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# Ultrasonic Properties of Phenolic and Poly(phenylquinoxaline) Polymers

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## Synopsis

Longitudinal and shear sound speeds and absorptions were measured for a phenolic polymer and a poly(phenylquinoxaline) (PPQ) polymer, from room temperature to 70°C, at a frequency of 1.8 MHz. Phenolic specimens were cured at a maximum temperature of either 120°C, 135°C, or 180°C. The specimens varied in density from 1.217 to 1.229 g/cm$^3$ with no correlation to curing temperature. Longitudinal sound speed in phenolic was found to depend only on density (or specific volume) and not directly on temperature or degree of crosslinking. Sound speeds and elastic constants, in phenolic, are not sensitive to cure temperature but sound absorption is: the higher the cure temperature, the lower the absorption. Hence ultrasonic absorption is a possible way to monitor or measure degree of crosslinking. Sound absorption is higher in phenolic than in PPQ, contrary to what is expected for a polymer with high sound speed. This high absorption indicates an additional mechanism of absorption in phenolic not found in PPQ. Also, the sound absorption increases with temperature in phenolic but is constant in PPQ. The Gruneisen parameter of phenolic appears high and that of PPQ about right when compared with other polymers. All of these results suggest there is a molecular transition in phenolic, but not PPQ. Further evidence for a transition comes from specific volume measurements as a function of temperature. The exact temperature of the transition and the molecular process responsible cannot, however, be determined from the measurements reported here.

## INTRODUCTION

Even though phenolics are the oldest purely synthetic plastics and date back to 1907, there are many gaps in our knowledge of the physical properties of these materials. Thus, there is much to be learned from a study of phenolics since they are prime examples of highly crosslinked polymers. Linear polymers have received most attention to date, but there is now considerable interest in the properties of crosslinked polymers. In addition to phenolic, another polymer of interest is a crosslinked poly(phenylquinoxaline) (PPQ), which, like phenolic, is a high-temperature polymer with benzene rings in the chain backbone, but is not as highly crosslinked.

In this paper, the properties of interest are the longitudinal and shear sound speeds and absorptions as functions of temperature. Knowing the sound speeds, the elastic constants can be calculated. It is also of interest to determine the Gruneisen parameters of the polymers. (This parameter is widely used in equation of state calculations.) To determine the Gruneisen parameter, the ultrasonic measurements must be supplemented with thermal expansion and specific heat measurements.

The goal of this work was to determine the properties of interest for the phenolic and PPQ and to relate these properties to polymer structure whenever possible. There were three specific questions that were of interest. What are the properties of phenolic and PPQ? How do these properties compare with those of linear polymers and with each other? How do the properties of phenolic vary with amount of crosslinking?

In the following sections of this paper, the materials used will be described and the ultrasonic apparatus used to make the measurements; then the results will be presented, first at room temperature, then at elevated temperature; then the Gruneisen parameter will be considered; finally, the conclusions based on the above work will be presented.

It will be shown that sound speed in phenolic varies less than 1% for curing temperatures between 120°C and 180°C, but absorption varies by 35% so that sound absorption may be useful in monitoring or measuring degree of crosslinking in thermosetting polymers. The temperature dependence of the sound speeds in phenolic is more than twice as high as in PPQ. Also, the absorption in phenolic doubles over the temperature range from 25°C to 70°C while the absorption in PPQ is constant. These strong temperature dependencies in phenolic are assumed to result from a transition occurring in this polymer.

## EXPERIMENTAL

### Materials

The phenolic used was a commercial resole type manufactured by the Monsanto Company, St. Louis, Missouri, under the trade name Resinox SC 1008. It was supplied as a prepolymer in a 62% solids solution in isopropyl alcohol. This prepolymer cures on application of heat to give a rigid crosslinked polymer. Martin[1] points out that below about 170°C, the primary reactions are formation of methylene bridges, either ortho or para, and dibenzyl ether linkages. Starting around 160° to 170°C, dibenzyl ether linkages begin to be converted to the more stable methylene bridges. This conversion may not become extensive until a temperature as high as 200°C is reached. As the temperature is raised even higher, degradation becomes important. An idealized representation of the structure of the polymer is shown in Figure 1. The general features portrayed there are: (1) most of the phenols are connected with methylene bridges; (2) ortho is favored over para; (3) overall, about two of the three potentially reactive sites on the phenol are reacted.

The curing cycle used on the phenolic was to heat the prepolymer in a forced-air oven for 24 hr at each of the following temperatures: 65°C, 80°C,

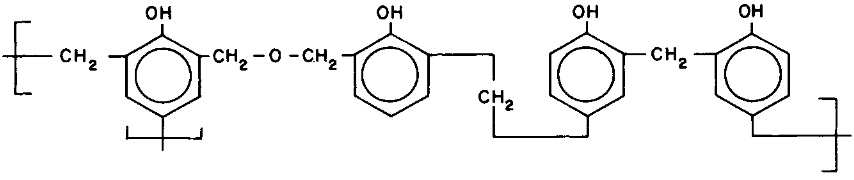

Fig. 1. Idealized structure of resole-type phenolic.

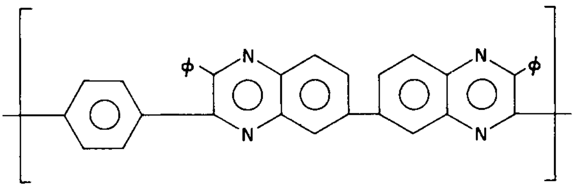

Fig. 2. Idealized structure of linear poly(phenylquinoxaline).

95°C, 110°C, 120°C, 135°C, 150°C, and 165°C. Finally, the polymer was cured for 2 hr at 180°C and allowed to cool to room temperature in about 2 hr before being removed from the oven. In addition to the two specimens prepared using this "high" temperature cure, two specimens were removed at 120°C, giving a "low" temperature cure, and one specimen was removed at 135°C, giving a "medium" temperature cure. In this manner, it was hoped to obtain a variation in the degree of crosslinking, even though we have no way of knowing to what extent crosslinking occurred.

After curing, the phenolic specimens were clear and had no visible voids. Thicknesses varied from 0.6 cm to 1.2 cm. All specimens were a nominal 5-cm diameter. The five specimens varied in density from 1.217 to 1.229 g/cm$^3$, with no correlation between curing temperature and density.

The PPQ used in this study was a crosslinked analog of a linear PPQ. The linear polymer has previously been discussed in detail.[2] It is derived from the condensation reaction of 3,3′-diaminobenzidine and 1,4-bis(phenylglyoxalyl)benzene in *m*-cresol solvent. The idealized structure of this polymer is shown in Figure 2. By using a trifunctional monomer, a tris benzil, in place of the difunctional 1,4-bis(phenylglyoxalyl)benzene, a crosslinked PPQ can be prepared. An idealized representation of the completely crosslinked polymer is shown in Figure 3. The specimen used in this study was made using one equivalent of 3,3′-diaminobenzidine and a mixture of 36 equivalent per

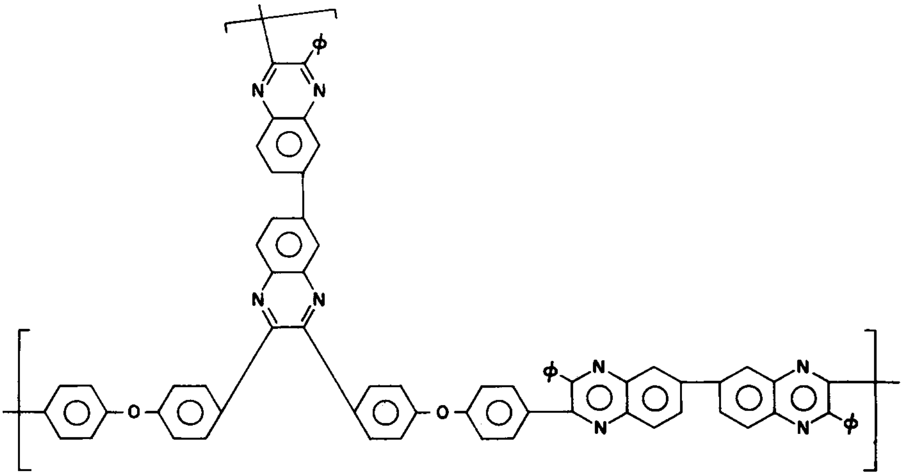

Fig. 3. Idealized structure of crosslinked poly(phenylquinoxaline).

cent of the tris benzil monomer and 64 equivalent per cent of the 1,4-bis-(phenylglyoxalyl)benzene. Therefore, the structure of the polymer used here was a mixture of the structures shown in Figures 2 and 3, with the crosslinks occurring at random.

The crosslinked PPQ was prepared in the following manner.[3] The low molecular weight prepolymer was isolated by quenching the *m*-cresol solution in a nonsolvent (acetone or methanol) prior to gelation. This precipitated prepolymer was filtered, washed with methanol, and then dried in a forced-air oven at 80°C for 1 hr, yielding a bright-yellow powder with a volatile content of about 1%. The powder was pulverized and pressed into a steel mold at ambient temperature to make a preform. The preform was then placed in a press held at 370°C. In the approximately 15 min it took for the specimen to reach the press temperature, the mold was vented periodically to release volatiles. Once the specimen had reached 370°C, it was held at that temperature and 70 bar pressure for 4 hr. At that time the heat to the press was turned off and the specimen cooled, under constant pressure, to near room temperature in about 2 hr. The specimen was then machined to finished dimensions, 5 cm diameter and 1.15 cm thick, on a silicon-carbide grinding wheel to avoid surface contamination. A single specimen was used, of density 1.209 g/cm$^3$.

## Ultrasonic Apparatus

The ultrasonic apparatus used has already been described in detail.[4] In brief, the specimen and two transducers are immersed in a silicone liquid. Pulses are sent from one transducer to the other, both with and without the specimen in the path of the sound beam. Shear measurements are made by holding the specimen at an angle to the sound beam. Temperature control is maintained with two 2-kilowatt heaters. The heaters are placed in the immersion tank, which is completely insulated. A variable resistor is used to control the heat input. In this manner, the temperature can be controlled to ±0.5°C. While the apparatus is capable of measurements over a range of frequencies, all the measurements reported here were done at 1.8 MHz.

All of the absorption results reported here were calculated from measurements on a single specimen. As pointed out earlier,[4] this requires knowledge of the density, sound speed, and absorption of the immersion liquid. Density, as a function of temperature, was obtained from the manufacturer's data sheet (Dow Corning Bulletin 05-145, July, 1968). Sound speed in the silicone liquid was determined by comparison with an aluminum standard, as discussed before.[4] Sound absorption in the liquid was found assuming the usual second power frequency dependence and fitting a quadratic curve to the temperature dependence data measured by McSkimin.[5]

An alternate method of calculating absorption is to use two specimens of different thickness. Calculations of this type were done in the two cases where specimens of different thickness were available: the high- and low-temperature cured phenolics. The results were in good agreement with the single specimen calculations and will not be presented in any further detail.

Sound speed measurements are estimated to be accurate to ±1%, while absorption measurements are accurate to ±5%.

## ULTRASONIC RESULTS

### Room Temperature

Room-temperature (25°C) ultrasonic results for phenolic are given in the first column of Table I. All of the values are averages from the five specimens, since there was no significant variation of sound speed with cure temperature. In other words, the sound speed varies less than 1% for the curing temperatures used here. In comparing these values with those in the literature, two points must be kept in mind. First, ultrasonic properties in polymers are correlated with density so that comparisons should be made with polymers of the same density. Second, phenolic is a generic name covering a variety of polymers, having somewhat different properties.

Several references were found in the literature for comparison. Wada and Yamamoto[6] made measurements on a phenolic of density 1.27 g/cm$^3$ and found a longitudinal sound speed of 2780 m/sec. Michaels, Christman, and Isbell[7] made measurements on a phenolic manufactured by Ironsides Resins, Inc., Columbus, Ohio under the designation FF17. Their specimen had a density of 1.29 g/cm$^3$ and sound speeds of 3250 ±20 m/sec and 1530 ±30 m/sec. Tarbell, Washington, and Scammon[8] made measurements on SC1008 of density 1.22 g/cm$^3$ and found sound speeds of 2770 m/sec and 1300 m/sec. Finally, Felix[9] reported measurements on SC1008 of density 1.205 g/cm$^3$ and found a sound speed of 2640 m/sec. In addition, Felix added phenolic microballons to the SC1008, lowering the density to 1.189 g/cm$^3$ and the sound speed to 2510 m/sec.

It has been pointed out by others[6,10,11] that sound speed increases approximately linearly with density. A plot of longitudinal sound speed vs density for phenolic is shown in Figure 4. On this plot are all of the literature results given in the last paragraph as well as the room temperature result found in this work. Also included on Figure 4 are the results obtained here as a function of temperature (to be discussed in more detail later in this paper). As can be seen, all of these results appear to be well correlated with the exception of that of Wada and Yamamoto.[6] However, it is not known how similar the structure of their polymer was to that used here. It is concluded from Figure 4 that the sound speed determined here is in excellent agreement with

TABLE I
Sound Speeds, Absorptions, and Elastic Constants for Phenolic Polymer

| | Value at 25°C | Temperature derivative | Logarithmic derivative[a] |
|---|---|---|---|
| Longitudinal sound speed | 2840 m/sec | —7.1 m/sec/deg | —25 × $10^{-4}$ deg$^{-1}$ |
| Shear sound speed | 1320 m/sec | —4.0 m/sec/deg | —30 × $10^{-4}$ deg$^{-1}$ |
| Longitudinal absorption | 4.1 dB/cm | — | — |
| Shear absorption | 19.0 dB/cm | — | — |
| Bulk modulus | 70.2 kbar | —0.33 kbar/deg | —47 × $10^{-4}$ deg$^{-1}$ |
| Young's modulus | 57.9 kbar | —0.34 kbar/deg | —49 × $10^{-4}$ deg$^{-1}$ |
| Shear modulus | 21.3 kbar | —0.13 kbar/deg | —61 × $10^{-4}$ deg$^{-1}$ |
| Poisson's ratio | 0.362 | 2.0 × $10^{-4}$ deg$^{-1}$ | 5 × $10^{-4}$ deg$^{-1}$ |

[a] $\frac{d \ln X}{dT}$, where $X$ is one of the quantities in the first column.

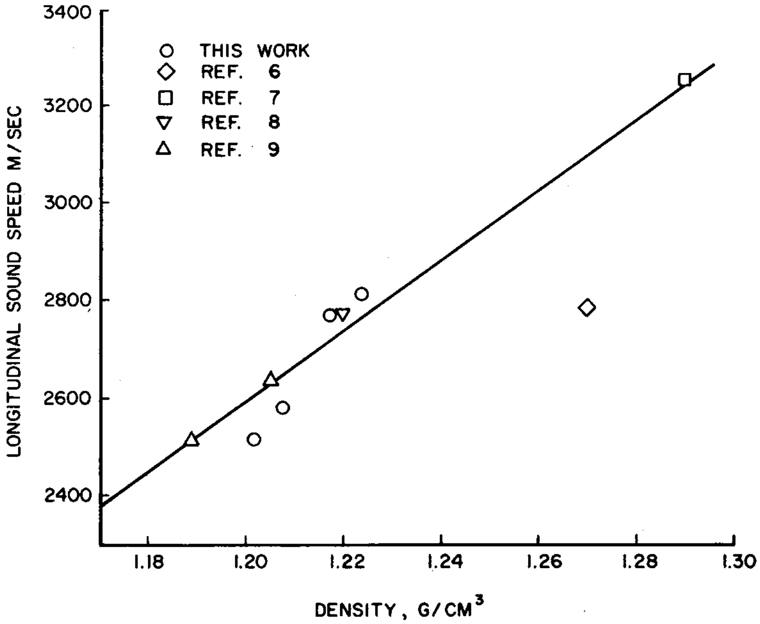

Fig. 4. Longitudinal sound speed vs. density for phenolic.

literature values when differences in density and structure are taken into account. It is also concluded that the sound speed in phenolic depends only on density (or its reciprocal, specific volume) and not directly on temperature or degree of crosslinking but only insofar as these factors change the density.

In comparing sound absorption measurements, one must compare at the same frequency. Wada and Yamamoto[6] measured a longitudinal absorption at 1.46 MHz which would be between 2.5 and 3 dB/cm, depending on the method of extrapolation to a frequency of 1.8 MHz as used here, compared with our value of 4.1 dB/cm. Michaels, Christman, and Isbell[7] made measurements at several frequencies. Interpolating to 1.8 MHz, they found a longitudinal absorption of 5 dB/cm. No shear absorption measurements could be found for comparison. Considering the differences in the materials used and the sensitivity of absorption measurements to small differences, the above agreement with literature values is considered good. Note that the longitudinal absorption of 4.1 dB/cm corresponds to an absorption of 0.65 dB/wavelength, and the shear absorption of 19.0 dB/cm corresponds to 1.4 dB/wavelength.

From the measured sound speeds, the elastic constants for phenolic can be calculated, and these values at room temperature are also given in the first column of Table I. Yamamoto and Wada[12] found a Young's modulus of 64 kbar compared with 57.9 kbar determined here. Drumm, Dodge, and Nielsen[13] measured a shear modulus of 21 kbar using a torsional pendulum compared with 21.3 kbar determined here. Michaels, Christman, and Isbell[7] obtain moduli values all significantly higher than those found here because their sound speeds were significantly greater. (Recall that they used a material of higher density.) Tarbell, Washington, and Scammon[8] did not report elastic constants but since the sound speeds were close to those found here,.the elastic constants calculated from these speeds will also be close.

TABLE II
Sound Speeds, Absorptions, and Elastic Constants for PPQ Polymer

| | Value at 25°C | Temperature derivative | Logarithmic derivative[a] |
|---|---|---|---|
| Longitudinal sound speed | 2460 m/sec | —3.0 m/sec/deg | $-12 \times 10^{-4}$ deg$^{-1}$ |
| Shear sound speed | 1130 m/sec | —1.3 m/sec/deg | $-11 \times 10^{-4}$ deg$^{-1}$ |
| Longitudinal absorption | 3.5 dB/cm | — | — |
| Shear absorption | 15.5 dB/cm | — | — |
| Bulk modulus | 52.1 kbar | —0.12 kbar/deg | $-23 \times 10^{-4}$ deg$^{-1}$ |
| Young's modulus | 42.0 kbar | —0.11 kbar/deg | $-26 \times 10^{-4}$ deg$^{-1}$ |
| Shear modulus | 15.4 kbar | —0.041 kbar/deg | $-27 \times 10^{-4}$ deg$^{-1}$ |
| Poisson's ratio | 0.366 | $1.9 \times 10^{-5}$ deg$^{-1}$ | $0.5 \times 10^{-4}$ deg$^{-1}$ |

[a] $\frac{d \ln X}{dT}$, where $X$ is one of the quantities in the first column.

Room temperature (25°C) ultrasonic results for PPQ are given the first column of Table II. No values could be found in the literature for comparison. Note that the longitudinal absorption of 3.5 dB/cm corresponds to 0.47 dB/wavelength and the shear absorption of 15.5 dB/cm corresponds to 1.1 dB/wavelength.

In comparing phenolic and PPQ, the sound speeds (and hence elastic constants) of phenolic are higher than PPQ. This can be understood as resulting from the highly crosslinked nature of phenolic. On the other hand, the absorptions in phenolic are also higher than PPQ, which one would not expect. Generally, materials with high sound speeds have low absorption. It would appear then that there is some additional mechanism of sound absorption in phenolic that is not present in PPQ.

In comparing the above values with those for linear polymers,[4] phenolic has the highest longitudinal sound speed by at least 5% and the second highest shear sound speed of the 12 common linear polymers listed. PPQ has sound speeds about in the middle of the range of linear polymers.

## Thermal Expansion Coefficient

In order to make ultrasonic measurements as a function of temperature, it is necessary to know the thermal expansion coefficient of the material being measured. There are two reasons for this. First, the thickness of the specimen at each temperature must be known in order to calculate the sound speeds and absorptions. Second, in the calculation of elastic constants from the sound speeds, the density of the specimen must be known at the temperature of interest. In addition to these requirements for the ultrasonic measurements, the thermal expansion coefficient is also needed in the determination of the Gruneisen parameter, as will be discussed later.

Thermal expansion coefficient measurements were made in a standard mercury dilatometer. Results of these measurements on a phenolic are shown in Figure 5. (The specimen used was a medium temperature cure.) In the vicinity of room temperature, the thermal expansion coefficient is $3.1 \times 10^{-4}$ deg$^{-1}$, in good agreement with the value of $2.8 \times 10^{-4}$ deg$^{-1}$ found by Wada and Yamamoto.[6]

The most interesting feature of Figure 5 is the change in slope at 70°C, more than doubling the expansion coefficient. Such a change in slope is in-

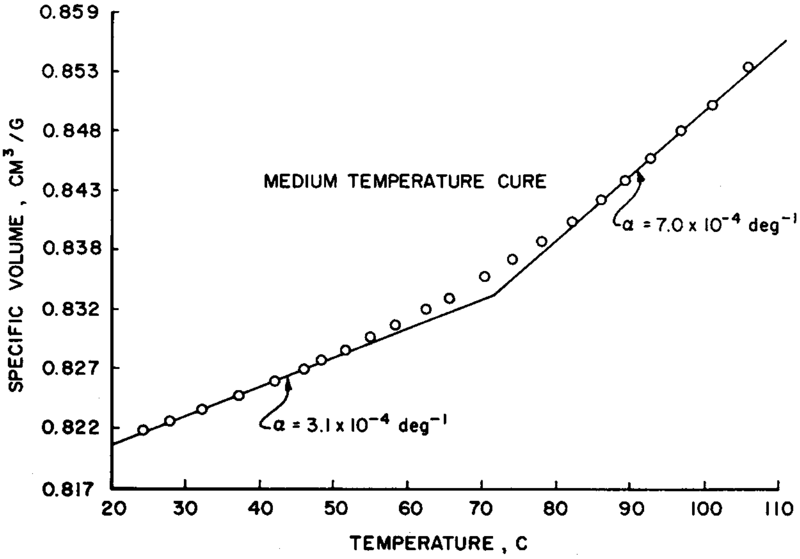

Fig. 5. Specific volume vs. temperature for phenolic.

dicative of some sort of transition in the phenolic. Further measurements on polymers cured at different temperatures and extending to higher temperature than was used here would have to be made in order to accurately determine the transition temperature. It is not clear whether the transition occurs in the crosslinked polymer, the uncrosslinked portions of the polymer, as an interaction with the solvent, or as an interaction with water of reaction.

Thermal expansion measurements were also made on PPQ. In this case there was no indication of a transition, and the expansion coefficient was 2.6 $\times 10^{-4}$ deg$^{-1}$, i.e., only slightly less than the phenolic.

## Temperature Dependence

Longitudinal and shear sound speeds from room temperature to 70°C for phenolic are shown in Figure 6. The straight lines shown are least-square fits to the data, each data point being the average of the five specimens, since there was no significant variation of sound speed with cure temperature. (Note that the 25°C results quoted earlier were taken from these lines.) For both longitudinal and shear speeds, the average scatter about the line is less than 1%. The temperature derivatives of the sound speeds are given in Table I along with the logarithmic derivatives ($d \ln V/dT$). Only Wada and Yamamoto[6] have any temperature dependent data for comparison. They found a temperature derivative of the longitudinal sound speed of −3.4 m/sec/deg compared with the value found here of −7.1 m/sec/deg. No shear speed measurements, as a function of temperature, could be found for comparison. Similar results for PPQ are shown in Figure 7. In this case, the scatter is less than 0.5%. Temperature derivatives are given in Table II. No literature values could be found for comparison. It is interesting that for both phenolic and PPQ, while the temperature derivative of the longitudinal speed is about twice that of the spear speed, the logarithmic derivatives are about the same for longitudinal and shear speeds, namely $-25 \times 10^{-4}$ deg$^{-1}$ for phenolic and

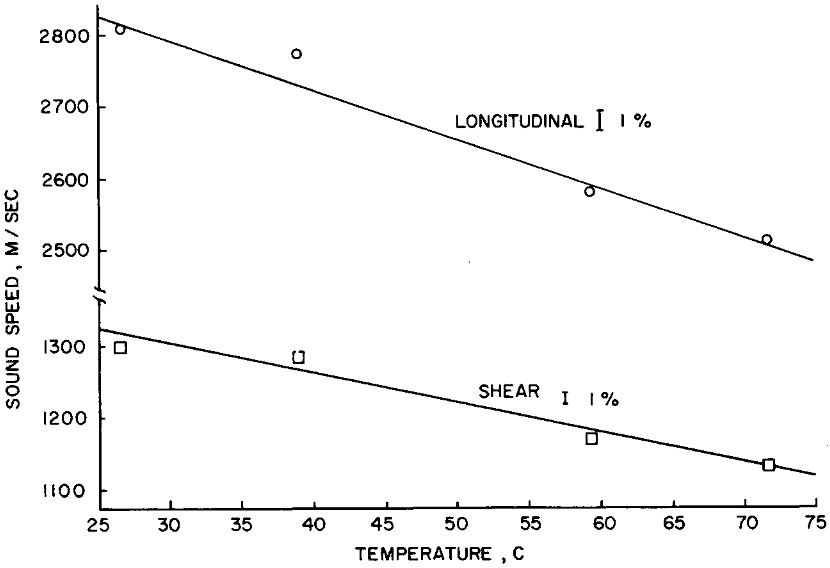

Fig. 6. Sound speeds vs. temperature for phenolic.

$-12 \times 10^{-4}$ deg$^{-1}$ for PPQ. Comparing with other materials,[4,14] phenolic has a high temperature dependence, but not the highest, while PPQ is about average.

Elastic constants as functions of temperature for phenolic are shown in Figure 8. Linear least-squares fit values are given in Table I. The only value available for comparison is Yamamoto and Wada's result[12] of −0.35 kbar/deg for Young's modulus, in excellent agreement with our value of −0.34 kbar/deg. Elastic constants for PPQ are shown in Figure 9 and least-square values in Table II. No literature values were found for comparison. As with

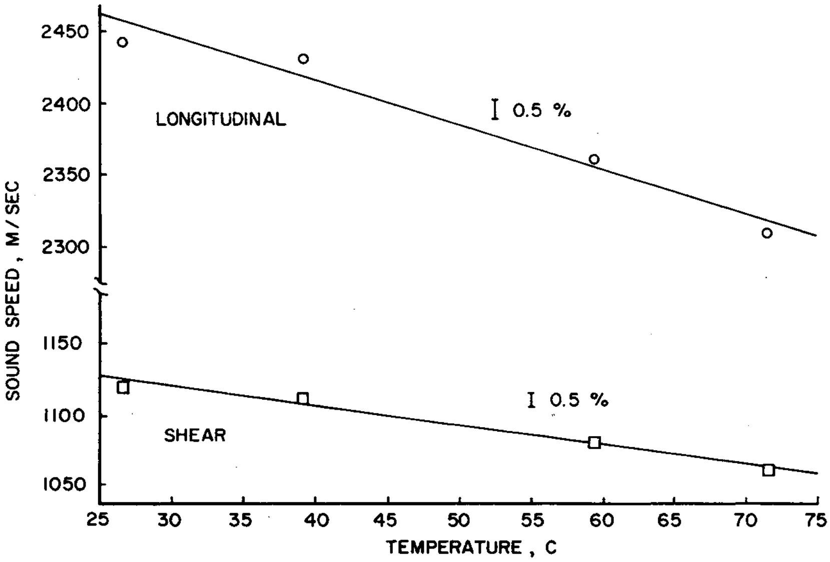

Fig. 7. Sound speeds vs. temperature for PPQ.

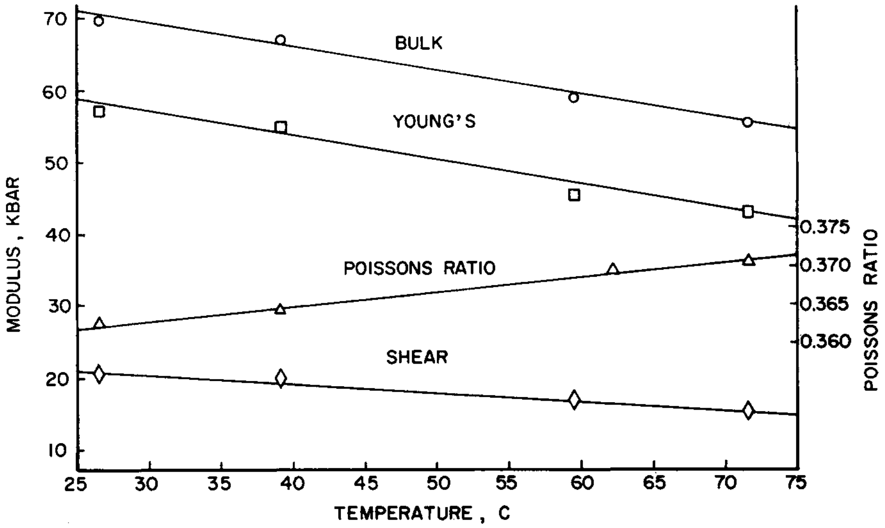

Fig. 8. Elastic constants vs. temperature for phenolic.

the sound speeds, even though the temperature derivative of the moduli are different, the logarithmic derivatives of the elastic constants are the same, namely $-60 \times 10^{-4}$ deg$^{-1}$ for phenolic and $-30 \times 10^{-4}$ deg$^{-1}$ for PPQ. As one would expect from the sound speeds, the elastic constants of phenolic have a temperature dependence more than twice that of PPQ.

Longitudinal absorption in phenolic as a function of temperature is shown in Figure 10 and shear absorption in Figure 11. Longitudinal absorption at 25°C averages 3.5 dB/cm, while shear absorption averages 19.0 dB/cm. Both these values have doubled at 70°C. Each single-specimen absorption is shown in the figures. There are two specimens, of different thickness, for both the high and low temperature cure and one specimen with a medium temperature cure. While there is some scatter among the replicates, for both

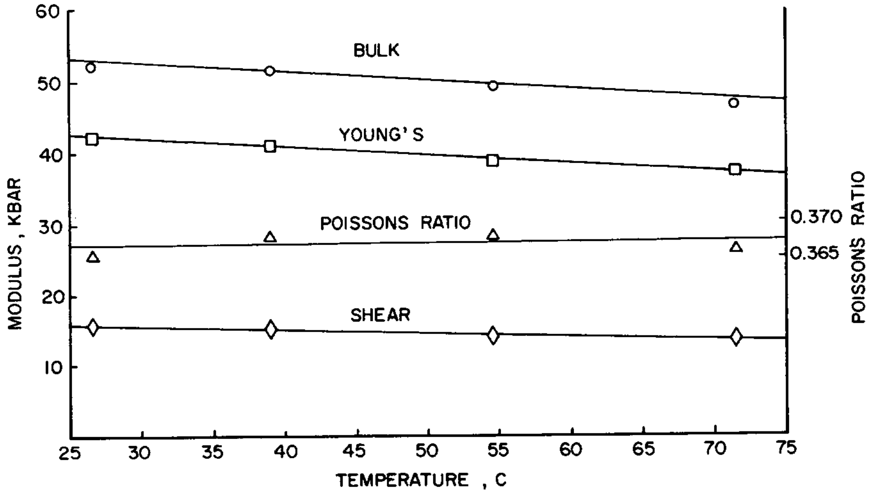

Fig. 9. Elastic constants vs. temperature for PPQ.

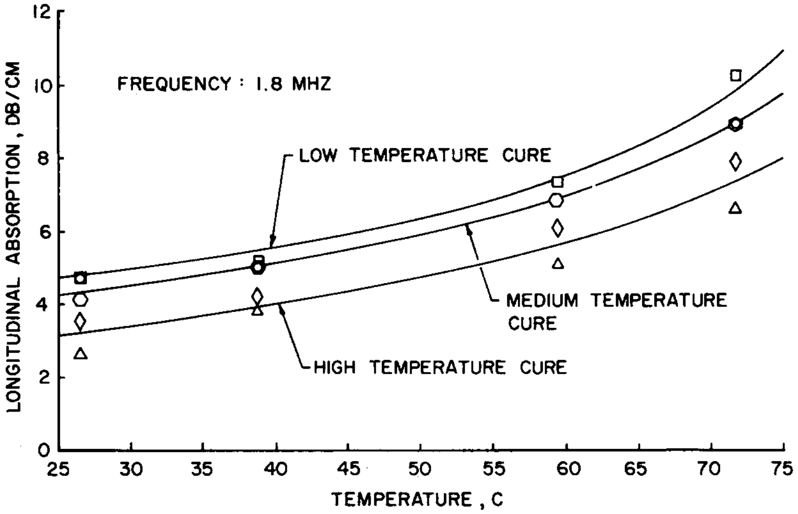

Fig. 10. Longitudinal absorption vs. temperature for phenolic.

longitudinal and shear absorption, the difference between the different cure temperatures is clearly seen. As expected, the higher the cure temperature, the lower the absorption. Also note that the absorption increases significantly with temperature. This temperature behavior is consistent with the idea that there is a transition in phenolic at 70°C. At ultrasonic frequencies, the absorption would have a peak at a higher temperature than was covered here. Wada and Yamamoto[6] also found that the longitudinal absorption increased with temperature in this temperature range. Their value at 70°C would extrapolate to between 6.1 and 7.5 dB/cm at 1.8 MHz, which is in excellent

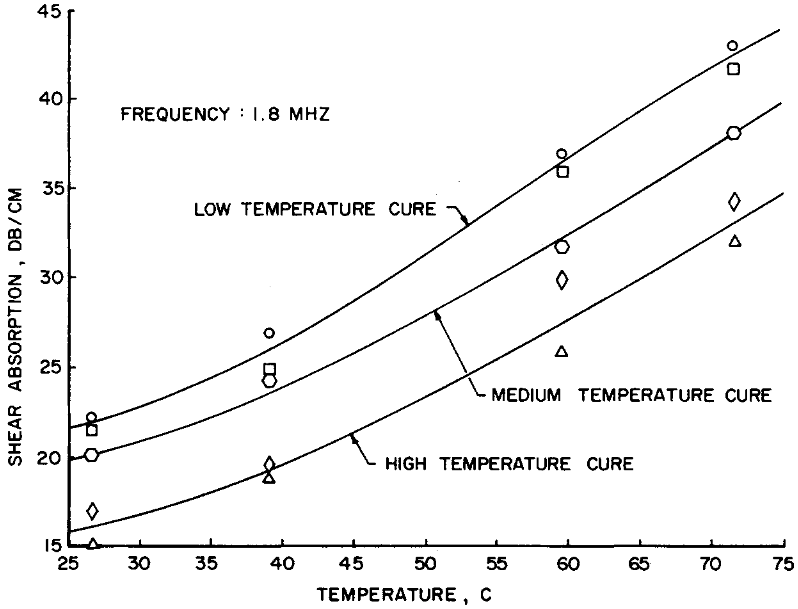

Fig. 11. Shear absorption vs. temperature for phenolic.

agreement with the value found here of 7.2 dB/cm for the high temperature cure.

Both longitudinal and shear absorption for PPQ showed no temperature dependence in the range from 25° to 70°C. The longitudinal absorption was constant at 3.5 dB/cm and the shear absorption was constant at 15.5 dB/cm. Again, there are no literature values to use for comparison. Absorption in PPQ is about 15% lower than in phenolic. At room temperature, both polymers have a lower absorption than the 7 dB/cm reported by Sutherland and Lingle[15] on epoxies.

## GRUNEISEN PARAMETER

### Background

One of the most useful parameters in describing the equation of state of solids is the Gruneisen parameter, $\gamma$. Not only is $\gamma$ useful in equation of state work, it is also invaluable in describing the molecular vibrations in solids. General background for this parameter is given by Slater.[16] Briefly, assuming that bulk modulus depends only on volume (just as the sound speed in phenolic was shown earlier to be a function only of volume), the Gruneisen parameter can be determined either by using temperature measurements with the relation

$$\gamma_T = -\frac{1}{2\alpha}\left(\frac{\partial \ln B}{\partial T}\right)_p \tag{1}$$

where $\alpha$ is the thermal expansion coefficient, or by using pressure measurements with the relation

$$\gamma_p = \frac{1}{2}\left(\frac{\partial B}{\partial p}\right)_T \tag{2}$$

Evaluating $\gamma$ either from eq. (1) or eq. (2) should give the same result, and this is generally the case, i.e., $\gamma_T = \gamma_p = \gamma$.

Alternately, one can define an average Gruneisen parameter by the relation

$$\bar{\gamma} = \frac{\alpha B V}{C_p} \tag{3}$$

where $C_p$ is the specific heat at constant pressure. As first pointed out by Wada,[17] however, to establish agreement between eq. (3) and eq. (1) or (2), only the interchain vibrations should be included in the specific heat,

$$\gamma = \frac{\alpha B V}{C_{p,i}} \tag{4}$$

where $C_{p,i}$ is that part of the specific heat due to interchain vibrations.

### Specific Heat

As seen in eq. (1), $\gamma$ can be calculated from data already presented in this paper. From eq. (3), $\bar{\gamma}$ can be calculated if the specific heat is known. Fur-

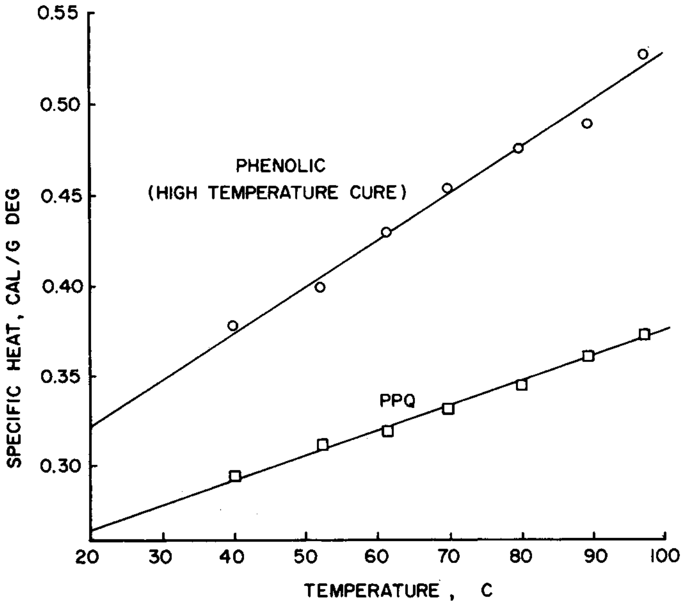

Fig. 12. Specific heat vs. temperature for phenolic and PPQ.

ther, if $\gamma$ and $\bar{\gamma}$ are known, one can calculate the interchain specific heat. For this reason, measurements were made of the specific heats of phenolic (high temperature cure) and PPQ. A differential scanning calorimeter was used over the temperature range from 40 to 100°C. The results are shown in Figure 12. A linear least-squares fit to the data gave

$$C_p(\text{Phenolic}) = 0.273 + 2.56 \times 10^{-3}t \qquad (5)$$

$$C_p(\text{PPQ}) = 0.239 + 1.37 \times 10^{-3}t \qquad (6)$$

for $t$ in degrees Celsius and $C_p$ in cal/g deg. At 30°C, the (extrapolated) specific heat of phenolic is 0.35 cal/g deg, in good agreement with the value of 0.31 cal/g deg found by von Meysenbug,[18] for a different type of phenolic. In addition, the temperature dependence of eq. (5) is about the same as found

TABLE III
Gruneisen Parameters for Phenolic and PPQ Polymers

| | Phenolic | PPQ |
|---|---|---|
| $\gamma_T = -\frac{1}{2\alpha}\left(\frac{\partial \ln B}{\partial T}\right)_p$ | 7.6 | 4.4 |
| $\gamma_p = \frac{1}{2}\left(\frac{\partial B}{\partial p}\right)_T$ | 6.3[a] | 3.5[a] |
| $\bar{\gamma} = \frac{\alpha B V}{C_p}$ | 1.3 | 1.0 |
| $\bar{\gamma}/\gamma_T = C_{p,i}/C_p$ | 0.17 | 0.23 |

[a] Reference 19.

by von Meysenbug. At 100°C, the specific heat of PPQ found here is 0.38 cal/g deg, which compares favorably with 0.36 cal/g deg found by Wrasidlo[2] on a linear PPQ (Fig. 2). Wrasidlo, however, found an even smaller temperature dependence than was found here.

## Calculated Results

Gruneisen parameters for phenolic and PPQ, calculated from eqs. (1), (2), and (3), are shown in Table III, using measurements of Warfield[19] for $\gamma_p$. (He measured the isothermal rather than the adiabatic bulk modulus, but this is not expected to alter the results appreciably.) These values of $\gamma_T$ and $\gamma_p$ are in agreement within the experimental uncertainty of the measurements, phenolic having a value of about 7 and PPQ about 4. Comparing these values with those for other polymers,[19] PPQ has about the lowest Gruneisen parameter of all, as expected. Phenolic, however, has about an average value, rather than the very low value that was expected.

Taking the ratio of eqs. (3) and (1), i.e., $\bar{\gamma}/\gamma_T$, gives the fraction of the specific heat resulting from interchain vibrations, i.e., $C_{p,i}/C_p$. These values are also given in Table III. Compared with other polymers,[19] these values are about average. As expected, the phenolic has a smaller percentage of its total in the form of interchain vibrations.

## CONCLUSIONS

Ultrasonic measurements of longitudinal and shear sound speeds and absorptions were made on phenolic and PPQ polymers. These measurements were made at a frequency of 1.8 MHz and covered the temperature range from 25°C to 70°C. Supplementing the ultrasonic measurements, specific volume and specific heat measurements, as a function of temperature, were also made. These measurements and the quantities calculated from the measurements are all summarized in the tables and figures contained in this paper. In addition to the presentation of this data, four major conclusions were reached during the course of this work:

1. Density dependence of speed: the longitudinal sound speed in phenolic depends only on density (or specific volume) and not directly on temperature or degree of crosslinking.
2. Effect of cure temperature on phenolic: for cure temperatures between 120°C and 180°C, ultrasonic sound speeds do not vary within the accuracy of these measurements, about ±1%. As a result, the elastic constants are not sensitive to cure temperature. On the other hand, both longitudinal and shear sound absorptions vary by 35% with cure; the higher the cure temperature, the lower the absorption. Hence, ultrasonic absorption is a possible way to monitor or measure degree of crosslinking in thermosetting polymers.
3. Comparison with other polymers: sound speeds and elastic constants are at least 5% higher in phenolic than in typical linear polymers. PPQ values are about the same. The high phenolic values are assumed to result from the high degree of crosslinking. Sound absorption is 15% higher in phenolic than in PPQ, contrary to what is expected for a polymer with high sound speed. This high absorption indicates an additional mechanism of ab-

sorption in phenolic not found in PPQ. In the temperature range covered here, phenolic has a higher temperature dependence of sound speeds than does PPQ. Again, this is not expected. Sound absorption increases with temperature in phenolic but is constant in PPQ. Finally, the Gruneisen parameter of phenolic seems high and that of PPQ about right when compared with other polymers.

4. Transitions: there is no suggestion of any transition in PPQ in the temperature range used here. A transition is indicated in phenolic, based on specific volume measurements. A transition is also suggested by the high value of sound absorption and the fact that the absorption increases with temperature. Furthermore, the existence of a transition explains the high temperature dependence of sound speeds in phenolic and the high Gruneisen parameter.

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