NOLTR 72-187

ULTRASONIC HYSTERESIS ABSORPTION IN POLYMERS

By
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21 AUGUST 1972

NOL
NAVAL ORDNANCE LABORATORY, WHITE OAK, SILVER SPRING, MARYLAND

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NOLTR 72-187

UNCLASSIFIED
Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author)
Naval Ordnance Laboratory
Silver Spring, Maryland 20910

2a. REPORT SECURITY CLASSIFICATION
UNCLASSIFIED

2b. GROUP

3. REPORT TITLE
Ultrasonic Hysteresis Absorption in Polymers

4. DESCRIPTIVE NOTES (Type of report and inclusive dates)

5. AUTHOR(S) (First name, middle initial, last name)
Bruce Hartmann and Jacek Jarzynski

6. REPORT DATE
21 August 1972

7a. TOTAL NO. OF PAGES
28

7b. NO. OF REFS
38

8a. CONTRACT OR GRANT NO

b. PROJECT NO
Task ORD 333 004/092-1/UF51-543-30

c. and NOL 278/ONR

d.

9a. ORIGINATOR'S REPORT NUMBER(S)
NOLTR 72-187

9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)

10. DISTRIBUTION STATEMENT
Approved for public release; distribution unlimited.

11. SUPPLEMENTARY NOTES

12. SPONSORING MILITARY ACTIVITY
Naval Ordnance Systems Command
Navy Department, Washington, D.C.
and Office of Naval Research,
Washington, D. C.

13. ABSTRACT

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DD FORM 1473 (PAGE 1)
1 NOV 65
S/N 0101-807-6801

1a

UNCLASSIFIED
Security Classification

14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Ultrasonic properties						
Ultrasonic absorption						
Polymer properties						
Absorption mechanism						

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NOLTR 72-187 **21 August 1972**

ULTRASONIC HYSTERESIS ABSORPTION IN POLYMERS

This report describes experimental work done in measuring ultrasonic absorption in polymers as a function of temperature, frequency, and strain. In addition, an interpretation of the results in terms of a molecular model is also given. The purpose of these measurements is to gain an understanding of the mechanism of sound absorption in polymers so that improved acoustic materials can be developed for a variety of ordnance applications.

This report was taken from a dissertation submitted by Bruce Hartmann to the faculty of the American University in partial fulfillment of the requirements for the degree of Doctor of Philosophy in physics.

This work was conducted in part under Task ORD 333 004/092-1/UF51-543-301 and in part under Task NOL 278/ONR. The materials used in this report were obtained from commercial sources. Their evaluation by the Laboratory in no way implies Navy endorsement.

ROBERT WILLIAMSON II
Captain, USN
Commander

ALBERT LIGHTBODY
By direction

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INTRODUCTION

Dynamic measurements have been shown to give valuable insight into the physical properties of matter.[1-4] While there is a large amount of data on polymers at low frequency,[3] to date there has been no systematic study of sound absorption at ultrasonic frequencies. Some ultrasonic studies of high polymers have been made, but generally only one frequency is used or the measurements are only made at room temperature. For example, reliable absorption measurements were made by Eby[5] on polyethylene (PE) over a wide temperature range but only at one frequency, 12 MHz. Absorption measurements on polymethylmethacrylate (PMMA) were made by Asay, Lamberson, and Guenther[6] as a function of frequency, but only at room temperature.

The polymers chosen for study here are PMMA, PE, and polyethylene oxide (PEO). PMMA and PE were chosen partly because they represent extremes of crystallinity, PMMA being amorphous and PE highly crystalline. PEO was chosen because low frequency (1 Hz) sound absorption measurements have been done[7] but no ultrasonic measurements are available on it.

The principal conclusions of this work are that the sound absorption in polymers has a strain independent hysteresis background throughout the temperature-frequency plane. Superimposed on this background are various relaxation processes. The mechanism responsible for the hysteresis absorption is postulated to be the trapping of the polymer in one of its many local metastable potential energy minima.

MATERIALS USED

The polymethylmethacrylate used here was made by the Rohm and Haas Company, Philadelphia, Pennsylvania, under the trade name Plexiglas II UVA, and was received in the form of a cast block. This is a special grade that has been annealed and is of high optical clarity. The polymer is amorphous but is on the order of 60 percent syndiotactic.[8] Its measured density was 1.191 g/cm^3. The glass transition temperature of PMMA is generally accepted[8] to be 105°C. For this material, the reported[9] number average molecular weight is 7.2×10^5 g/mole and the weight average molecular weight is 4.4×10^6 g/mole.

The polyethylene used here was made by the Allied Chemical Corporation, Morristown, New Jersey, under the trade name FF 50-001, and received in the form of an extruded block. This block had a measured density of 0.957 g/cm^3. The manufacturer gives a weight average molecular weight of 2×10^5 g/mole. For the polymer used here, the melting point is taken[10] as 137°C.

The polyethylene oxide used here was made by the Union Carbide Corporation, New York, under the trade name WSR-301 and received in the form of a powder. The weight average molecular weight of this polymer is reported[11,12] to be 2.9×10^6 g/mole, and the melting point is given[11] as 68.5°C. The powder was compression molded at 1000 atm and 180°C for one hour and allowed to cool to room temperature before the pressure was released. After molding, the measured density of the specimens used in this study was an average of 1.208 g/cm^3, indicating[11] a degree of crystallinity of about 80 percent. The molded specimens were then machined to exact size.

EXPERIMENTAL EQUIPMENT

Most of the data presented here was obtained using an immersion apparatus. In this apparatus, the specimen and transducers are all immersed in a bath of silicone liquid. Ultrasonic pulses are sent from one transducer to the other, both with and without the specimen in the path of the sound beam. Measurements of longitudinal and shear sound speeds and absorptions can be made as functions of frequency, temperature, and strain. Specimen strain was estimated using the measured voltage applied to the transducer and the manufacturer's values of the piezoelectric constants.

Some ultrasonic measurements were made using an aluminum delay rod apparatus. The difficulty with this type of equipment lies in trying to get a reproducible silicone grease or liquid bond between the delay rods and the specimen. With some difficulty, reliable measurements can be made with this type of equipment. To improve the accuracy of the delay rod results, the room temperature absorption measurements reported here were made using four different specimen thicknesses rather than just two. These measurements were all repeated several times in order to check the reproducibility of the data. Based on these repeated measurements, the absorption measurements are estimated to be precise to within ±10%.

Some low frequency measurements were made in an Instron Universal Test Machine which applied the load at a cross-head speed of 0.05 cm/min. The load is applied at this rate up to the desired maximum, then the machine is reversed, releasing the load at the same rate. When zero load is reached, the machine is again reversed and the process is repeated as often as desired. The frequency of these measurements was 10^{-3} Hz. The specimens used were 20 cm long, 1.27 cm wide, and 0.318 cm thick, in the region between the grips. In the grips, the specimen was 1.91 cm wide, following the ASTM standard method for this type of test (test method number ASTM 638-68).

EXPERIMENTAL RESULTS AND DISCUSSION

All of the experimental results will be given in this section. Ultrasonic data from both the immersion apparatus and the delay rod apparatus will be presented as well as some low frequency stress-strain measurements. Where possible, comparison with other data will be made.

Some of the conclusions that follow more or less directly from the measurements will be given in this section. More detailed analysis will be given in subsequent sections.

Ultrasonic Measurements in PMMA

Ultrasonic measurements were made in the immersion apparatus on four PMMA specimens of thickness 0.632, 1.270, 1.903, and 2.540 cm respectively. Longitudinal absorption at room temperature was measured at frequencies of 0.6, 2.2, and 5.5 MHz. The results are shown in Figure 1 along with literature values.[6,13,14] All of the data fall very close to a straight line. A similar frequency plot for the shear absorption is shown in Figure 2. Again, the frequency dependence is a straight line. Both plots indicate a nonzero extrapolated absorption at zero frequency. The data for both longitudinal and shear absorption is of the form

$$\alpha = A + Bf \qquad (1)$$

where α is the absorption (dB/cm), f is the frequency and A and B are constants. Litovitz and Lyon[15] found a similar behavior for ultrasonic absorption in viscous liquids at frequencies above the structural relaxation peak. They attributed the zero frequency component to the tail end of a relaxation.

The major component of the room temperature absorption, both longitudinal and shear, in PMMA has a linear dependence on frequency,

$$\alpha = Bf \qquad (2)$$

This type of absorption is referred to as a hysteresis absorption. From equation (2), a hysteresis absorption is one for which

$$\alpha\lambda = \text{constant} \qquad (3)$$

where the constant is independent of frequency and λ is the wavelength.

Since the absorption is of the hysteresis type, it would be desirable to express Figures 1 and 2 in terms of $\alpha\lambda$, the absorption per wavelength, as the dependent variable rather than α, the absorption per centimeter. The longitudinal and shear sound speeds for this material were found to be v_ℓ = 2690 m/sec and v_s = 1340 m/sec. Then $\alpha\lambda$ (longitudinal) = 0.19 dB and $\alpha\lambda$ (shear) = 0.29 dB.

The above measurements were all done at room temperature. The longitudinal absorption in PMMA as a function of temperature at frequencies of 2.2 and 5.5 MHz is shown in Figure 3. Using the longitudinal sound speed as a function of temperature (to be published elsewhere), $\alpha\lambda$ as a function of temperature was calculated and is shown in Figure 4. Results for the two frequencies fall on the same line. Thus the absorption is a hysteresis type over this temperature interval.

Some of the temperature dependence in Figure 3 is seen to result from the change in sound speed with temperature. Another point of interest is that about half of the difference between longitudinal absorption and shear absorption is due to the fact that shear waves travel only half as fast as longitudinal waves.

Further ultrasonic measurements were done on PMMA to determine whether or not the absorption has a strain dependence. This information is of interest in determining the mechanism of the absorption. These measurements were all made at room temperature and a frequency of 2.2 MHz. For both longitudinal and shear waves, the absorption has no measurable strain dependence for strains in the range from 10^{-9} to 10^{-6}.

Ultrasonic Measurements in PE

Ultrasonic measurements were made in the immersion apparatus on three PE specimens of thickness 1.270, 2.032, and 2.526 cm, respectively. Longitudinal absorption at room temperature was measured at frequencies of 0.6, 2.2, and 5.5 MHz. Measurements were also made in the delay rod apparatus at 3, 5, 7, 8.8, and 11 MHz. The results are shown in Figure 5. As with PMMA, the data follows a straight line, but in this case the zero frequency intercept is zero, within experimental error. Shear waves are highly attenuated in PE and no values at 5.5 MHz could be obtained. Values for the lower two frequencies are shown in Figure 5. The points are consistent, within experimental error, with a zero frequency intercept of zero.

The longitudinal and shear sound speeds for this material were found to be v_ℓ = 2430 m/sec and v_s = 950 m/sec. Then $\alpha\lambda$ (longitudinal) = 0.40 dB and $\alpha\lambda$ (shear) = 1.20 dB at room temperature.

The absorption per wavelength as a function of temperature at 2.2 and 5.5 MHz was calculated and is shown in Figure 6. Within experimental accuracy, the two frequencies have the same $\alpha\lambda$ at room temperature (compare with Fig. 5) and near the melting point. In between, however, there is a deviation from hysteresis behavior due to a relaxation process. This relaxation behavior will be considered elsewhere.

As with PMMA, there is no strain dependence in the longitudinal absorption at room temperature and 2.2 MHz over the region of strain covered here.

Ultrasonic Measurements in PEO

Ultrasonic measurements were made in the immersion apparatus on four PEO specimens of thickness 0.411, 1.021, 1.533, and 2.038 cm, respectively. Longitudinal absorption at room temperature was measured at frequencies of 0.6, 2.2, and 5.5 MHz. Measurements were also made in the delay rod apparatus at 3, 7, 9, and 11 MHz. The results are shown in Figure 7. As with PE and PMMA the frequency dependence is a straight line and as with PE the zero frequency intercept is zero.

Shear waves are so highly attenuated in PEO that no shear measurements could be made even at room temperature.

To express Figure 7 in terms of $\alpha\lambda$, we measured the longitudinal sound speed at room temperature and found that $v_\ell = 2250$ m/sec. Then $\alpha\lambda$ (longitudinal) = 0.8 dB at room temperature.

The measured longitudinal sound speed as a function of temperature for PEO is shown in Figure 8. No literature values could be found for comparison. Using the above sound speed, $\alpha\lambda$ as a function of temperature at 5.5 MHz was calculated and is shown in Figure 9. The data at 2.2 MHz for this polymer had a lot of scatter in it and is not shown in Figure 9. Qualitatively, however, as with PE, there is hysteresis behavior at room temperature and again in the melt but a deviation from hysteresis in between.

As with the other two polymers, there is no strain dependence in the longitudinal absorption at room temperature and 2.2 MHz over the region of strain covered here.

Low Frequency Stress-Strain Measurements

At room temperature for all three polymers, the absorption is of hysteresis type. If this behavior extends over a wide frequency range, then it should be possible to measure the stress-strain hysteresis curve directly at low frequency and correlate this measurement with the ultrasonic measurements. An attempt was made to do this using the low frequency tester described earlier. These tests were all done at room temperature, and different maximum loads were used.

These results showed that the shape of the hysteresis loop depends on the load. Nielsen[16] points out that for PE at room temperature, the creep compliance is independent of stress up to a stress of about 3.5×10^6 dyne/cm^2. Beyond this, the compliance increases with load. With a 30 kg load in our tests, the stress is 7.2×10^7 dyne/cm^2, well above the linear range. Another way to put the above results is that the maximum allowable strain for PE is 5×10^{-4} to ensure linearity, while at 30 kg load the strain is 75×10^{-4}. (Recall that the maximum strain in the ultrasonic measurements is 10^{-6}.) Therefore, the results at the higher loads should be ignored and only the lowest load for each polymer will be considered further. Here the maximum stress is 9.8×10^6 dyne/cm^2 and the maximum strain is 12×10^{-4}. These values are marginal as far as being in the linear region, but this is as low a strain as can be measured with this instrument.

Qualitatively, the results are as expected. The hysteresis loop is the smallest for PMMA and the largest for PEO, just the same ranking as the acoustic absorptions per wavelength. Unfortunately, quantitative measurements of the area of the hysteresis loop for PMMA and even PE are not possible because of the small areas involved. In addition, the magnitude of the "instrument hysteresis," i.e., backlash in the gears, etc., is not known, but is probably comparable to the area we are trying to measure. For PEO, however, with its high loss per cycle, measurements are marginally possible. From Gemant[17] we see that

$$\alpha\lambda = 8.686 \frac{A}{\sigma\epsilon}, \quad \text{dB} \qquad (4)$$

A is the area of the hysteresis loop and σ and ϵ are the maximum values of stress and strain. For PEO, we find $\alpha\lambda$ (tensile) = 2.4 dB. It has been shown[18] that to a good approximation the tensile absorption per wavelength is just equal to the shear absorption per wavelength. Unfortunately, we don't know the shear absorption in PEO. However, the ratio of shear to longitudinal absorption per wavelength in PE is 3 to 1. If we assume the same ratio of shear to longitudinal absorption holds in PEO, we would expect an ultrasonic $\alpha\lambda$ of 3 x 0.7 dB = 2.1 dB, in excellent agreement with the measured tensile value of 2.4 dB.

Comparison with Torsional Pendulum Data

In a further attempt to determine if the hysteresis absorption extends to low frequencies, comparisons were made with torsional pendulum measurements in the literature, all nominally at 1 Hz. For PMMA, the shear absorption per wavelength as measured in a torsional pendulum, $\alpha\lambda$(TP), has been measured as a function of temperature by Nielsen.[19] Unfortunately, we cannot compare the room temperature ultrasonic value with the room temperature torsional pendulum value because PMMA has a broad relaxation peak at 1 Hz and room temperature due to the rotation of the $COOCH_3$ groups. On the higher temperature side this relaxation overlaps the major relaxation in this polymer, the glass transition. On the lower temperature side $\alpha\lambda$(TP) drops off markedly and is still dropping at -50°C, the limit of the experimental data. At -50°C, $\alpha\lambda$(TP) = 0.5 dB. It is entirely consistent with the data to assume that at still lower temperature (i.e., sufficiently far from the relaxation) $\alpha\lambda$(TP) will be the same as the ultrasonic value of 0.29 dB.

Although this comparison of ultrasonic and torsional pendulum data is not entirely conclusive, as well as can be determined from the available data, PMMA has a constant value of $\alpha\lambda$ at least over the frequency range from 1 Hz to 10^7 Hz, except in the vicinity of a relaxation.

For PE, Nielsen[20] finds $\alpha\lambda(TP) = 1.7$ dB and Thornton[21] finds $\alpha\lambda(TP) = 1.6$ dB. These values are in excellent agreement with the ultrasonic value of 1.2 dB. Thus, at least over the frequency range from 1 Hz to 10^7 Hz at room temperature, $\alpha\lambda$ for PE is a constant.

For PEO, the reported[7,22] $\alpha\lambda(TP) = 1.7$ dB for a material of slightly lower crystallinity than that used here. This value is in good agreement with the 2.1 dB estimated for the ultrasonic measurement and the 2.4 dB found in the tensile measurement. Thus, at least over the frequency range from 10^{-3} Hz to 10^7 Hz at room temperature, $\alpha\lambda$ for PEO is a constant.

A summary of the comparisons between the ultrasonic measurements and low frequency measurements is given in Table I.

MOLECULAR MODELS OF HYSTERESIS ABSORPTION

The major result of the experimental measurements has been to show that a hysteresis absorption is characteristic of both crystalline and amorphous polymers and that this hysteresis behavior extends for at least ten decades of frequency. In this section we will attempt to interpret this behavior in terms of the molecular processes responsible. The analysis is divided into two parts: existing general molecular theories of absorption and a proposed molecular theory specifically for polymers.

Existing Theories

Perhaps the most common model for absorption is that of relaxation absorption. A single relaxation absorption increases as the square of the frequency, not linearly. A distribution of relaxation times can result in a hysteresis absorption. Ferry[23] points out that an $\alpha\lambda$ independent of frequency results from a fractional power law distribution of relaxation times (provided the power is small). The disadvantage of this model is that attempts to quantitatively justify this distribution of relaxation times on a molecular basis have not been successful. Mathematically, almost any experimental result can be expressed in terms of a distribution of relaxation times, but this does not mean that any particular motion of the polymer occurs in the relaxation times found. It is unlikely that the fractional power law distribution of relaxation times has any physical significance.

A second possible mechanism, for the crystalline polymers at least, would be scattering, either from voids or from spherulites. The frequency dependence of such an absorption depends on the ratio of the wavelength to the size of the scatterer. For this reason it is of interest to know the crystallite size and the void size. These dimensions were found by using a scanning electron microscope. The void size in PEO is 30 μm or less. At 5.5 MHz and room temperature for PEO, the wavelength is 400 μm so that the scattering is in the long wavelength limit, which has an f^4 dependence. The spherulite size can be as much as 200 μm, i.e., on the order of, but less than, the wavelength. Papadakis[24] has shown that in this case the absorption is proportional to the square of the frequency. Therefore, scattering, whether from spherulites or voids, cannot be the explanation for the absorption in PEO. Similar considerations apply to PE. This mechanism is presumably absent from PMMA because it is amorphous (and hence has no spherulites) and has no appreciable voids.

Another possible cause of absorption is phonon-phonon interaction. It was this type of loss that Litovitz and Lyon[15] suggested would explain the observed hysteresis loss in viscous liquids. The simplest case to consider is the thermoelastic loss. If the sound wavelength is much larger than the mean free path of the thermal phonons in the material, the thermal phonons can be treated as a fluid with a viscosity which results in an f^2 absorption. Another way to express the condition for this result to hold is

$$\omega\tau_{th} \ll 1 \tag{5}$$

where ω is the angular frequency and τ_{th} is the thermal relaxation time, i.e., the mean time between phonon collisions. A second mechanism is also possible when equation (5) holds. This is the Akhiezer[25] mechanism whereby the strain modulates the frequencies of the thermal phonons. The equilibrium population of these modes is therefore modulated also, but with a time lag that results in absorption. It has been shown[26] that the absorption in this case also has an f^2 dependence.

Phonon-phonon interaction for the case

$$\omega\tau_{th} \gg 1 \tag{6}$$

was considered by Woodruff and Ehrenreich[27] and found to produce a hysteresis absorption. It is therefore of interest to find the thermal phonon relaxation time. This time may be taken to be approximately the same as that appearing in the expression for the thermal conductivity of an insulator

$$K = 1/3\ C_v <v>^2\ \tau_{th} \qquad (7)$$

where K is the thermal conductivity, <v> is the Debye average sound speed, and C_v is the specific heat at constant volume. For PMMA, the thermal conductivity at room temperature is[28] 5×10^{-4} cal cm/cm^2 sec deg, the specific heat is[29] 0.3 cal/cm^3 deg, so that the thermal phonon relaxation time is about 10^{-13} sec. For the highest frequency used here $\omega = 10^7$ sec^{-1} so that $\omega\tau_{th} = 10^{-6}$ $<< 1$. As shown earlier, we would therefore not expect to see any hysteresis.

A further point against phonon-phonon interaction is that such an interaction is inherently anharmonic and thus strain dependent. However, as shown above, there is no strain dependence to the absorption. Finally, the strong temperature dependence found for this type of loss is not seen experimentally.

The last of the possible mechanisms to be considered here is that of dislocation damping, a mechanism which has been found useful for metals and rocks. Dislocations may produce absorption in four general ways: (1) A resonance absorption of the dislocation length. This loss has an f^2 dependence. (2) A dislocation relaxation mechanism (Bordoni loss), also with an f^2 dependence. (3) A strain dependent hysteresis loss caused by a dislocation breaking away from the impurity pinning points. (4) A strain independent hysteresis loss caused by the motion of kinks in the dislocation length.

Only the last of these dislocation mechanisms agrees with the experimental results, namely a strain independent hysteresis loss. Mason[30] suggested that the kinks may behave differently under increasing and decreasing stress, but did not give a molecular reason why this should be so. This mechanism is therefore unsatisfactory from the point of view that it is not specific in the molecular mechanism involved, and no one has ever applied this mechanism in detail to polymers.

Polymer Model

None of the above models was specifically proposed for explaining absorption in polymers, and none is completely satisfactory. Let us now consider specifically a mechanism of hysteresis absorption in polymers.

In general, hysteresis can be attributed[31] to the existence of a large number of independent domains at least some of which can exhibit metastability. Here a domain means only some element of the system which can exist in one or other of two states. As applied to magnetic domains, Levy[32] points out that there are potential energy irregularities in a crystal that determine the domain wall positions. Irreversible domain wall motion (and hence magnetic hysteresis) occurs when a potential hill is crossed. This general idea should also hold for polymers because there are many independent configurations possible for a polymer chain. Further, due to steric effects (excluded volume) there are many irregularities in the potential energy, leading to many positions of metastability. Qualitatively, then, elastic hysteresis in polymers could be anticipated.

Mason[33] proposed a similar mechanism when he speculated that the dislocation hysteresis loss in metals is connected with irreversible changes in the bonding mechanism between the atoms as they approach each other under the stress of the sound wave. These changes occur over an energy barrier which has to be surmounted by thermal agitation. The absorption is independent of applied frequency so long as the frequency of jumping is greater than the applied frequency. The frequency of jumping, f_i, is related to the energy barrier, H_i, by

$$f_i = f_o e^{-H_i/RT} \tag{8}$$

where f_o is approximately 10^{13} Hz, i.e., equal to the reciprocal of the thermal phonon relaxation time (see previous section). As applied to polymers, Mason et al[34] suggest that the motion involved is a twisting of chain segments which cannot quite jump from one stable potential well to a neighboring one but are displaced to intermediate metastable potential minima and held there by steric restrictions. Sauer et al[35] noted that the slipping of chains past one another was a possible mechanism of loss.

At this point, we would like to suggest a molecular model which qualitatively accounts for our experimental data. In brief, the suggested model involves rotation about the covalent bonds in the main chain such that the polymer becomes trapped in one of its many local metastable potential energy minima. It is well known[36] that for a single small hydrocarbon molecule, for example, rotation about the carbon-carbon bond is not completely free; there are three preferred positions. The same qualitative features hold in a solid polymer, but the energy barriers to rotation are accentuated and multiplied.

Guided by the above considerations, we make the following assumptions:

I. Under the applied stress of the sound wave, some reorientation of the polymer occurs (by way of rotation of individual mers). Upon release of the stress, not all the mer units return to their original orientation because they are trapped in one of the many metastable configurations possible for a polymer chain. This dissymmetry of behavior under stressing and unstressing is the origin of hysteresis.

II. The magnitude of the hysteresis absorption is dependent on free volume because of two competing effects: (a) the number of segments that reorient themselves decreases with decreasing free volume, (b) the fraction of these segments which do not return to their original orientation increases with decreasing free volume. The second effect dominates, and the hysteresis absorption increases with decreasing free volume.

III. The free volume in a polymer decreases with increasing degree of crystallinity.

According to assumption II,

$$\alpha\lambda = F(V_f) \tag{9}$$

where V_f is the free volume and F is some undetermined function. Recall that

$$V_f = V - V_o \tag{10}$$

where V is the volume of the polymer and V_o is the volume extrapolated to absolute zero temperature without change of phase.

Substituting equation (10) into equation (9) and expanding in terms of V yields

$$\alpha\lambda = a - bV + \cdot \cdot \cdot \tag{11}$$

where a and b are positive constants and the minus sign results because $\alpha\lambda$ increases as V decreases. Thus, the absorption is best expressed as a function of volume rather than temperature, a result which was first suggested by Slawsky[37] on somewhat more intuitive grounds.

To a first approximation then, the hysteresis absorption should be a linearly decreasing function of specific volume. Qualitatively, this is so, at least for the crystalline polymers, by inspection of the data, Figures 6 and 9, neglecting the relaxation peaks. For PMMA (Figure 3), there is an increase of absorption with increasing temperature (increasing volume) but this may be explained as due to the influence of the relaxation absorption associated with the glass transition. This absorption may increase with temperature (as the glass transition temperature is approached) more than the decrease in hysteresis absorption which the very slight decrease in volume would produce.

A plot of $\alpha\lambda$ vs V for PE is shown in Figure 10. The data used for this plot is given in Table II. V(T) was taken from Mandelkern[38] and $\alpha\lambda$(T) was taken from Figure 6. Only the hysteresis absorption from this figure is used. Thus, only the room temperature values and values near the melting point are used. These are the values that are known to be hysteresis type. As can be seen, there is reasonably good agreement with equation (11).

A similar plot for PEO is not possible because accurate V(T) data is not available for the particular polymer used here. As shown in Figure 9, the decrease in $\alpha\lambda$ at the melting point is very rapid and accurate volume data would be required to test the relationship expressed in equation (11). Qualitatively, there is agreement between equation (11) and our results for PEO. The absorption is lowest in the melt, where the volume is greatest. Near the melting point, where the volume is increasing most rapidly, the absorption is decreasing most rapidly.

According to assumption III, free volume and crystallinity are related so that we can also expand $\alpha\lambda$ in terms of degree of crystallinity, x, to obtain

$$\alpha\lambda = a' + b'x + \cdots \qquad (12)$$

where a′ and b′ are positive constants and the plus sign results because $\alpha\lambda$ increases as x increases. Equation (12) can also be derived from equation (11) using the relation

$$V = xV_c + (1 - x)V_A \qquad (13)$$

where V_c is the specific volume of the crystalline regions and V_A is the specific volume of the amorphous regions. By equation (12), sound absorption is related to the degree of crystallinity of a polymer and may offer a method of determining crystallinity, provided a′ and b′ are measurable. The constant a′ should be measurable in the melt $(x = 0)$, but it is doubtful that the proposed molecular model applies to a completely crystalline polymer $(x = 1)$ since eventually the free volume must become so small that applied ultrasonic stresses cause negligible reorientation of the polymer. Apparently this limit was not reached for the polymers studied in this work. An independent measurement of crystallinity is required to determine b′.

One of the primary physical parameters of the above molecular model is the energy barrier to rotation. An upper limit for this parameter can be obtained from equation (8). At room temperature, assuming that $f_o = 10^{13}$ Hz, f_i must be at least as high as the highest frequency used in this work, 10^7 Hz. Then the energy barrier to rotation, H_i, can be at most 8 kcal/mole. If the hysteresis behavior persists up to 10^9 Hz, H_i can be at most 5.5 kcal/mole. These estimates are somewhat greater than the 1 kcal/mole typical of the enthalpy of fusion of one mer but are certainly of the right order of magnitude to be consistent with the suggested molecular model of the hysteresis absorption in polymers.

CONCLUSIONS AND RECOMMENDATIONS

Ultrasonic absorption measurements for both longitudinal and shear waves have been made as functions of temperature, frequency, and strain in three high polymers: polymethylmethacrylate, high density polyethylene, and polyethylene oxide.

At room temperature, all three of these polymers show a hysteresis type absorption for both longitudinal and shear waves. For this reason, use of the variable $\alpha\lambda$ is preferred rather than α in order to exhibit the frequency dependence explicitly. There are two other benefits to using the variable $\alpha\lambda$. Part of the temperature dependence of α is determined by the temperature dependence of the sound speed. Also a major part of the difference in magnitude between longitudinal and shear absorption is due to the difference between longitudinal and shear sound speeds.

There is no strain dependence to the absorption in any of the polymers in the strain range from 10^{-9} to 10^{-6}. A strain dependence becomes apparent for strains above 10^{-4}.

For PEO at room temperature, $\alpha\lambda$ is independent of frequency at least over the range from the highest ultrasonic frequency of 10^7 Hz to a frequency of 10^{-3} Hz, used in the low frequency measurements. For PE at room temperature, $\alpha\lambda$ is independent of frequency at least from 10^7 Hz to 1 Hz, using literature values of torsional pendulum results. For PMMA, at room temperature, such a correlation of ultrasonic and torsional pendulum measurements cannot be made due to the dominance of the $COOCH_3$ rotation relaxation in the torsional pendulum results. However, there is reasonable agreement with the room temperature ultrasonic measurements and low temperature torsional pendulum measurements (that is, well away from any relaxations).

As a function of temperature, the ultrasonic measurements on PE and PEO indicate a hysteresis absorption at room temperature and near the melting point. PMMA shows a hysteresis absorption over the entire limited temperature range covered for that polymer.

On the molecular level, various mechanisms have been examined to see if they could explain the hysteresis absorption. Mechanisms that were ruled out as being inconsistent with the data were relaxations, scattering, phonon-phonon interaction, and dislocation damping. The mechanism postulated was the trapping of the polymer in one of its many local potential energy minima. This mechanism should result in a hysteresis absorption from very low frequency to 10^{13} Hz. For the crystalline polymers at least, this suggests a volume dependence of the absorption, which in turn means that the absorption is directly related to the degree of crystallinity.

Based on the above measurements, it appears that the sound absorption in high polymers has a hysteresis background throughout the temperature-frequency plane. Superimposed on this background are various relaxation processes. The relatively complicated shape of the hysteresis α vs T plot is reduced to a straight line by plotting $\alpha\lambda$ vs volume, V. The temperature, frequency, and strain dependence of the hysteresis absorption in partially crystalline polymers can be expressed as

$$\alpha(T,f,\epsilon) = \frac{a - bV(T)}{v(T)/f} \qquad (14)$$

where a and b are constants for a given polymer and v is the speed of sound.

Based on the above work, we recommend the following experiments be performed:

a. Measurements similar to the above should be conducted on other polymers to verify that the hysteresis background behavior is a characteristic of all long chain polymers.

b. Measurements should be made on polymers to very high frequencies, 10^{13} Hz, to verify that the hysteresis absorption is eliminated at some very high frequency and, from the value of the frequency at which this occurs, to calculate the energy barrier to reorientation.

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Table I. Comparison of Ultrasonic and Low Frequency Measurements

Polymer	$\alpha\lambda_s$ Ultrasonic $f \sim 10^7$ Hz	$\alpha\lambda_s$ Torsional Pendulum $f \sim 1$ Hz	$\alpha\lambda_s$ Low Frequency Tester $f \sim 10^{-3}$ Hz
PMMA	0.29	<.5	--
PE	1.2	1.6	--
PEO	2.1	1.7	2.4

Table II. Absorption and Volume as Functions of Temperature for Polyethylene

T, °C	V, cm^3/g	$\alpha\lambda$, dB
25	1.045	.40
129	1.149	.175
130	1.169	.15
131	1.212	.12
132	1.227	.09
133	1.242	.06
134	1.244	.035

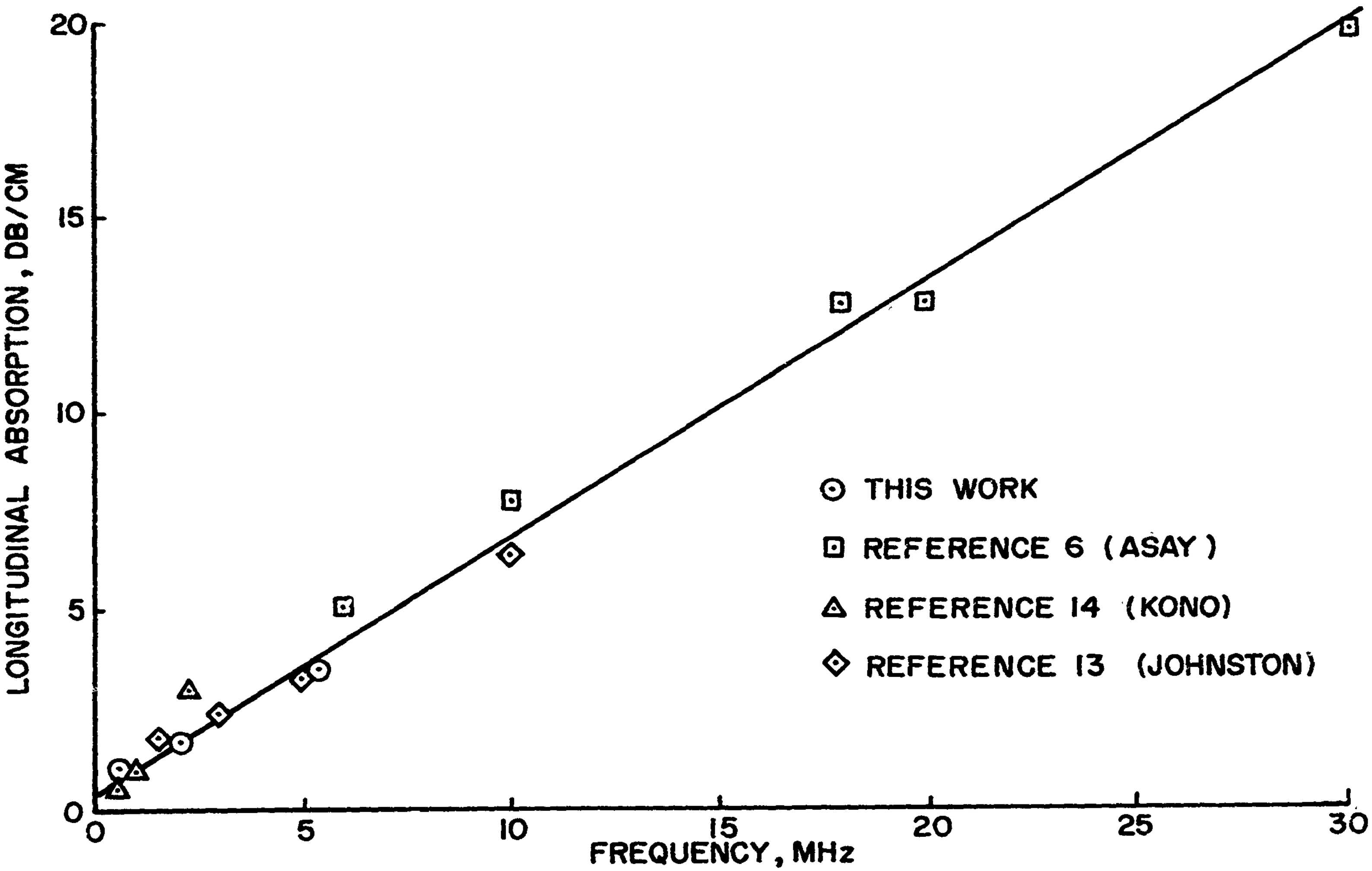

FIG. 1 LONGITUDINAL ABSORPTION VS FREQUENCY AT ROOM TEMPERATURE FOR POLYMETHYLMETHACRYLATE

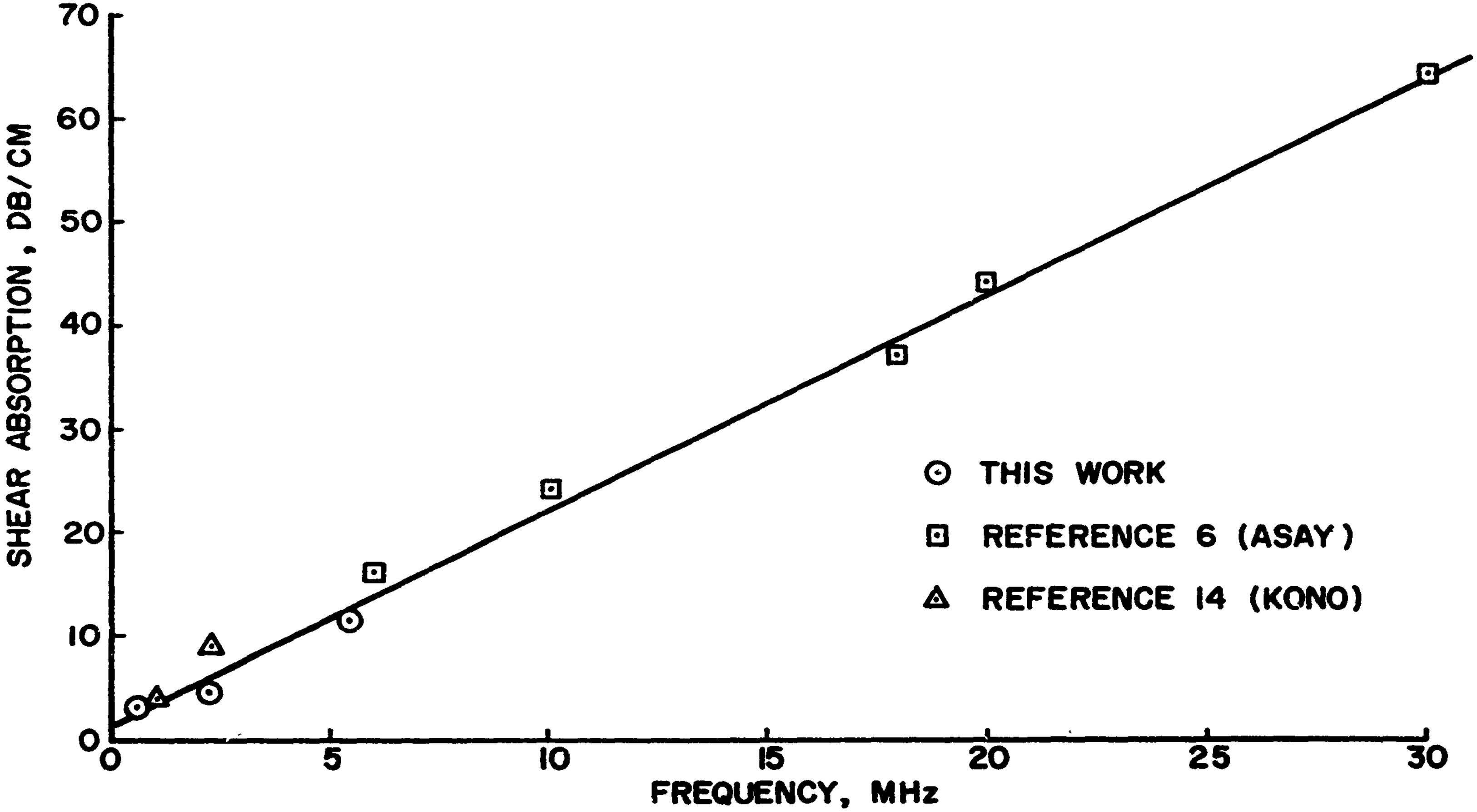

FIG. 2 SHEAR ABSORPTION VS FREQUENCY AT ROOM TEMPERATURE FOR POLYMETHYLMETHACRYLATE

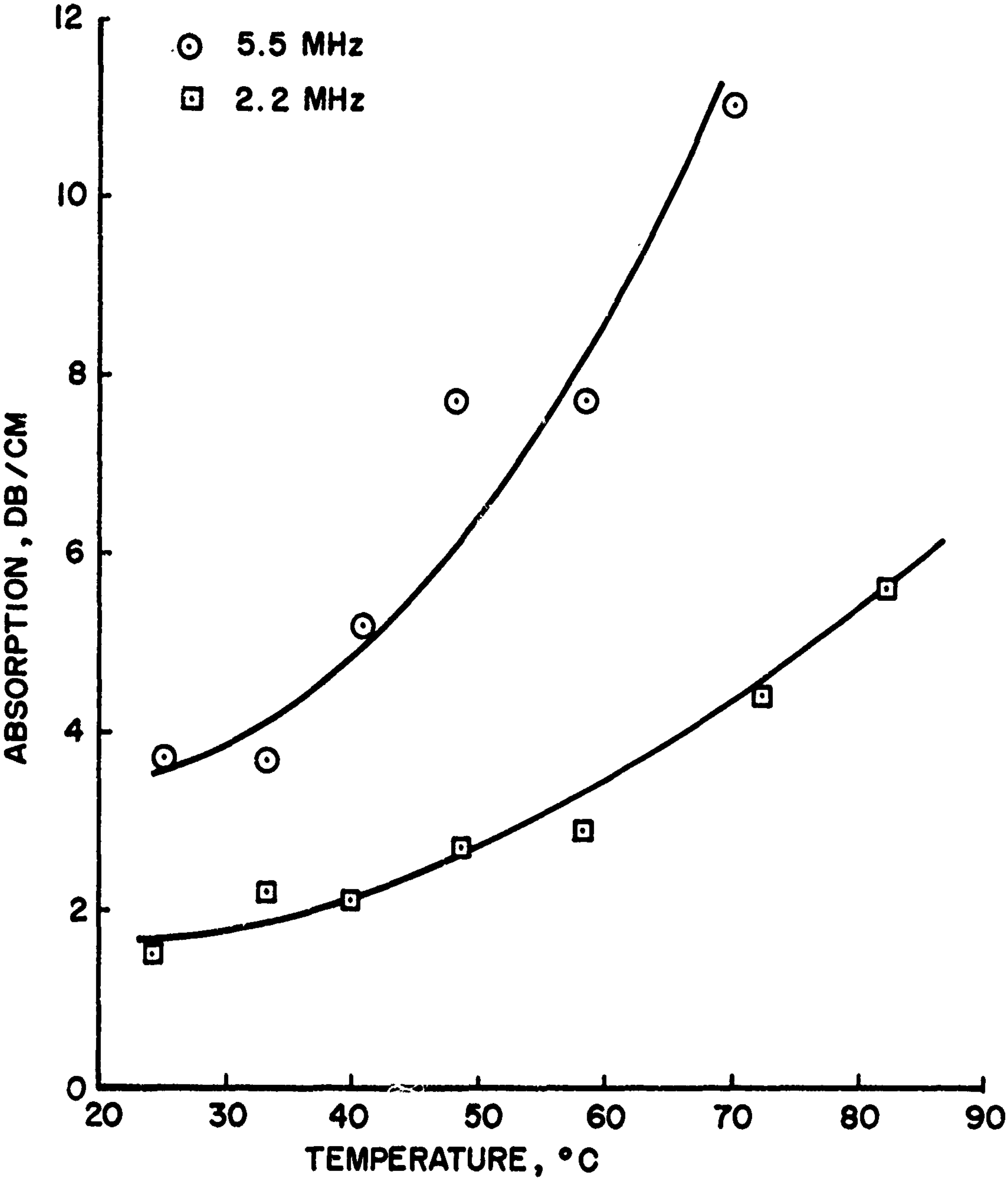

FIG. 3 LONGITUDINAL ABSORPTION VS TEMPERATURE FOR POLYMETHYLMETHACRYLATE

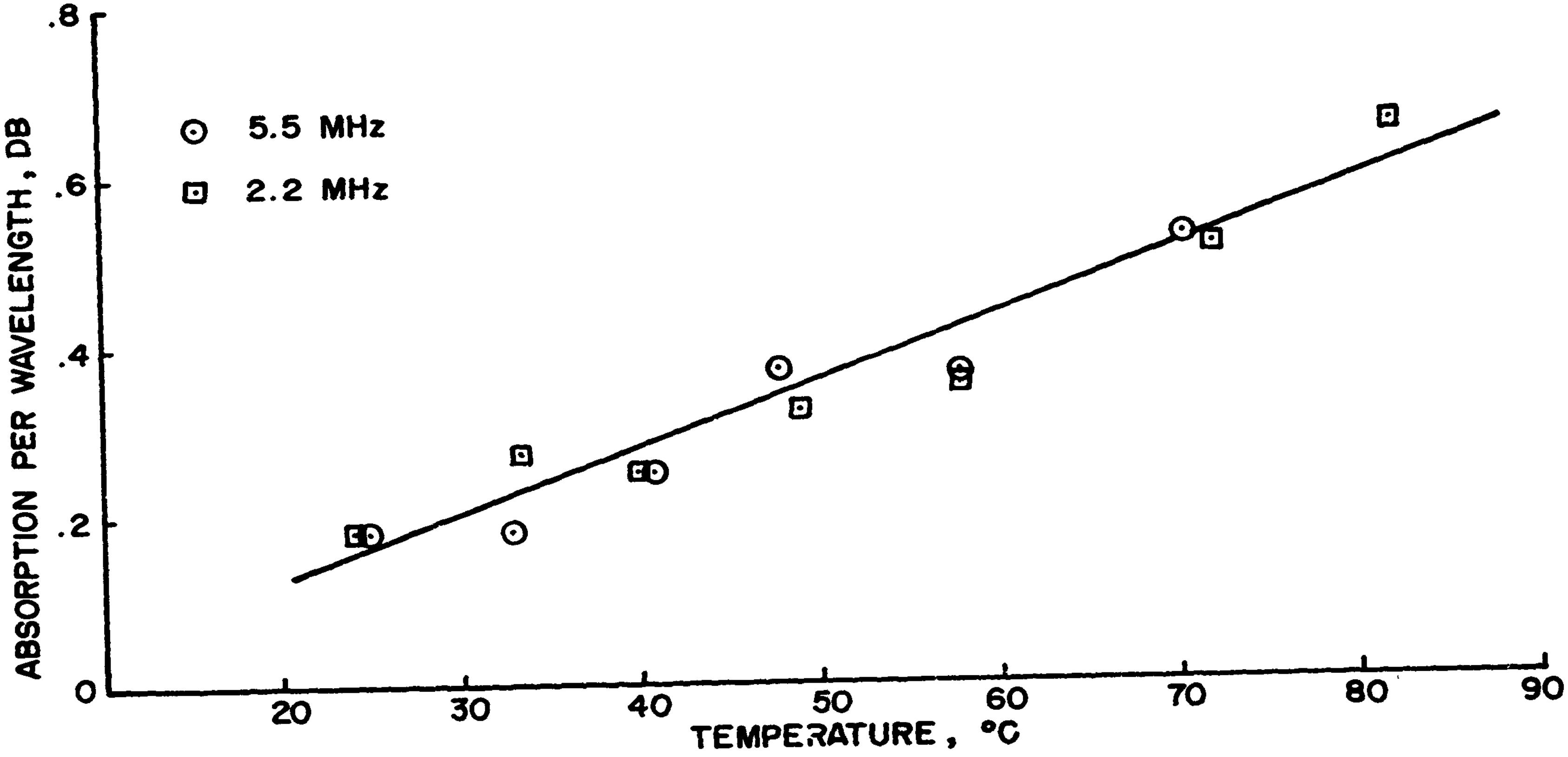

FIG. 4 LONGITUDINAL ABSORPTION PER WAVELENGTH VS TEMPERATURE FOR POLYMETHYLMETHACRYLATE

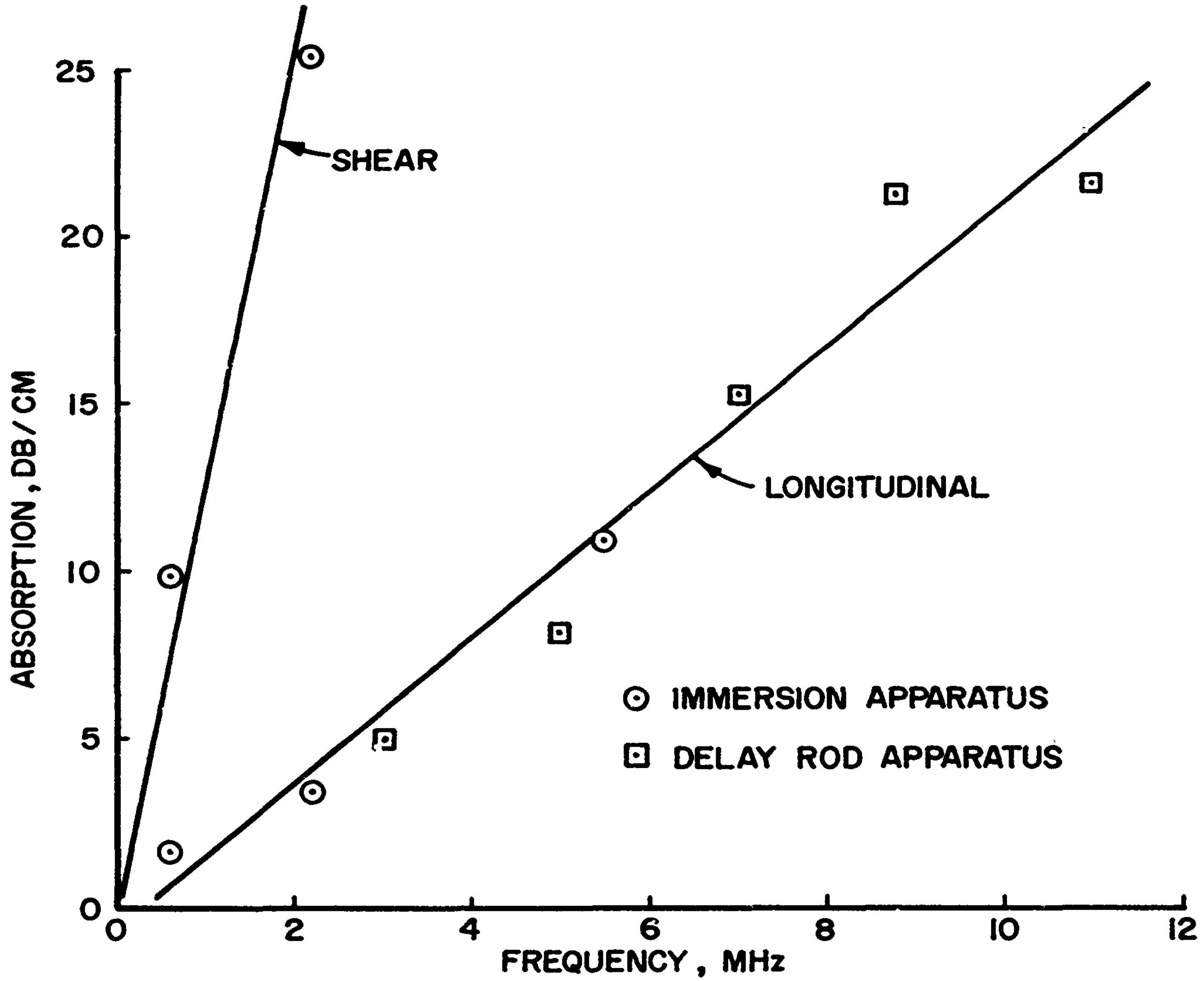

FIG. 5 ABSORPTION VS FREQUENCY AT ROOM TEMPERATURE FOR POLYETHYLENE

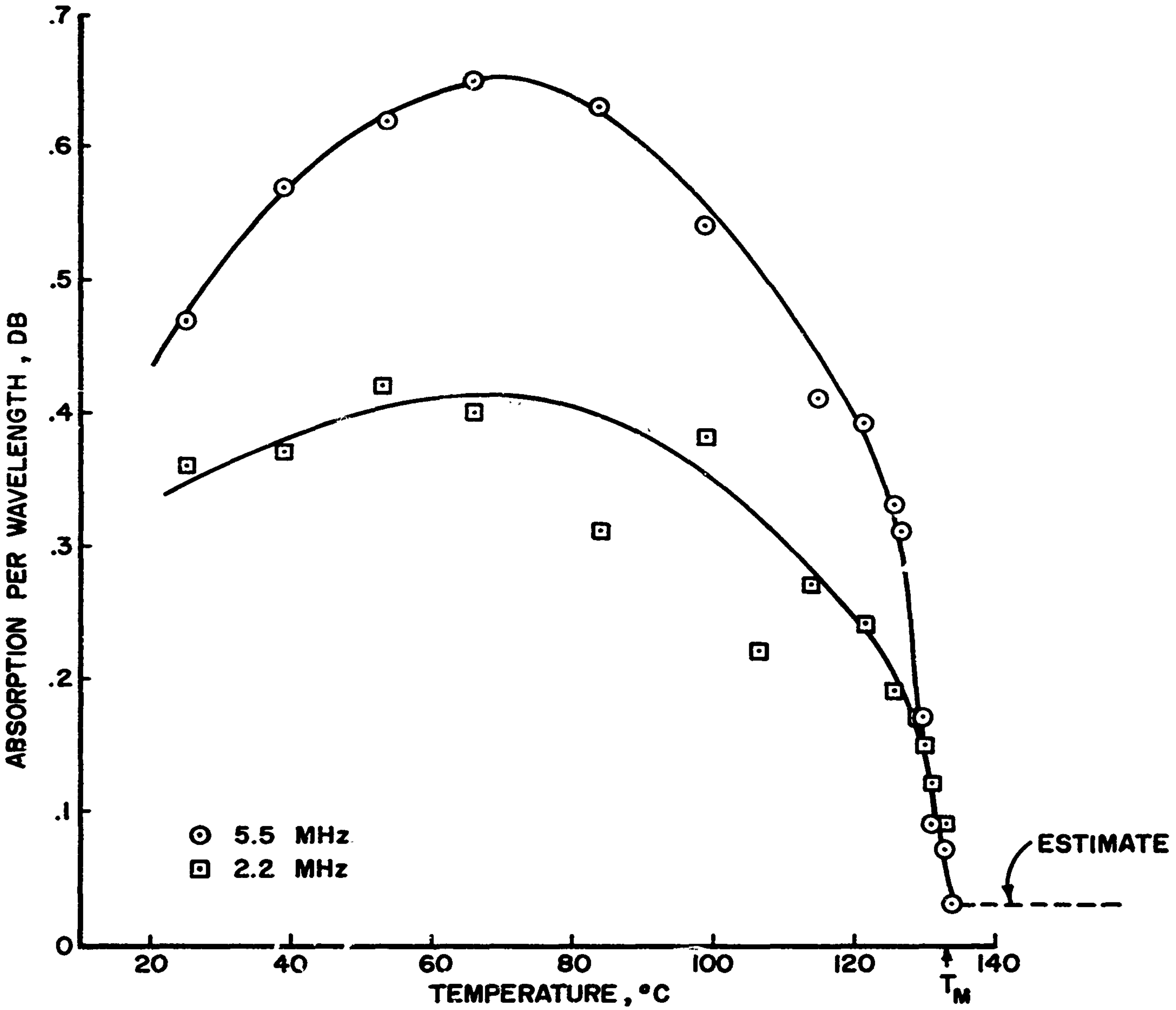

FIG. 6 LONGITUDINAL ABSORPTION PER WAVELENGTH VS TEMPERATURE FOR POLYETHYLENE

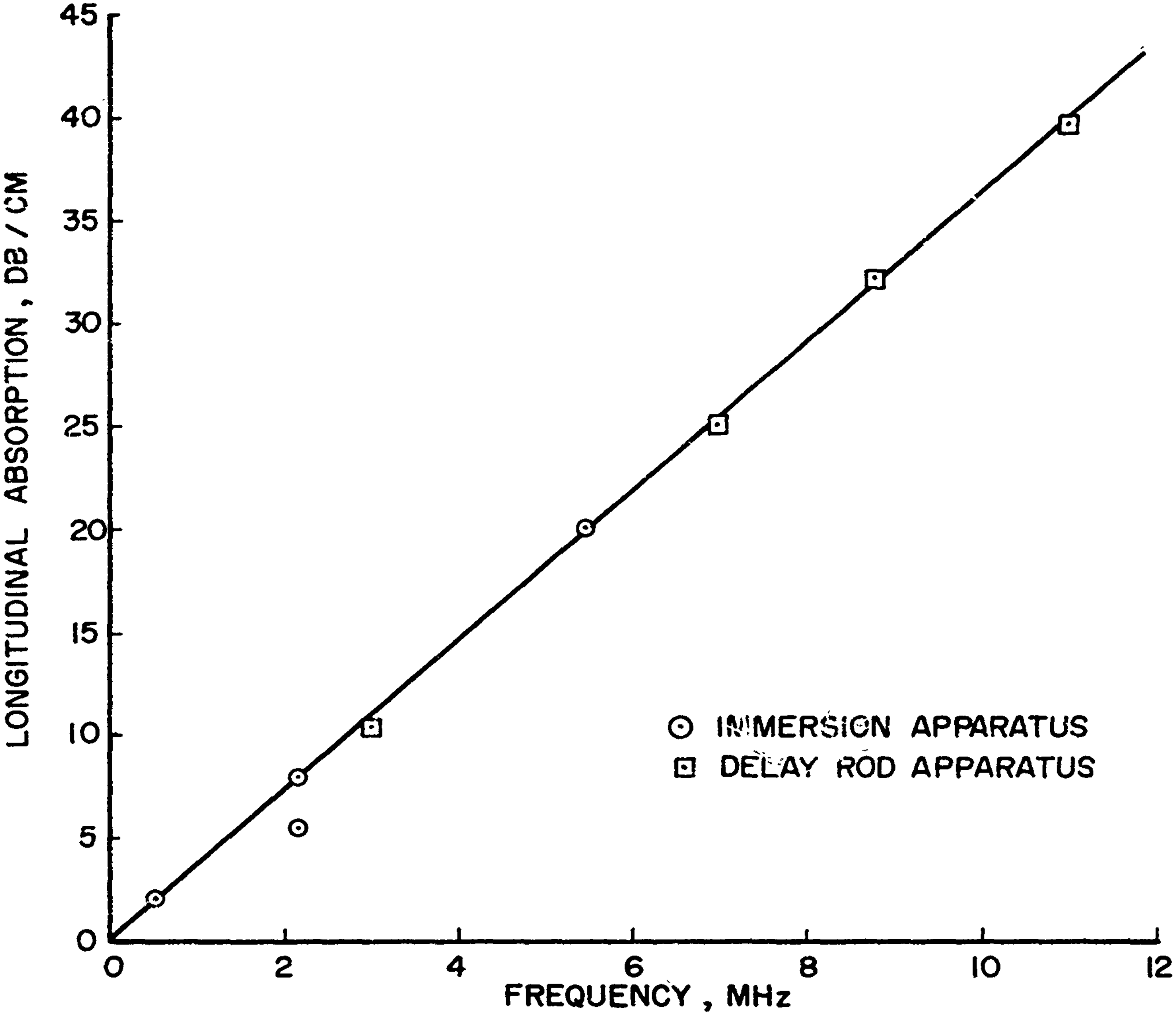

FIG. 7 LONGITUDINAL ABSORPTION VS FREQUENCY AT ROOM TEMPERATURE FOR POLYETHYLENE OXIDE

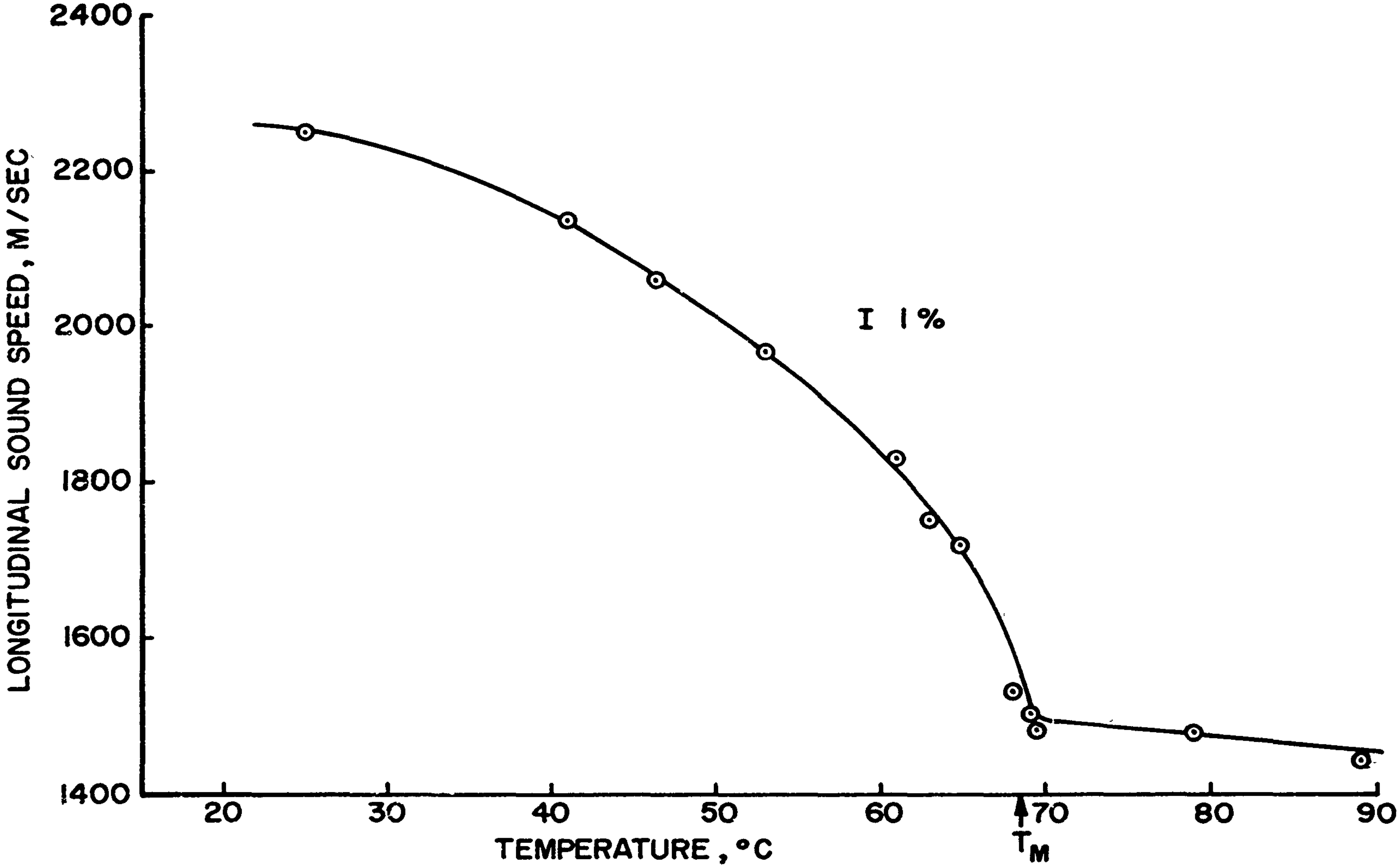

FIG. 8 LONGITUDINAL SOUND SPEED VS TEMPERATURE FOR POLYETHYLENE OXIDE

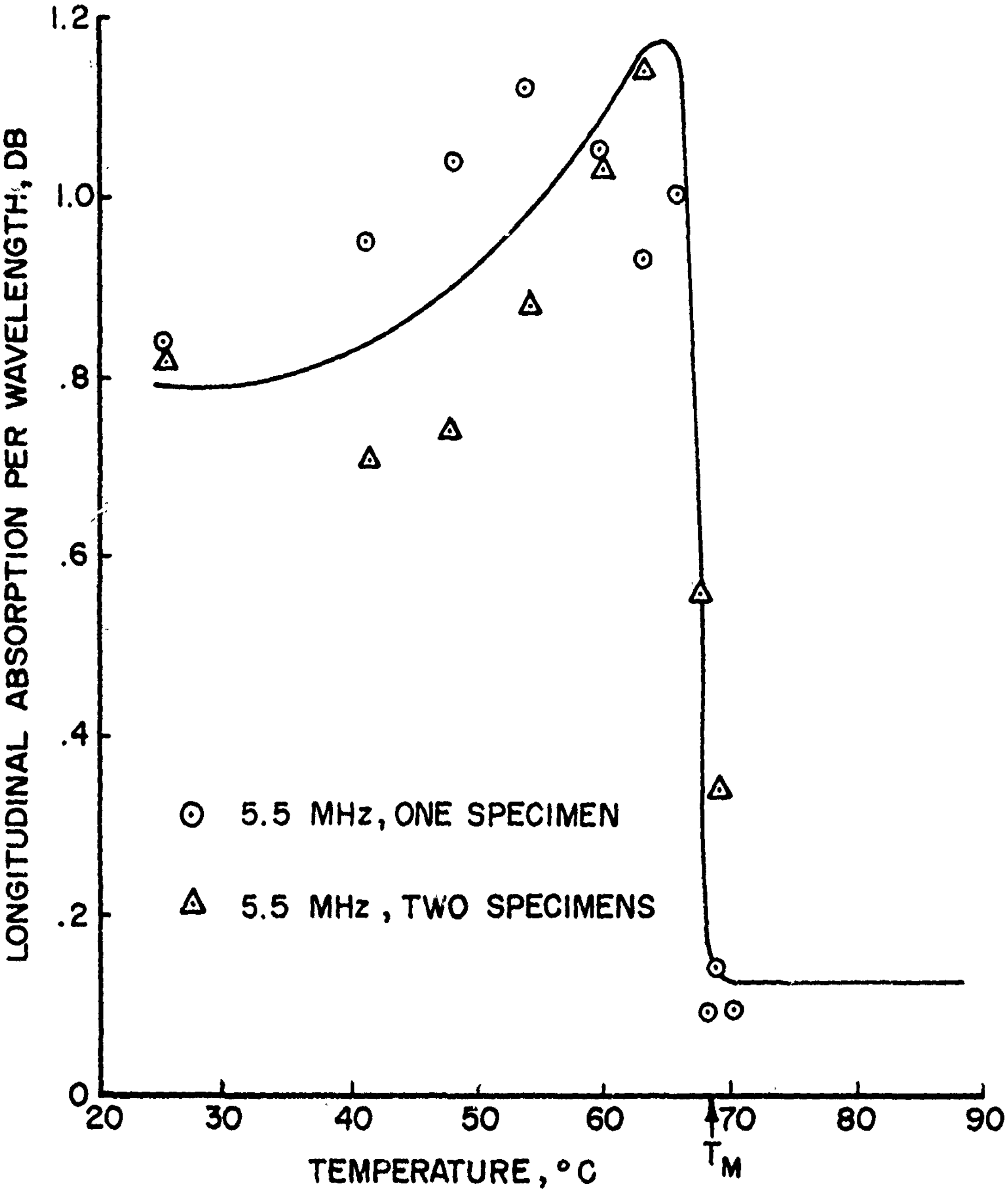

FIG. 9 LONGITUDINAL ABSORPTION PER WAVELENGTH VS TEMPERATURE FOR POLYETHYLENE OXIDE AT 5.5 MHz

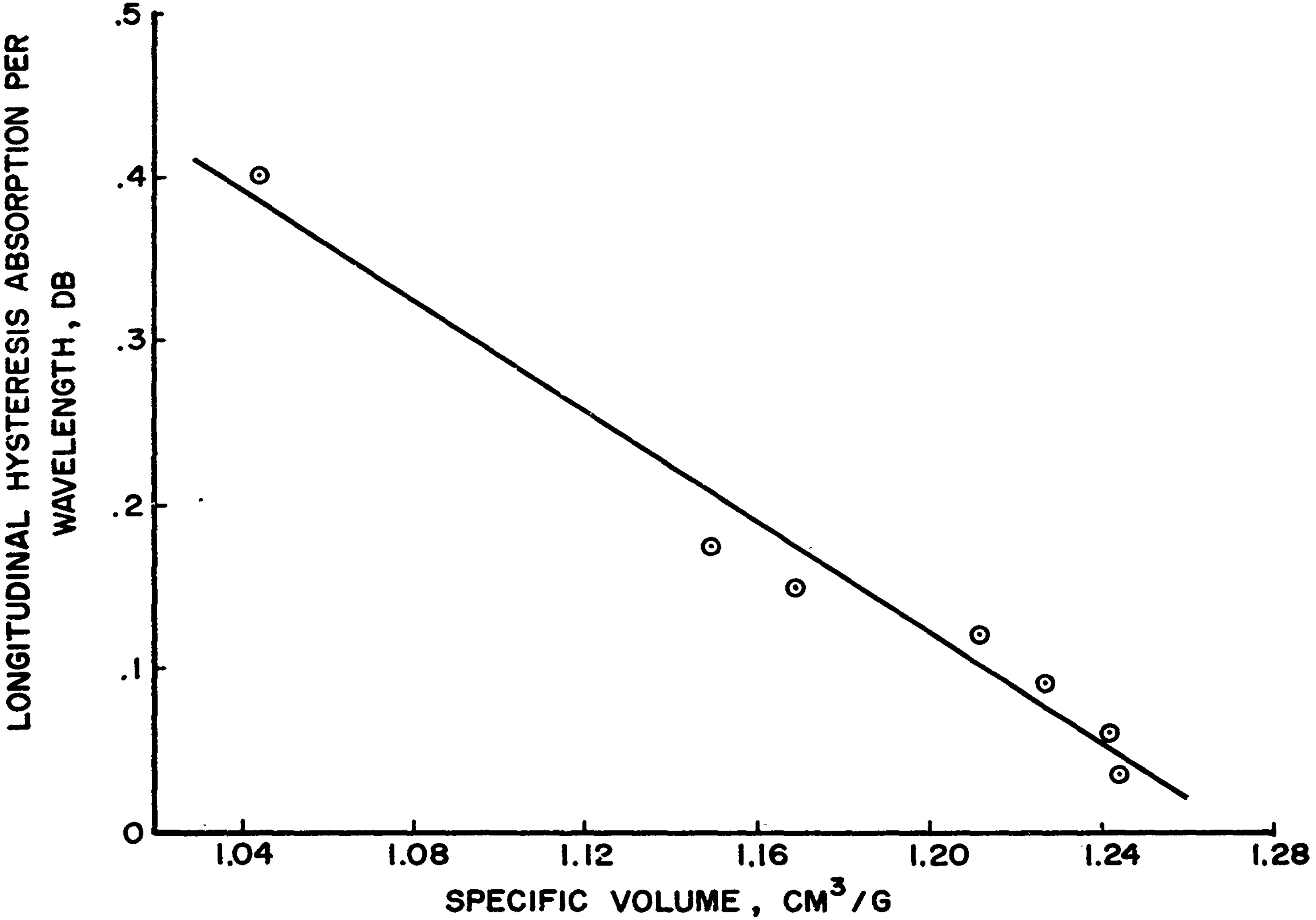

FIG.10 LONGITUDINAL HYSTERESIS ABSORPTION PER WAVELENGTH VS SPECIFIC VOLUME FOR POLYETHYLENE