

# Accelerated Heat Age Testing of Phenolics: Applicable Temperature Range

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## Synopsis

An upper bound in temperature for accelerated heat aging of a phenolic molding compound has been determined. Oxidative degradation based on time and temperature follows the Arrhenius relationship up to this upper temperature bound, after which thermal shock becomes the primary mode of failure.

## INTRODUCTION

During development of heat-resistant phenolic molding compounds, it is advantageous to have an accelerated elevated temperature test that accurately predicts behavior at lower actual use temperatures. With an accelerated test that can be used with confidence, experimental results can be evaluated in much shorter times.

Ultimately, any heat resistant molding compound used commercially must receive an Underwriters Laboratory (UL) thermal index designation. This involves rigorous thermal aging and subsequent testing procedures, which are spelled out in detail in UL bulletin 746B. The method requires testing at four temperatures, the lowest of which can take considerable time (9–12 months). While this is necessary and desirable as an ultimate criterion of performance, it is too long for screening results in a materials development program.

A review of the literature subsequent to 1965 revealed no information on accelerated heat aging for phenolics. Information on conventional long-term heat aging of phenolics was limited to the following test methods: ASTM D3045, D1870, and UL746B "Long Time Heat Aging."

The literature was more fruitful in the area of thermal degradation of phenolics. These papers dealt with mechanisms,<sup>1,2</sup> kinetics,<sup>3,4</sup> degradation products,<sup>5,6</sup> and techniques used for degradation studies.<sup>7</sup> The work in this area was primarily concerned with phenolics used for ablative purposes<sup>8,9</sup> or forming chars for a variety of reasons.<sup>10,11</sup> Most of the reported work dealt with resoles, although a few papers were concerned with novolacs.<sup>12,13</sup>

## EXPERIMENTAL

**Molding Compound.** A "textbook" phenolic molding compound<sup>14</sup> was

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TABLE I  
Phenolic Molding Compound

Phenolic resin (novolac + HEXA)	1472 g
Magnesium oxide	32 g
1/8 in. Fiber glass	960 g
Silica	640 g
Stearic acid	32 g
Carbon black	64 g
Synasol solvent	64 g

prepared for this study on a two-roll laboratory mill. The composition is given in Table I.

**Molding.** The specimens were transfer molded ASTM flexural strength test bars.<sup>15</sup> The nominal dimensions were 0.5 in.  $\times$  5 in.  $\times$  0.125 in. These specimens were then cut in half to give two 2.5-in. long samples for heat aging. All test bars were given a typical postbake to stabilize them prior to heat aging. This was 2 h at 105°C, followed by 4 h at 150°C, and finally 2 h at 188°C.

**Heat Aging.** The heat aging exposures at 190°C, 235°C, 260°C, 270°C, 285°C, and 313°C were done in circulating air ovens equipped with iron-constantan thermocouples monitoring all eight corners and the center of the oven.

Samples were randomly arranged in groups of five to give five replicate values for a given time at a given exposure.

**Physical Testing.** All samples were equilibrated at 25°C and 50% relative humidity for 48 h after oven aging and prior to flexural strength testing. Flexural strength and modulus measurements were made in accordance with ASTM Test Method D790.

## RESULTS AND DISCUSSION

A single continuous relationship was found to exist between weight loss and flexural strength loss, up to 260°C. This is shown in Figure 1, where % weight

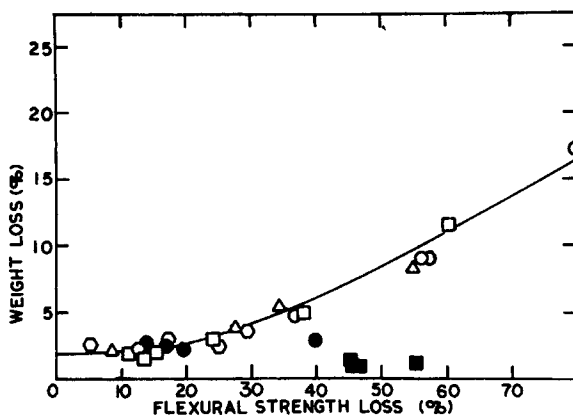


Fig. 1. Relationship of weight loss to flexural strength loss for specimens aged at 190°C ( $\Delta$ ), 235°C ( $\circ$ ), 260°C ( $\square$ ), 270°C ( $\circ$ ), 285°C ( $\bullet$ ), and 313°C ( $\blacksquare$ ).

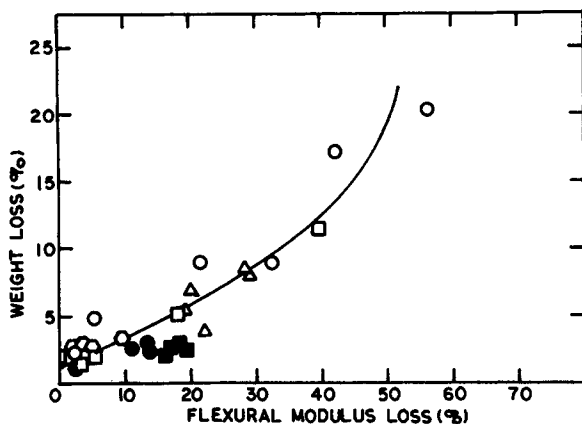


Fig. 2. Relationship of weight loss to flexural modulus loss for specimens aged at 190°C ( $\Delta$ ), 235°C ( $\circ$ ), 260°C ( $\square$ ), 270°C ( $\circ$ ), 285°C ( $\bullet$ ) and 313°C ( $\blacksquare$ ).

loss and % flexural strength loss are plotted for data obtained at each of the aging temperatures 190°C, 235°C, 260°C, 270°C, 285°C, and 313°C. The 270°C data do not follow the curve as closely as the 190–260°C data, but they do not deviate from it to the extreme exhibited by the 285°C and 313°C data. The 285°C and 313°C data are seen to deviate significantly from the basic curve; that is, they show high losses in flexural strength for very little weight loss. These specimens were found to have internal cracks and fissures, indicating a change in the failure mode from gradual decomposition by oxidation and scission<sup>2,12</sup> to one of thermal shock. Though weight loss is a convenient experimental method of following heat aging, there must be some realistic correlation to the primary property of interest.

A similar relationship is found between flexural modulus and weight loss (Fig. 2). The general shape of this curve is similar to that in Figure 1. Again we see that the data from the 285°C and 313°C aging fall away from the general curve.

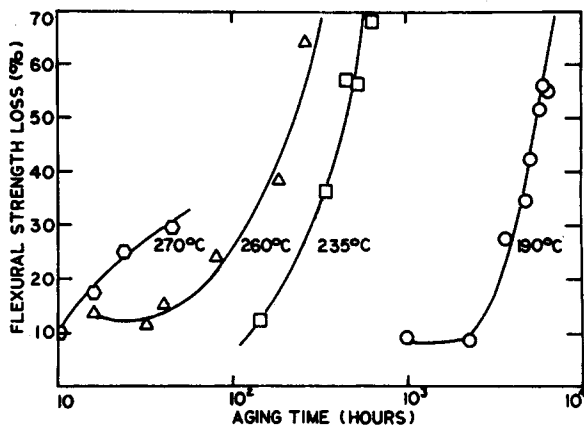


Fig. 3. Comparison of flexural strength loss for specimens aged at 190°C, 235°C, 260°C, and 270°C shown on a log time scale.

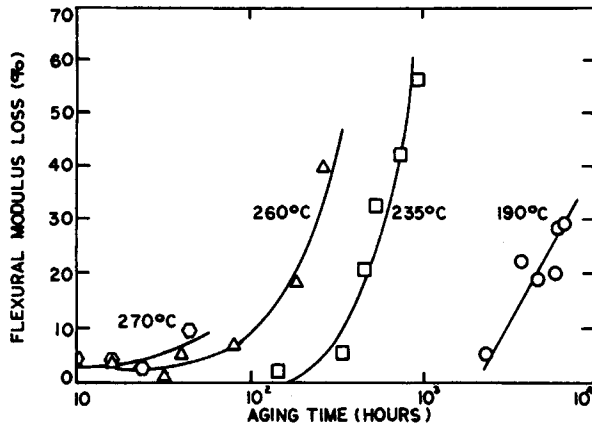


Fig. 4. Loss in flexural modulus with log time for specimens aged at 190°C, 235°C, 260°C, and 270°C.

Percent flexural strength loss versus log aging time for aging temperatures up to 270°C are compared in Figure 3. It can be seen that in the temperature range of 190–260°C there is good agreement of data and that by applying appropriate shift factors along the time axis the curves are approximately superposable. The 270°C data do not fit as neatly, and as indicated above has to be considered questionable as the upper temperature bound.

Flexural modulus loss, and weight loss vs. log of aging time are shown in Figures 4 and 5. In both cases we again find that the curves are superposable along the time axis. The 270°C data also fit better.

The results shown in Figures 1–5 demonstrate that there is an appropriate testing range over which the aging mechanism does not change by any significant degree. This is bounded at the lower end by a practical time limit. The upper temperature is the highest temperature at which the aging mechanism is still valid, in this case about 270°C.

Figure 6 is an Arrhenius curve plotted on the basis of time to 50% loss in flexural strength at each aging temperature. The activation energy calculated from

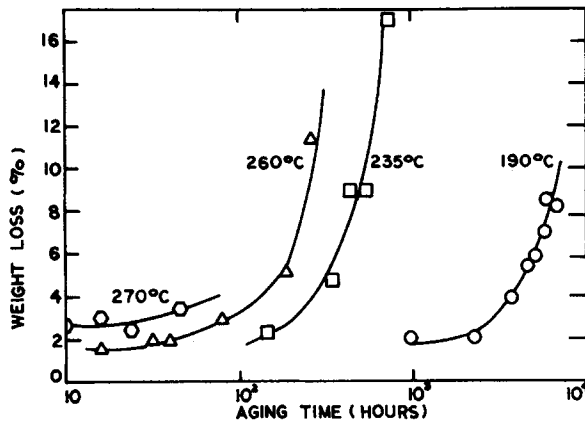


Fig. 5. Weight loss vs. log time for specimens aged at 190°C, 235°C, 260°C, and 270°C.

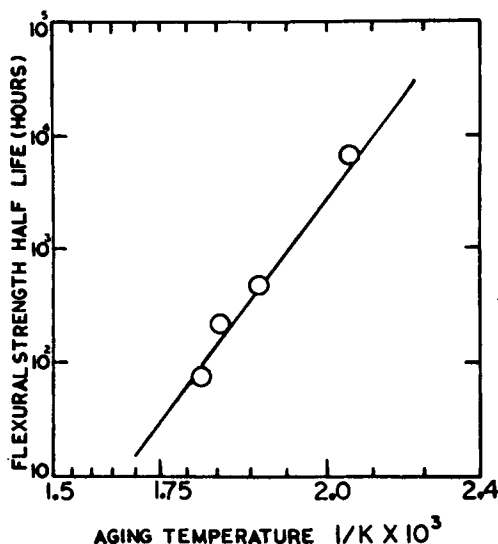


Fig. 6. Arrhenius relationship—log time to 50% loss in flexural strength vs. aging temperature.

best fit least squares line in the Arrhenius plot was 25.0 kcal/mol. This agrees reasonably well with other literature values reported for phenolic molding compounds.<sup>12,16,17</sup>

The Arrhenius relationship is the basis for extrapolating heat aging data to predict suitable use temperatures for long-term use.<sup>18,19</sup> From Figure 6 we can see that valid test results were obtained on this material within 100 h.

## CONCLUSIONS

1. There is an upper limit beyond which accelerated heat age tests cannot be extended for phenolic molding compounds. This upper limit is defined as the highest temperature for which the failure mechanism is still one of oxidative degradation. For the materials studied, this temperature was determined to be 270°C.

2. A good linear relationship was found between weight loss and flexural strength loss. This correlation was sensitive to important changes in failure mechanism that occur at temperatures above 270°C.

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