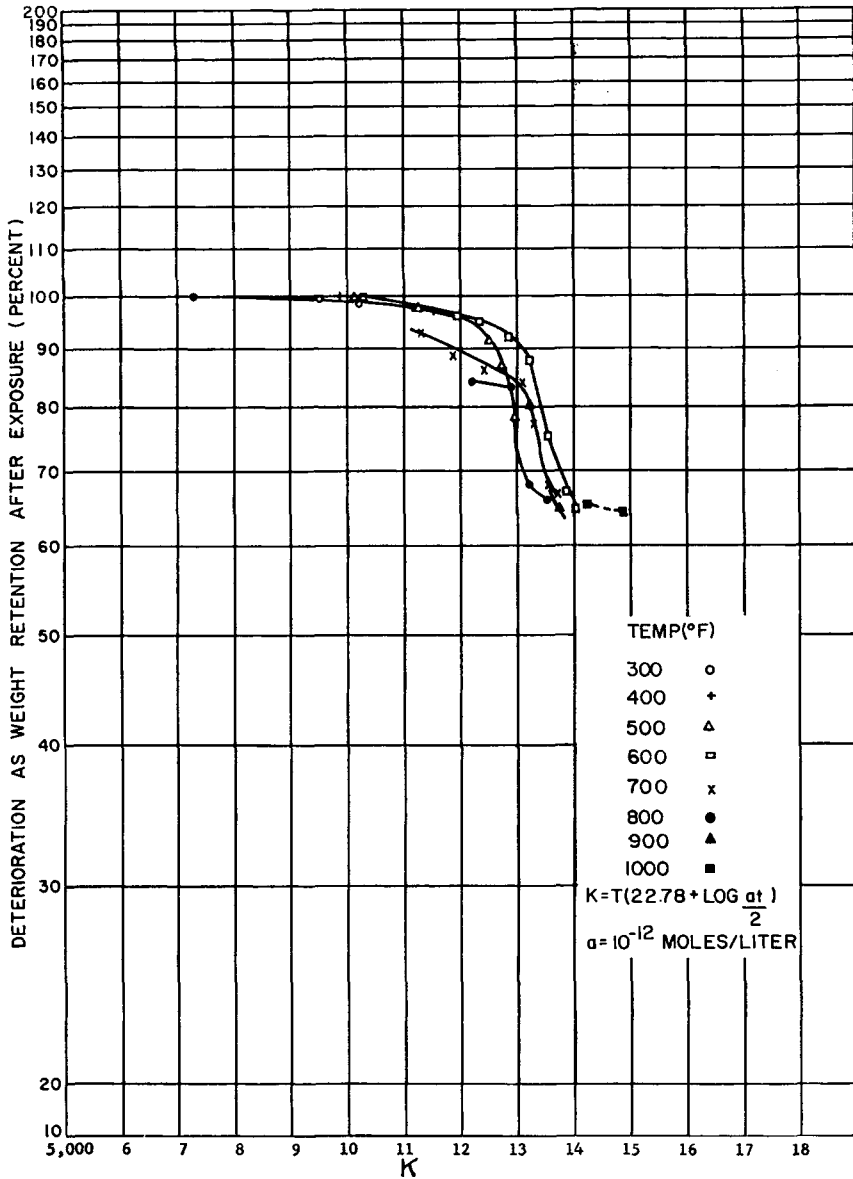Fig. 6. Variation of tensile strength with temperature of heat treatment.

Fig. 7. Deterioration master curve.

temperature parametric isothermals were at the lower end of the curve with the highest temperature (700°F.) at the bottom for the compressive curve, the situation was almost reversed in the tensile curves. When those isothermals which have data in the $K = 12,000$ region are examined, it is observed that the 500°F. one is at the bottom followed by the 600°F. one immediately above it, the 700°F. above this, and finally the 800°F. one on top. Since the strength of the glass fibers is a major factor in the tensile

strength, it might explain this paradox. In the absence of strength–temperature data for S fiber, Figure 6, which shows how E fiber varies with temperature, is presented.[4] The effect of elevated temperatures on E and S fibers is very similar and is irreversible around 500°F. Figure 6 shows that at 500°F. the fiber retained approximately 65% of its strength; at 600°F., 58%; and at 700°F., 50%. Thus, while the laminate was losing large portions of its compressive strength caused by viscoelastic effects in the plastic (which only constituted 35% of the laminate), the losses sustained by the tensile strength were less severe since the bulk of this property came from the glass fiber which constituted 65% of the laminate. This effect, then, may have masked the large viscoelastic effects which occurred in the plastic.

The deterioration master curve (Fig. 7) displayed a more conventional shape. Although it too did not coalesce into one single curve with congruent isothermals, the isothermals were close. It had been hoped that the deterioration curve would be so located and shaped that it would correlate with the master rupture curves so that the strengths might be predicted from deterioration data which is far easier to obtain. Actually, the main region of activity was in the $K = 13,000$ area for tensile, compressive, and deterioration data. It was in an area of relative uselessness, however, since it represented the laminate in its last stages of degradation. If the laminate could be considered to be a homogeneous material, it is in the area just before $K = 10,000$ shown in Figure 4, the tensile master rupture curve. This correlates with the deterioration curve (Fig. 7) at the point where the laminate had lost about 2% of its weight. Since only the plastic component deteriorated within the temperature range considered, it was too much to expect correlation with the entire laminate which was composed of only one-third plastic. Study is required first in the correlation of weight deterioration with strength in a completely organic plastic polymer. It is believed that all the curves go through a maximum, but sufficient experimental data in the pertinent temperature and time range were not available to indicate this.

References

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