

Accelerated Heat Age Testing of Phenolics: Morphological Changes

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Synopsis

The morphological changes that occur in molded phenolic specimens during long-term heat aging tests have been observed in optical and scanning electron microscopy. The changes in morphology include shrinking and the formation of both cracks and charred zones in the phenolic matrix. The relationship of these morphological changes to weight losses and flexural strength losses was demonstrated.

INTRODUCTION

To aid in the development of new heat-resistant phenolic molding compounds, it is advantageous to have an accelerated testing procedure which accurately predicts behavior over the very long times of actual use. Test materials are typically aged at elevated temperatures in the laboratory, and interpretation of results is based on the assumption that all important aspects of product degradation are simply speeded up at the higher temperature of the test. It stands to reason, however, that there is an upper temperature limit to the range over which this is true, and above which additional reactions and physical changes start to occur. An earlier report¹ showed that this was indeed true for a typical novolac phenolic molding compound, and that the upper limit was about 270°C. Below 270°C weight losses correlated well with flexural strength and modulus losses, but appeared to follow a distinctly different pattern above it. Data obtained correlated by shifting plots of the measured property versus time along the time axis. Additionally, the times to attain a loss of one-half the original strength property were amenable to a simple Arrhenius 1/T correlation, indicating the basic chemical nature of the material changes accompanying aging. The activation energy calculated from this Arrhenius relation (25.0 kcal/mol) agrees with some literature values reported for other phenolic molding compounds.² However, it is higher than most, as can be seen from examination of the literature values shown in Table I.

The two-stage mechanism of degradation in such compounds, as revealed in our study, has support from several earlier research efforts. Conley⁴ studied both resole and novolac resins using analytical methods such as (IR) infrared thermogravimetric analysis (TGA), and elemental analysis, and described the primary mode of degradation to consist of oxidation of methylene bridges to

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TABLE I
Activation Energies for Phenolics Reported in the Literature

Authors	E _a (kcal/mol)	Phenolic material	Reference
Dixon	18.1-25.5	Molding compounds	2
Shulman & Lochte	22	Resin (unfilled)	3
Conley	16.8, 19.5	Resins (unfilled)	4, 5
Landi, Fitts, & Mersereau	21.7-24	Molding compounds	5
Landi & Walters	18.3, 18.5	Molding compounds	6

ketones, with some quinoidal structures also being formed and later converted to acidic functional groups. All these reactions occurred below 225°C.

Shulman and Lochte³ studied phenolics between 200 and 800°C. Below 400°C, both postcuring and oxidative degradation occurred, the latter ultimately yielding formaldehyde and water as volatiles. Above 450°C, smaller molecules (such as CO, CO₂, and H₂O) were predominant among the volatiles, and over 600°C, char formation and liberation of H₂ and CO occurred, along with condensation to fused-ring structures.

EXPERIMENTAL

Test Materials

A "textbook" phenolic molding compound⁷ was prepared for the present study, using a two-roll laboratory mill. The composition of this material is given in Table II.

Molding

The specimens were transfer-molded ASTM flexural strength test bars⁸ with nominal dimensions of 0.5 × 5 × 0.125 inches. These specimens were cut in half to give two 2.5-inch long samples for heat aging. Prior to heat aging, all test bars were given a stabilizing postbake consisting of 2 h at 105°C, followed by 4 h at 150°C, and finally 2 h at 188°C.

TABLE II
Phenolic Molding Compound Composition

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

Heat Aging

Heat aging exposures at 190, 235, 260, 270, 285, and 313°C were carried out 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 samples for each exposure.

Physical Testing

All samples were equilibrated at 25°C and 50% relative humidity for 48 hours after oven aging and prior to flexural strength testing. Flexural strength and modulus measurements were done in accordance with ASTM D790-81⁸.

Microscopy

The heat-aged, molded phenolic test specimens were examined in both optical and scanning electron microscopy (SEM). Optical microscopy was done with a Unitron Series N metallograph, while the SEM work was carried out in an AMR Model 1200. Pack mounts for observing cross sections on both the optical and electron microscopes were made by casting a liquid plastic around the specimens in an aluminum ring. After the mounting media had hardened, the mounts were ground in succession with 120, 240, 320, 400, and 600 grit silicon carbide papers. This was followed by polishing with 6 μm , then 0.25 μm diamond pastes. Optical photomicrographs were taken on Polaroid type 107 film.

Samples selected for SEM evaluation were cemented on aluminum stubs. They were air dried, and then dried in an oven for several hours at 105°C and placed in a desiccator to cool. The mounted samples were gold/palladium coated in a sputter coater to a coating thickness of 200–300 Å. After coating, silver paint was used to make one or two conductive paths from the specimen onto the mounting stub. SEM photomicrographs were taken on Polaroid type 55 film.

RESULTS AND CONCLUSIONS

Previously reported results¹ showed that there was a good time-temperature correlation with both flexural strength and weight loss over the temperature range 190–270°C. At higher temperatures, the mode of failure appeared to change from one of gradual chemical degradation to a kind of catastrophic

TABLE III
Effect of Exposure Time and Temperature on Physical Properties at 235°C

Exposure time (h)	Flexural strength loss (%)	Flexural modulus loss (%)	Weight loss (%)	Resin loss (%)	Ratio-strength to resin losses
144	12.5	2.17	2.43	5.28	2.35
341	36.5	5.44	4.82	10.5	3.48
528	56.6	32.6	8.94	19.4	2.90

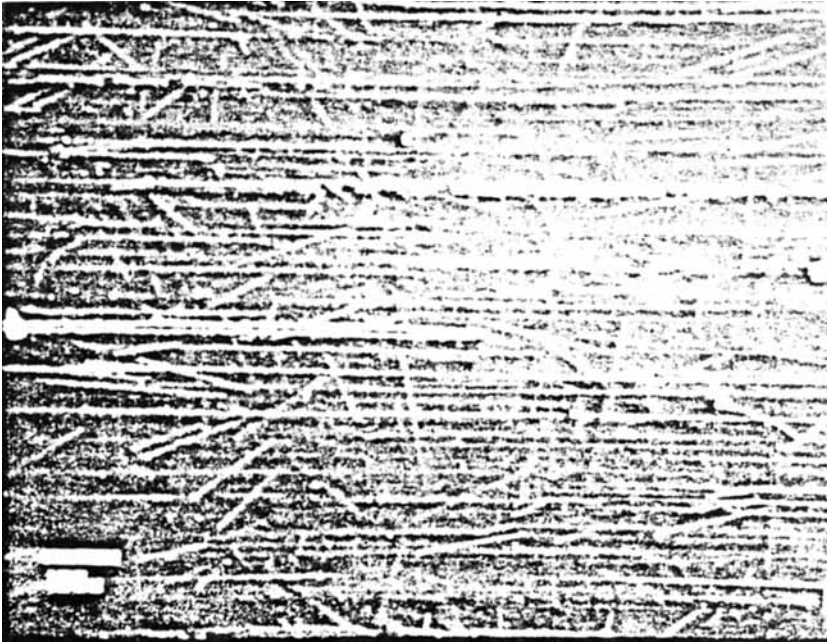


Fig. 1. Surface, unaged, 100 \times .

deterioration, perhaps similar to that suggested by the data of Shulman and Lochte,³ cited earlier.

Microscopy has now shown that the morphological changes at the lower temperatures ($< 270^{\circ}\text{C}$) follow a generally uniform pattern, with greater effects being observed as temperature increases. The results discussed here are based on specimens aged at 235°C and are typical of the morphological aspects of the degradation process up to 270°C . Table III shows the changes in physical properties with time at 235°C .

During the thermal aging process, physical changes took place on both the exterior surfaces and in the interior of the molded specimens. The progression of morphological change with increased aging times at 235°C is illustrated in Figures 1-8.

The micrographs in Figures 1-4 show pronounced and progressive effects of aging on the molded surfaces of the specimens. Figure 1 is an unaged sample; the machining marks of the mold are evident and many glass fibers are visible just below the phenolic surface. In Figure 2 (144 h), the glass fibers are much more pronounced on the surface, possibly due to gradual shrinkage of the resin matrix. Some fine hairline cracks (Fig. 4) have already started to form on the surface, also indicating shrinkage; these are more visible under the increased magnification of Figure 3. Weight loss after 144 h at 235°C is 2.43% and flexural strength loss is 12.5%. Initial shrinkage and weight loss up to a few percent is attributed to the loss of moisture from the molding compound, ammonia from the hexamethylenetetramine curing agent,^{9,10} and possibly some stearic acid mold release agent.



Fig. 2. Surface, 144 h, 235°C, 100 × .



Fig. 3. Surface, 144 h, 235°C, 400 × .

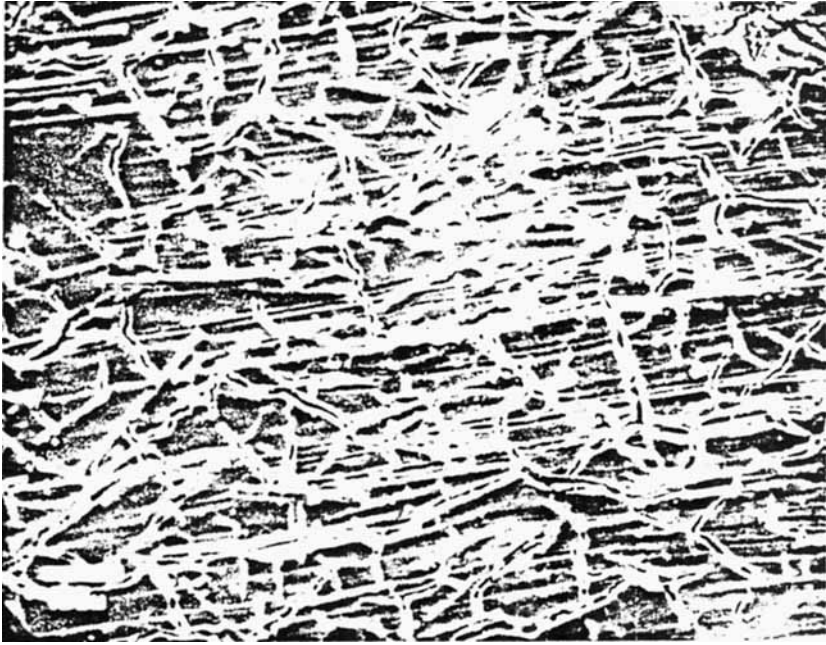


Fig. 4. Surface, 528 h, 235°C, 100 \times .

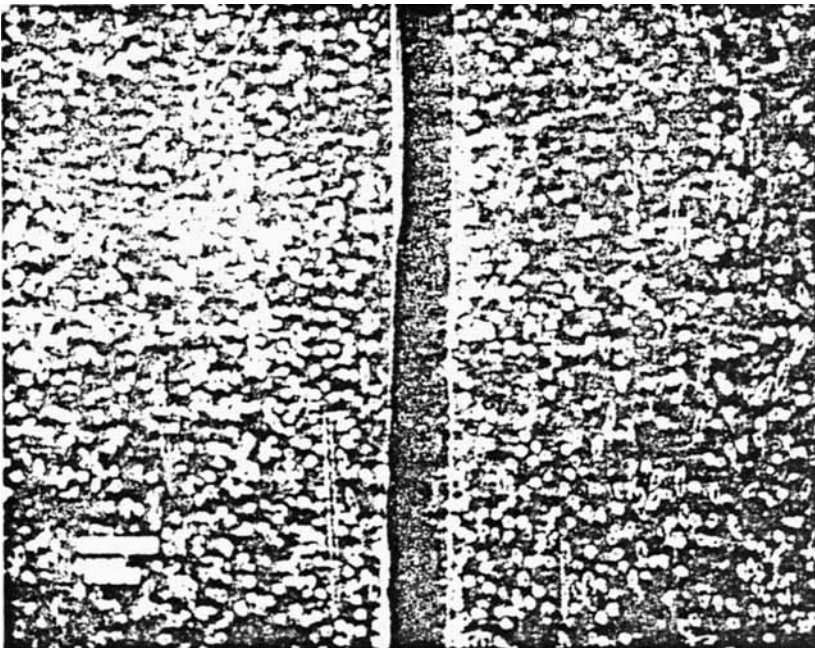


Fig. 5. Polished cross sections: left, unaged; right, 144 h 235°C; 100 \times .

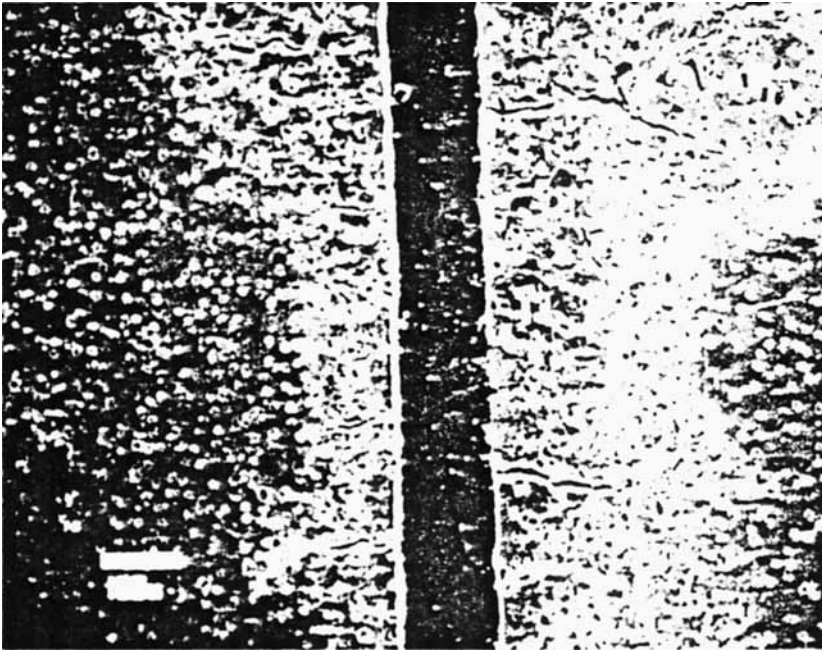


Fig. 6. Polished cross sections: left, 341 h, 235°C; right, 538 h, 235°C; 100 × .

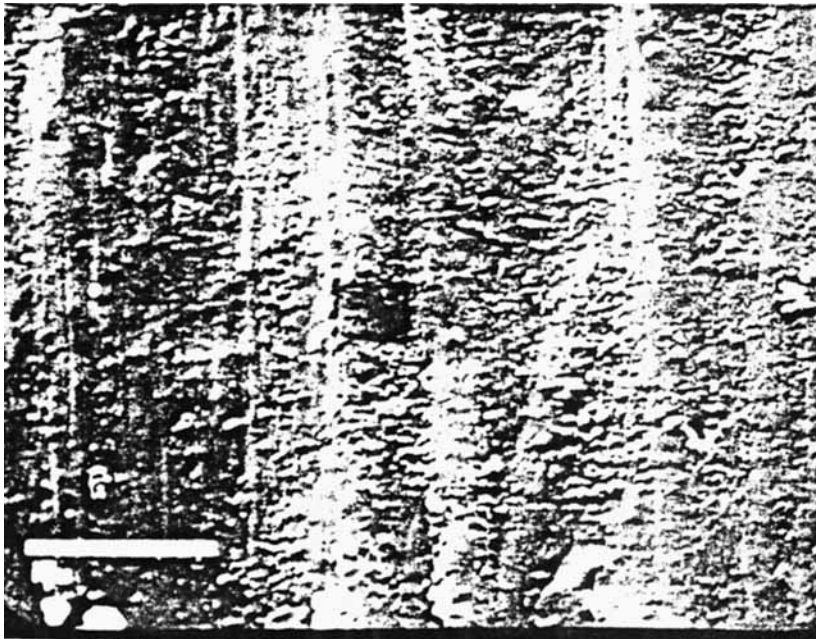


Fig. 7. Surface, unaged, 2500 × .

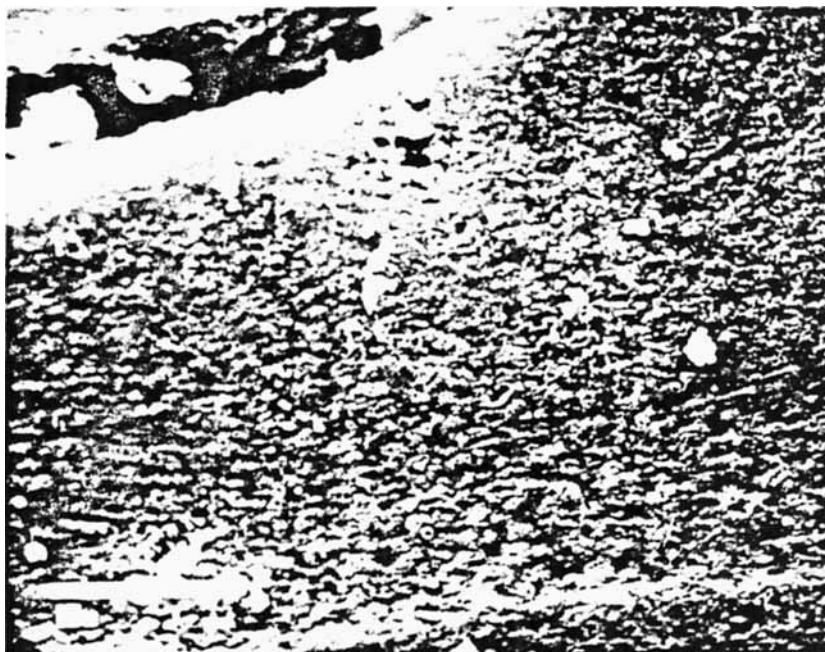


Fig. 8. Surface, 528 h, 235°C, 2500 \times .

Once the surface starts to degrade, oxidation proceeds toward the specimen interior. Figures 5 and 6 depict the formation of this oxidation layer of "char zone" with increasing time (341 h) at 235°C. The interiors of the specimens are shown in polished cross sections. In Figure 5, which contains the unaged and 144-h specimens adjacent to one another, there is no evidence of char zone. Figures 2 and 3 of the surfaces also show only the onset of very fine cracks for the 144-h exposure. The char zones are evident at longer aging times in Figure 6, where the increase in penetration with increase in exposure time can also be seen.

The weight loss at 341 h is 4.82%, and flexural strength loss is 36.48%. Beyond about 3%, weight loss must be attributed to the degradation of the phenolic resin, since sources of ammonia and water have by this time been exhausted.

The gradual shrinking ultimately leads to the "mud-crack" effect evident in Figure 4. The weight and flexural strength losses after 528 h at 235°C were 8.94 and 56.6%, respectively. In addition to the slow formation of shrinkage cracks, other effects are evident on a smaller scale. Figures 7 and 8 are 2500 \times SEM photomicrographs of the resin matrix surface, comparing the unaged surface (Fig. 7) with the surface after 528 h at 235°C (Fig. 8). It is evident that aging causes the surface to be degraded on a very much smaller scale (2500 \times) also.

These observations show that when a molded part degrades, even the most miniscule of the morphological changes which occur can have detrimental effects on strength properties. They not only accelerate the degradation

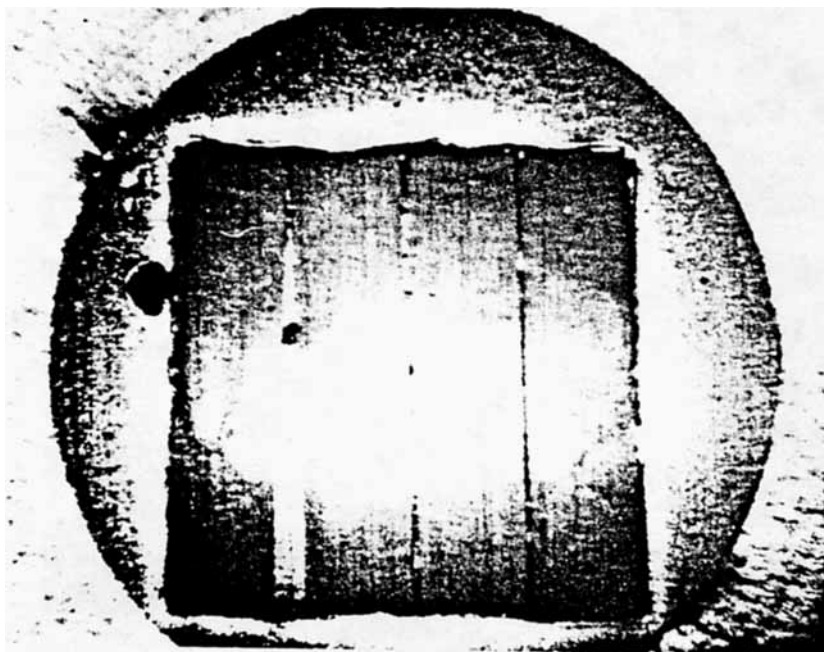


Fig. 9. Cross section of test bars aged at 313°C for 2, 4, 6, and 8 h, 5 × .

process (as seen in Figs. 5 and 6), but the presence of these cracks disproportionately weakens the composite.

Table III also shows the relationship of flexural strength loss to resin weight loss for various aging times at 235°C. It is seen that strength loss is almost a direct function of loss in weight of the resin (nonfiller) portion of the phenolic molding compound.

The morphological changes taking place during the degradation of these phenolic samples at 235°C can be summarized as follows: A gradual shrinkage of the resin matrix occurs, with the eventual formation of cracks in the exterior. Initial weight change is due to water and ammonia losses, but continued aging results in more catastrophic breakdown of the resin itself. There is a subsequent increase in the severity of surface cracking with time, and these cracks provide convenient avenues for oxidation to proceed rapidly into the interior of the molded part.

In contrast to these observations at 235°C, our measurements above 270°C present an entirely different picture. Flexural strength decays very rapidly with very little weight loss or surface damage, but severe internal cracking. This can be seen in Figure 9, which is a polished cross section of test bars aged for 2, 4, 6, and 8 h at 313°C. Large fissures are evident even in the 2-h sample. These samples did not look degraded, but were still dark and shiny. Closer inspection, however, showed the presence of minute cracks on the surfaces. Figures 10–13 are SEM photomicrographs of the aged surfaces shown at 500 × magnification.

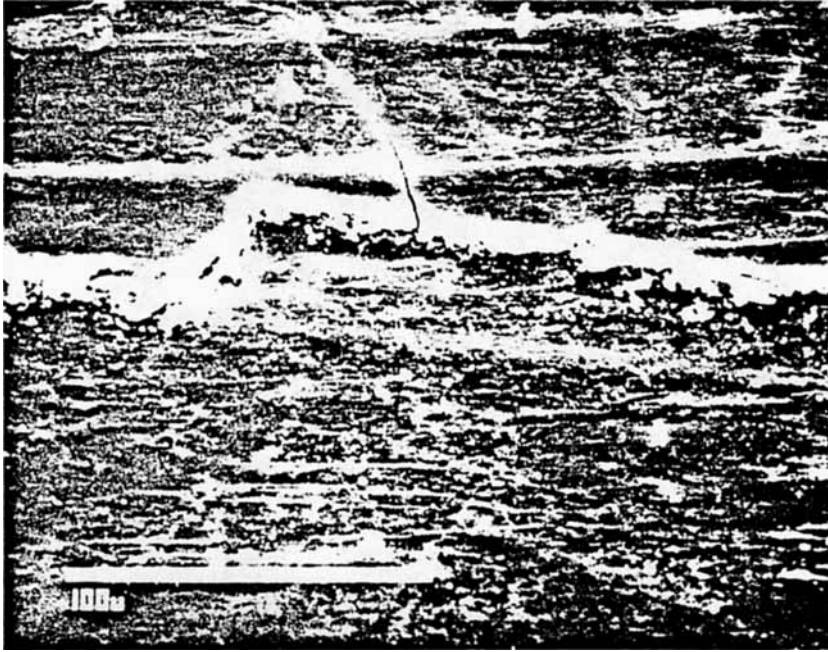


Fig. 10. Surface, 2 h, 313°C, 500 \times .

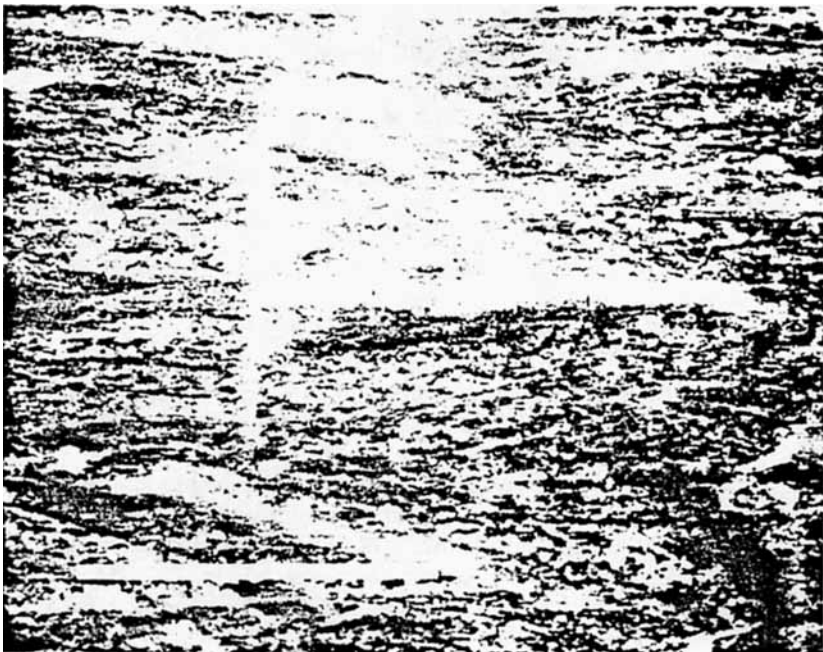


Fig. 11. Surface, 4 h, 313°C, 500 \times .



Fig. 12. Surface, 6 h, 313°C, 500 × .



Fig. 13. Surface, 8 h, 313°C, 500 × .

TABLE IV
Effect of Exposure Time and Temperature on Physical Properties at 313°C

Exposure time (h)	Flexural strength loss (%)	Flexural modulus loss (%)	Weight loss (%)	Resin loss (%)	Ratio-strength to resin losses
2	46.14	17.09	2.15	4.78	9.65
4	55.05	19.10	2.38	5.29	10.41
6	45.46	16.58	2.29	5.09	8.93
8	45.50	18.59	2.75	6.11	7.45

Table IV shows strength and weight losses for these samples. About 50% of the original strength is lost in less than 2 h at 313°C, and no additional loss is evident in the next 6 h. The weight loss is also stabilized, and at a value which can be approximately accounted for by the loss of water and ammonia only. This is in surprising contrast to the result at 235°C, where 50% strength loss did not occur until about 400 h of exposure, even though more than 10% of the resin had already been lost.

Thus, whereas loss of properties at 235°C and below is gradual and develops as a function of temperature, degradation at 313°C and higher is the result of catastrophic thermal shock wherein stress cracks occur quickly to cause the relatively rapid loss of flexural strength. The approximately 50% strength loss occurs within two hours at these high temperatures and only after very long exposures at lower temperatures. Figure 6, for example, shows deep internal cracking along with comparable strength losses only after 528 h at 235°C.

In overall conclusion, morphological changes in phenolic molding compounds aged at 235 and 313°C show very striking differences, the practical significance of which is great. Aging in such materials can be accelerated in ovens up to about 235°C with results which can be used to predict service life at lower temperatures. Aging above 313°C, however, produces an entirely different result wherein catastrophic degradation takes place, and no direct relationship exists to results obtained at lower temperatures or to service life under ambient conditions.

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