Transitions in Phenolic Polymer

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Synopsis

The solid-state properties of a highly crosslinked amorphous resole-type phenolic polymer have been studied by compressibility and torsional braid analysis measurements. Three secondary transitions were found over the temperature range of 123° to 623°K the largest of which occurs at about 393°K. These results confirm previously made electrical resistivity and specific heat measurements. These transitions are discussed in relation to the structure of this polymer.

INTRODUCTION

We have previously shown by electrical resistivity[1] and specific heat[2] measurements that a transition exists at about 120°C (393°K) in resole-type phenolic polymer. However, the experimental data do not clearly indicate what type of transition exists in this highly crosslinked system. Since few previous studies appear to have been made on the solid state properties of these polymers, we have now investigated the properties over the temperature range of 123° to 623°K by means of bulk compressibility and torsional braid analysis (TBA) measurements.

The results of this investigation are that over the temperature range considered there are at least three small secondary transitions in the completely polymerized polymer. The largest transition occurs between ~ 125°C (398°K) to 250°C (523°K). These transitions are discussed in terms of polymer structure.

EXPERIMENTAL

Material and Polymerization

The polymer employed in this investigation is a resole-type phenolic manufactured by Monsanto Polymer and Petrochemicals Company under the name Resinox SC 1008. It is supplied in the form of a 62% average solution in isopropyl alcohol which upon heating polymerizes to give a rigid crosslinked polymer. The primary reactions during polymerization are the formation of either ortho or para methylene linkages and dibenzyl ether linkages with the ortho being favored over the para position.[3] Generally, about two of the three potentially reactive sites on the phenolic molecule are reacted[4] and with the polymerization cycle em-

ployed here, about 70% of the linkages will be methylene. Hartmann[5] has recently presented an idealized representation of the structure of this polymer.

Specimens were thermally polymerized as follows: The specimens were heated for 24 hr at 38°C (311°K), the temperature being increased by 15° for each following 24-hr cycle, with the final cycle being 24 hr at 177°C (450°K). Samples for use in the compressibility and specific heat phases of this investigation were cut from the same cast bar while samples for the electrical resistivity and torsional braid measurements were cast separately but polymerized by the exact same cycle.

This very long cycle was employed in order to obtain complete thermal polymerization. At the end of this cycle, a clear, amber-brown solid was obtained of density 1.22 g/cm^3. Electrical resistivity measurements made as a function of temperature indicated that after the above polymerization cycle, thermal polymerization was complete.[1] No cracks were noted in any of the samples after this cycle, or after machining or after any of the experiments herein described.

Compressibility Measurements

Bulk compressibility measurements to a pressure of 9000 atmospheres and temperatures.as high as 190°C (463°K) were made using a Matsuoka-Maxwell compressibility device.[6] Briefly, use of this apparatus consists of placing a machined polymer specimen 7.62 cm long and 0.635 cm in diameter in the bore of the compressibility device and determining the volume change as a function of pressure and temperature. The source of pressure is a Baldwin-Southwark 30,000-kg capacity Universal Test Machine. Additional details of the experimental procedure have been given.[7,8,9]

Torsional Braid Analysis (TBA)

The dynamic thermomechanical spectra (~1 Hz) were determined over the temperature range of 150° to 350°C (123° to 623°K) by means of torsional braid analysis (TBA). This technique is an adaption of the torsional pendulum in which the specimen under study is a free-hanging supported composite consisting of a multifilamented glass braid impregnated with a polymer. The phenolic polymer solution as supplied by the manufacturer was diluted to about 20% concentration in isopropyl alcohol, the braid impregnated by the polymer solution and then allowed to air dry at 25°C (298°K) for 24 hr. Polymerization was then conducted in exactly the same manner as was given the cast specimens used in the compressibility, specific heat, and electrical resistivity phases of this investigation. A detailed description of the torsional braid analysis instrument and experimental technique has been given by Gillham.[10]

RESULTS

The results of this investigation are shown in Figures 1–3. Figure 1 is a plot of a typical isotherm showing the change in volume, $(-\Delta V/V_0)\%$, versus pressure for this polymer at 160°C. A very similar plot was obtained at 25°C, thus the temperature dependence of the compressibility is small.

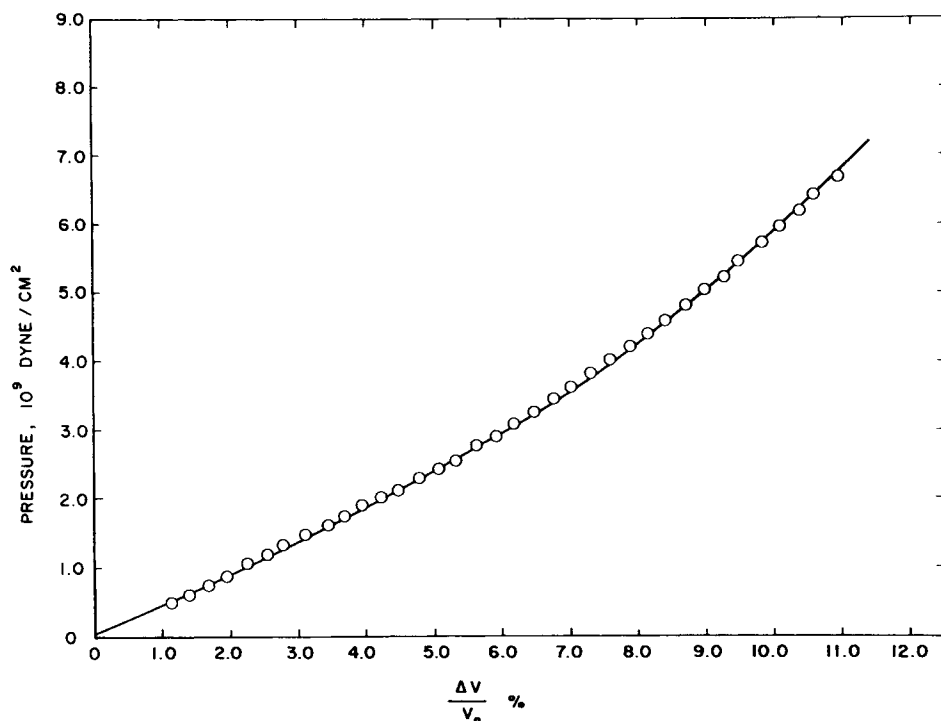A number of the higher temperature isotherms upon close examination re-

Fig. 1. Compressibility of phenolic polymer at 160 °C.

vealed small inflection points along the isotherm. Inflections of this type suggest that a small transition is occurring. On this assumption a series of stress-strain isotherms were obtained between 144° and 190°C and examined for inflection points. These were found, and the pressure and temperature of these inflection points are plotted on Figure 2.

Figure 3 is a plot of the thermomechanical spectra as determined by TBA over the temperature range of 123° to 623°K. This plot shows the various transitions exhibited by this polymer.

DISCUSSION

At the start of this investigation, we were unable to find any significant amount of experimental data on the physical properties of resole-type phenolic polymers. Many scattered references exist, particularly on the electrical properties, but almost all of the data are on uncharacterized polymer and are not suitable to be applied even generally to the phenolic polymer considered here.

Compressibility Measurements

We initially determined the compressibility of this polymer as a function of temperature, and the isotherm shown in Figure 1 is typical. The change in volume with pressure, $(\Delta V/V_0)\%$, is about 11% and exhibits a small temperature dependence at temperatures up to 190°C (463°K). This is a typical value for a glassy polymer.[7,8]
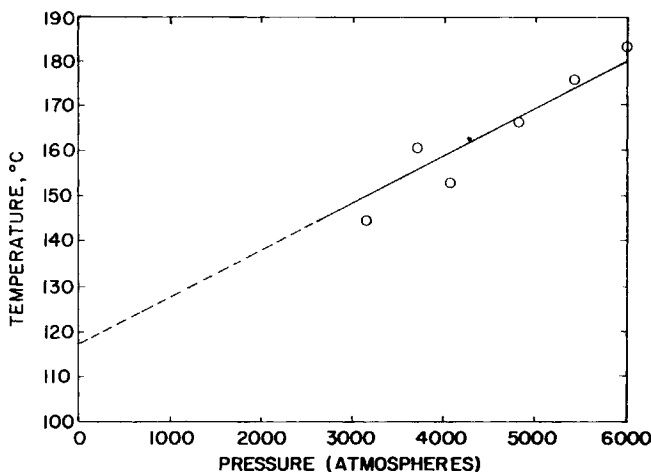
Fig. 2. Pressure dependence of transition in phenolic polymer.

Close examination of the stress–strain plots reveals[11] small inflection points along each of the isotherms above 144°C (417°K). Additional examination indicated that with increasing temperature, the pressure at which these inflections occur increases. Plotting the pressure at which the inflection occurs and the temperature of the isotherm yields the plot shown in Figure 2. The data points fall on approximately a straight line with the scatter of the points apparently caused by errors in determining the exact inflection points from the stress–strain plots. Drawing a straight line through the data points and extending it to zero pressure strongly suggests that a transition of some type is occurring at about 120°C (393°K). This procedure has been previously employed to locate pressure induced glass transitions[7,8] and pressure induced freezing points.[9,12]

The slope of this plot is 0.010°/atm. The pressure dependence of glass transitions, T_g, and the melting points, T_m, are higher, i.e., about 0.025° to 0.030°/atm. Thus, this transition appears to be of smaller magnitude and is most likely a secondary transition,[13] T_{sec}. This fact could also explain the scatter of the data points since small transitions are frequently sluggish due in part to the extremely high bulk viscosity which is characteristic of the glassy state. The change in volume, which is the driving force behind pressure induced transitions, is small here, i.e., of the order of a per cent or two. Hence, locating the transition is slightly uncertain. Heydemann and Houck[13] have noted that the small pressure dependence of transitions of this type is characteristic of processes consisting of the motion of small side groups rather than motion of the main chain. Parry and Tabor[14] have noted that the small pressure dependence of secondary transitions can be attributed to the small amount of free volume usually required for transitions of this type.

One may contrast the diffuse nature of this transition with the sharp, highly pressure- and temperature-dependent nature of the melting, T_m, of crystalline polymers. In crystalline polymers, the change in volume upon melting is large, i.e., about 20% while in many amorphous polymers the change in volume at the glass transition is of the order of 5% to 10%. However, while the above evidence suggests that a secondary transition occurs at about 120°C (393°K), additional evidence is necessary to make the case for a secondary transition.
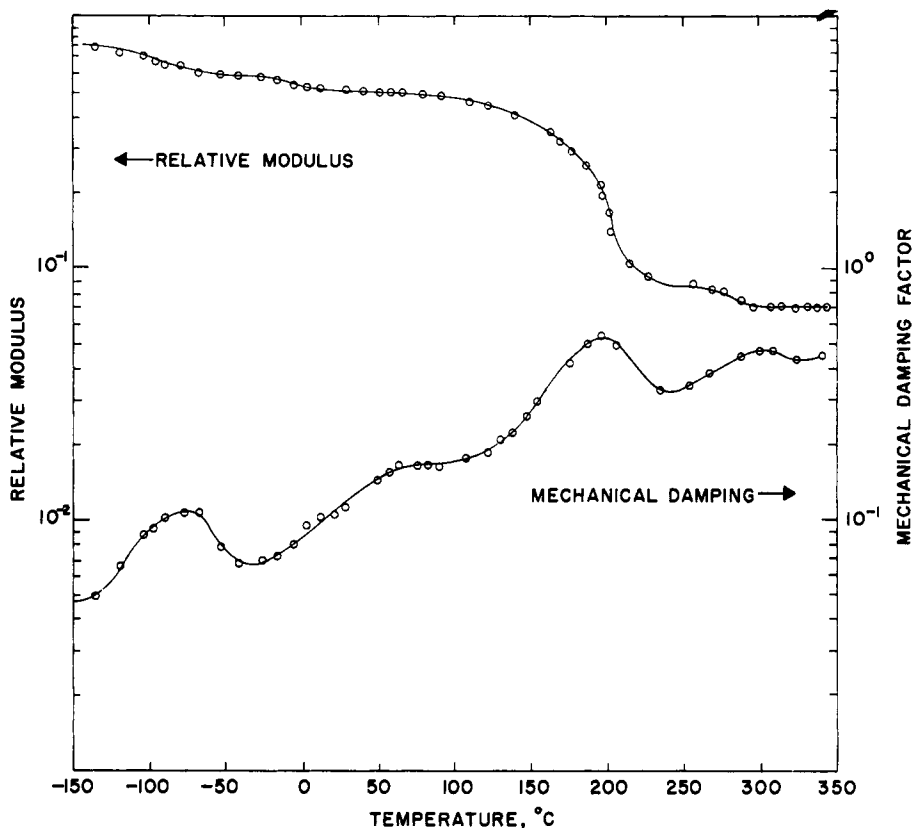
Fig. 3. Thermomechanical behavior of phenolic polymer.

The existence of this transition has been previously found by electrical resistivity[1] and specific heat measurements,[2] but neither of these experimental procedures give the type of transition.

Torsional Braid Analysis Measurements

The thermomechanical spectra reveal a small transition which attains a maximum value at about 200°K. Small low temperature transitions of this type are frequently observed[12,15] and are generally considered to arise from the motion of small numbers of molecules along the polymer chain. Pogany[16] has studied this transition in a resole-type phenolic polymer of apparently similar structure to ours and has pointed out that when benzene rings form part of the backbone of the system the low-temperature transition can be ascribed to a wiggle-type motion and since the motion involves only a small segment the presence of crosslinks makes little difference in the temperature range of the transition. Pogany noted this transition at 193°K which is in good agreement with our observation at about 200°K.

It has been previously shown by McCrum et al.[17] that the area under the dynamic mechanical loss factor or damping factor versus temperature curve in the vicinity of a transition is directly related to the activation energy for that tran-

sition. The technique has been demonstrated with a torsional pendulum. It has been assumed that with the TBA only a relative value of the loss factor can be obtained[18] and that this instrument could not be used to obtain activation energies. However, Hartmann and Lee[19] have found that absolute values of loss factor can be obtained and that the activation energy for a transition can be calculated from the area under the loss factor versus temperature curve obtained by the TBA. About the same degree of accuracy is obtained as with the torsional pendulum.

From TBA data, the activation energy for the low-temperature transition at about 200°K is 10 kcal/mole. This low value is consistent with the wiggle-type motion noted by Pogany.[16]

Another very small transition is noted at about 75°C (348°K) and is likely the same transition as was noted by Hartmann.[5] This transition is of small magnitude and occurs over a broad temperature range.

Commencing at about 125°C (398°K) and attaining a maximum at about 200°C (473°K) is another secondary transition. It occurs over a broad temperature range and may possibly overlap other transitions on each side. It is the start of this transition which has been observed by compressibility, electrical resistivity, and specific heat measurements and the question arises as to what type of transition is occurring. Experience with determining transitions with the TBA indicates that a glass transition in a crosslinked polymer will exhibit a sharp damping peak with a decrease of about two decades in relative modulus. Typical plots of this type have been presented by Gillham.[10]

In the case of the phenolic polymer, the decrease in the relative modulus is small, only about half a decade, and the increase in the mechanical damping, at about 200°C, is neither large nor sharp as would be the case if this were a typical glass transition.

By means of the TBA method the activation energy for this transition has been calculated to be 32 kcal/mole. Boyer[20] has considered activation energies for transitions in polymers and has suggested criteria for distinguishing between glass and secondary transitions. For a glass transition, the activation energy is proportional to the transition temperature, whereas for a secondary transition, the activation energy exhibits a small dependence on the transition temperature. He also presents a plot of activation energy versus transition temperature for both glass and secondary transitions.

Comparing our value of 32 kcal/mole with that predicted from Boyers plot, we find that for a glass transition occurring between 400° to 473°K an activation energy of about 120 kcal/mole would be expected whereas a secondary transition in this temperature range would have an activation energy of about 20 to 30 kcal/mole. We thus conclude that this is a secondary transition and based on Boyers concepts the calculated activation energies for both the low- and high-temperature transitions appear reasonable.

It is of interest to attempt to relate the available information on the high-temperature secondary transition to the underlying molecular motions which give rise to it. Boyer[20] has considered this problem and noted that in chain motion of subgroups which are smaller in size than the main inchain groups can give rise to a secondary transition. In the ether linkage, $-CH_2-O-CH_2-$, such a subgroup is present in the main chain of this polymer. Either some type of sterically restricted "crankshaft" motion and/or the oxygen atom serving as a

swivel could account for this transition. Boyer notes that for secondary transitions internal barriers to rotation appear to be the only consideration, the calculated activation energy of 32 kcal/mole appears to be consistent with some type of inchain motion of subgroups.

It is of interest that Lim et al.[21] have studied a somewhat similar transition in poly(2,6-dimethyl-p-phenylene oxide) (PDMPO) and suggest that a limited motion of ether oxygen atoms may be involved. They note that the activation energy of about 20 kcal/mole is greater than would be expected for torsional vibrations of phenylene groups.

At about 300°C (573°K), there is another small peak on the damping factor versus temperature plot for which an activation energy of 7 kcal/mole may be calculated. Based upon Boyers plot of secondary transitions at this temperature one would expect an activation energy of 30 to 40 kcal/mole. This strongly suggests that this peak is not a secondary transition but rather some form of molecular rearrangement and/or degradation. We have previously noted[11] that heating at high temperatures frequently produces some rearrangement within the solid polymer. This rearrangement could be additional crosslinking, conversion of ether linkages to methylene linkages, or degradation or a combination of all of these.

At some temperature above 623°K, it seems reasonable to assume that this polymer would undergo a glass transition. However, thermal degradation occurs before the transition temperature can be attained and the transition is thus not accessible to direct measurement.

CONCLUSIONS

The results presented in this paper lead to the following conclusions:

a. Three secondary transitions have been identified in phenolic polymer: (1) one at about 200°K; the activation energy for this transition is about 10 kcal/mole; (2) a very small transition at about 348°K; (3) a large transition which attains a maximum at about 473°K; the activation energy for this transition is about 32 kcal/mole.

b. These transitions have been observed by electrical resistivity, specific heat, bulk compressibility, and torsional braid analysis measurements.

c. The activation energy for each of the transitions, which can be calculated from the thermomechanical spectra, appear reasonable when considered along with possible mechanisms for the transition.

References

1. R. W. Warfield, *J. Appl. Polym. Sci.*, **19**, 1205 (1975).
2. R. W. Warfield, and E. G. Kayser, *J. Macromol. Sci.—Phys.*, **B11** (3), 325 (1975).
3. R. W. Martin, *Chemistry of Phenolic Resins,* Wiley, New York, 1956.
4. H. P. Higginbottom, Monsanto Co., private communication, March 7, 1975; P. W. King, R. H. Mitchell, and A. R. Westwood, *J. Appl. Polym. Sci.*, **18**, 1117 (1974).
5. B. Hartmann, *J. Appl. Polym. Sci.*, **19**, 3241 (1975).
6. S. Matsuoka, and B. Maxwell, *J. Polym. Sci.*, **32**, 131 (1959).
7. R. W. Warfield, *J. Appl. Chem. (London)*, **17**, 263 (1967).

8. R. W. Warfield, *Makromol. Chem.,* **116,** 78 (1968).

9. R. W. Warfield, and B. Hartmann, *J. Appl. Phys.,* **44,** 708 (1973).

10. J. K. Gillham, *Crit. Rev. Macromol. Sci.,* **1,** 83 (1972).

11. R. W. Warfield, *Proceedings of the 4th International Conference on High Pressure,* Kyoto, Japan, November 1974, p. 91.

12. R. W. Warfield, Naval Ordinance Laboratory Technical Report NOLTR 73-23, 1973.

13. P. L. M. Heydemann, and J. C. Houck, *J. Polym. Sci.,* **10A-2,** 1631 (1972).

14. E. J. Parry, and D. Tabor, *Polymer,* **14,** 628 (1973).

15. S. Matsuoka, and Y. Ishida, *J. Polym. Sci. C,* **14,** 247 (1966).

16. G. A. Pogany, *Polymer,* **11,** 66 (1970).

17. N. G. McCrum, B. E. Read, and G. Williams, *Anelastic and Dielectric Effects in Polymeric Solids* Wiley, London, 1967, pp. 122–126.

18. J. K. Gillham, *Amer. Inst. Chem. Eng. J.,* **20,** 1066 (1974).

19. B. Hartmann, and G. F. Lee, *J. Appl. Polym. Sci.,* in press.

20. R. F. Boyer, *Rubber Chem. Technol.,* **36,** 1303 (1963).

21. T. Lim, V. Frosini, V. Zaleckas, D. Marrow, and J. A. Sauer, *Polym. Eng. Sci.,* **13,** 51 (1973).