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**DETERMINATION OF PHYSICAL PARAMETERS FOR
POLYMERIC MATERIALS USING ULTRASONICS
TECHNIQUES**

**LONGITUDINAL AND SHEAR MEASUREMENTS ON
COMMERCIALY AVAILABLE PLASTICS**

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| 20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The background theory used in understanding longitudinal and shear velocities in isotropic and anisotropic materials is summarized. How these velocities are related to mechanical property evaluation is presented. Finally, the derived expressions are applied. Use of a described ultrasonics apparatus enabled the investigators to measure longitudinal and shear velocities in a variety of commercially available semicrystalline polymers. Measured results agree well with other published values. The use of this ultrasonic technique for polymer characterization is discussed. | | |

FOREWORD

This report was prepared by the University of Dayton Research Institute, Dayton, Ohio under Contract AF33615-75-C-5095, Project No. 7340, "Nonmetallic and Composite Materials", Task No. 734004, "New Organic and Inorganic Polymers", with Dr. I. Goldfarb (AFML/MBP) as project engineer.

This report describes research conducted from 1 September 1975 to 1 February 1976.

The research described in this report was performed at the Polymer Branch Laboratory, Nonmetallic Materials Division, Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio by Dr. D. R. Wiff and Mr. David E. Wright of the University of Dayton Research Institute. The manuscript was released by the authors in February 1976 for publication as a technical report.

The authors thank Dr. Bruce Hartman, Naval Ordnance Laboratory, for discussions regarding capabilities of commercially available equipment in initial equipment purchasing stages circa 1970. In addition, he supplied us with reprints of his laboratory's ultrasonics technical reports over the past six years, which gave us insight as to the necessary techniques to develop.

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SECTION I

INTRODUCTION

During the past 25 years, considerable research has been performed on determining elastic constants of plastics. Specifically, static mechanical constants were measured: (1) in order to provide a standard basis of comparison; (2) to compare changes occurring when studying the effects of plasticizers; and (3) to study the effects of variations in production and forming techniques upon the ultimate mechanical properties.

The characteristic general features of the dynamic mechanical behavior of high molecular weight amorphous polymers are well known and qualitatively understood. In particular, frequency/temperature measurements in the rubbery region can be correlated by the Williams, Landel and Ferry (Reference 1) expression and the molecular theories of Kirkwood (Reference 2), Rouse (Reference 3) and Bueche (Reference 4) meet with some success. The nature of the glass transition in polymers is still a subject of discussion and all treatments of dynamic behavior become empirical as the glassy state is approached.

Partially crystalline polymers present a much more complex picture. Even their simplest dynamic properties (Reference 5) cannot be treated theoretically with success. The present work describes an attempt to establish experimental capability to measure dynamic mechanical properties of the crystalline portion of polymers with the expectation of possible collaboration with data from other techniques, e.g. rheovibron, etc., which readily measure the amorphous phase contribution to a material's elastic mechanical properties (References 6-11).

SECTION II
BACKGROUND

In the theory of elasticity (References 12-14), it is assumed that elemental volumes of a macroscopic material are small but still not small enough that the atomic nature of a material must be considered. That is, each infinitesimal element still retains the continuous physical characteristics of the bulk material.

If one considers small but finite elemental volumes within a deformed material, their temperatures are not in general the same and their dimensions vary in both time and space. This considerably complicates the exact equations of motion for a specified small volume when arbitrary motions are allowed.

Usually, however, matters are simplified in that the transfer of heat from one such small volume within a body to another (by simple thermal conduction) occurs very slowly. If the heat exchange between these elemental volumes are negligible (over a time interval similar to the period of oscillatory motions in the volumes), the process is said to be adiabatic.

Consider an isotropic elastic medium containing a plane elastic wave in which the deformation \underline{u} is a function of only one coordinate, say x . Then

$$\frac{\partial^2 u_x}{\partial x^2} - \frac{1}{v_l^2} \frac{\partial^2 u_x}{\partial t^2} = 0 \quad (1)$$

and

$$\frac{\partial^2 u_y}{\partial x^2} - \frac{1}{v_s^2} \frac{\partial^2 u_y}{\partial t^2} = 0 ; \quad \frac{\partial^2 u_z}{\partial x^2} - \frac{1}{v_s^2} \frac{\partial^2 u_z}{\partial t^2} = 0 \quad (2)$$

where

$$v_l = \sqrt{\frac{E(1-\sigma)}{\rho(1+\sigma)(1-2\sigma)}} \quad (3)$$

and

$$v_s = \sqrt{E/2\rho(1+\sigma)} \quad (4)$$

Here E is the Young's modulus, ρ is the density and σ is Poisson's ratio, i. e., the ratio of the transverse compression to longitudinal extension. Thus, an elastic wave is composed of two waves propagated independently. In one (u_x) the displacement is in the direction of propagation, i. e., the longitudinal wave, and is propagated with velocity v_ℓ . In the other waves (u_y and u_z), the displacement is in a plane perpendicular to the direction of propagation, i. e., the transverse direction, and is propagated with velocity v_s .

We know that the volume change in a deformation is given by the sum of the diagonal terms in the strain tensor, i. e., by $u_{ii} \equiv \nabla \cdot \underline{u}$. In the transverse wave there is no component u_x , and since the other components do not depend on y or z , $\nabla \cdot \underline{u} = 0$ for such a wave. Thus, transverse waves do not involve any change in volume. For longitudinal waves, however, $\nabla \cdot \underline{u} \neq 0$, and these waves involve compressions and expansions in the body.

The separation of the wave into two parts propagated independently with different velocities can also be affected in the general case of an arbitrary (not plane) elastic wave in an infinite medium. However, in the specific study under discussion, the material being examined was immersed in silicone oil between two transducers, one a transmitter and the other a receiver. The silicone oil, acting as a coupling medium, served only to support compressional (or longitudinal) waves. Thus, the approximation of plane longitudinal waves in an isotropic medium agrees with the present experimental situation.

Consider the reflection and refraction of a plane, monochromatic, longitudinal wave at a boundary interface between two different elastic media, keeping in mind that the reflected and refracted waves will in general be a mixture of both transverse and longitudinal wave motions. In the situation at hand, the reflected wave will only consist of a longitudinal component

because it is propagated back through the silicone oil. The refracted wave, being in the plastic specimen under investigation, will be a mixture of both transverse (shear) and longitudinal (compressional) waves.

Referring to Figure 1, we see that the usual boundary value conditions applied to equations of plane wave motions at an interface will result in Snell's Law. Therefore,

$$\frac{\sin \theta_{l,1}}{\sin \theta_{l,2}} = \frac{v_{l,1}}{v_{l,2}} \quad (5)$$

If we consider the plane, compressional, wave fronts incident on a flat surface (see Figure 2), such that $\theta_{l,1} = (\theta_{l,1})_{\text{critical}}$ and $\theta_{l,2} = 90^\circ$, then only a shear (transverse) wave will be propagated in medium 2. In addition, because of the geometry of the transmitter-specimen-receiver experimental configuration used in this investigation, selective transverse displacements were achieved. This is shown in Figure 3 with compression waves incident on the solid specimen. For the present investigation of commercially available plastics, this fact is not significant because of the isotropic behavior of these specimens. More recent studies on unidirectional graphite composites made this feature of the experimental apparatus valuable. Similar studies on other anisotropic specimens (e.g., oriented bulk polymer specimens) are planned.

Once the longitudinal velocity (v_l), the shear velocity (v_s) and the mass density (ρ) have been measured, the elastic constants of the material can be determined by Equation 3, rewritten as:

$$v_l = \sqrt{(B+4G/3)/\rho} \quad (6)$$

and equation 4, rewritten as

$$v_s = \sqrt{G/\rho} \quad (7)$$

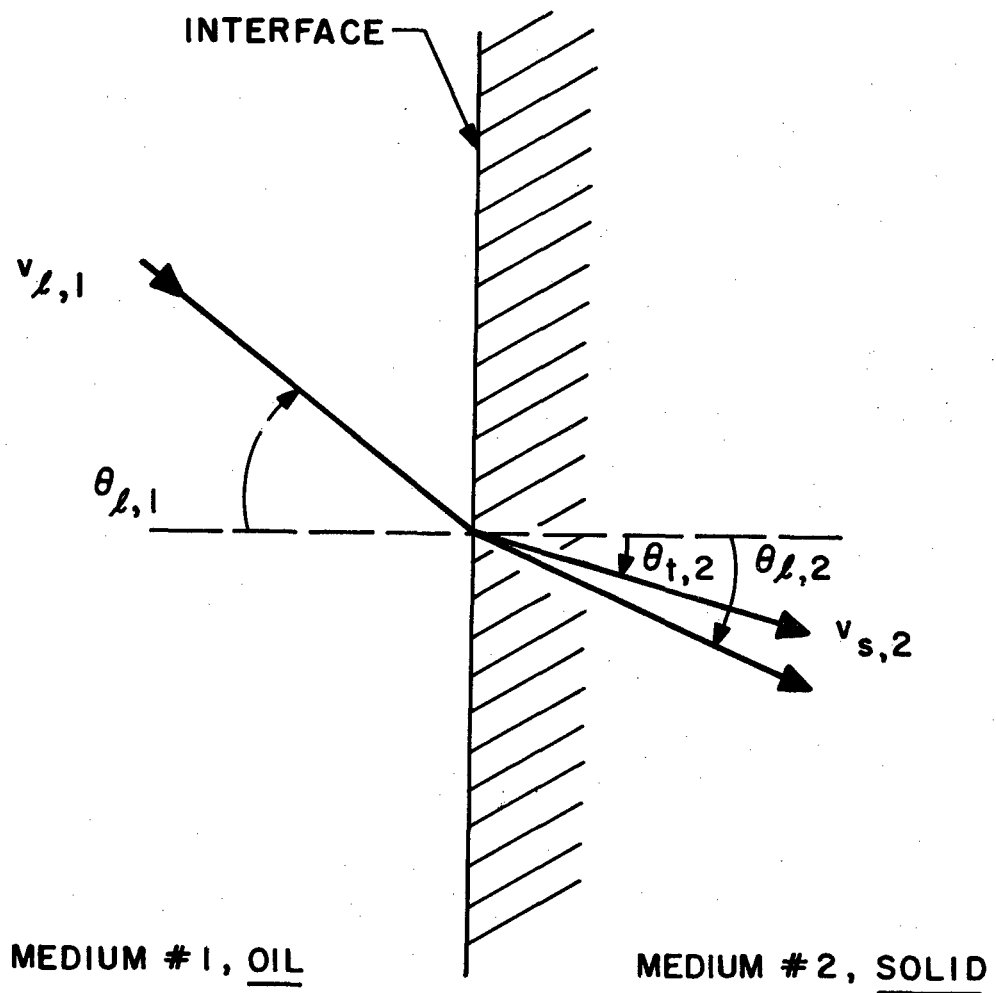


Figure 1. A Plane Wavefront Incident Upon an Infinite Plane Boundary. The refracted wave is a mixture of shear and compressional waves.

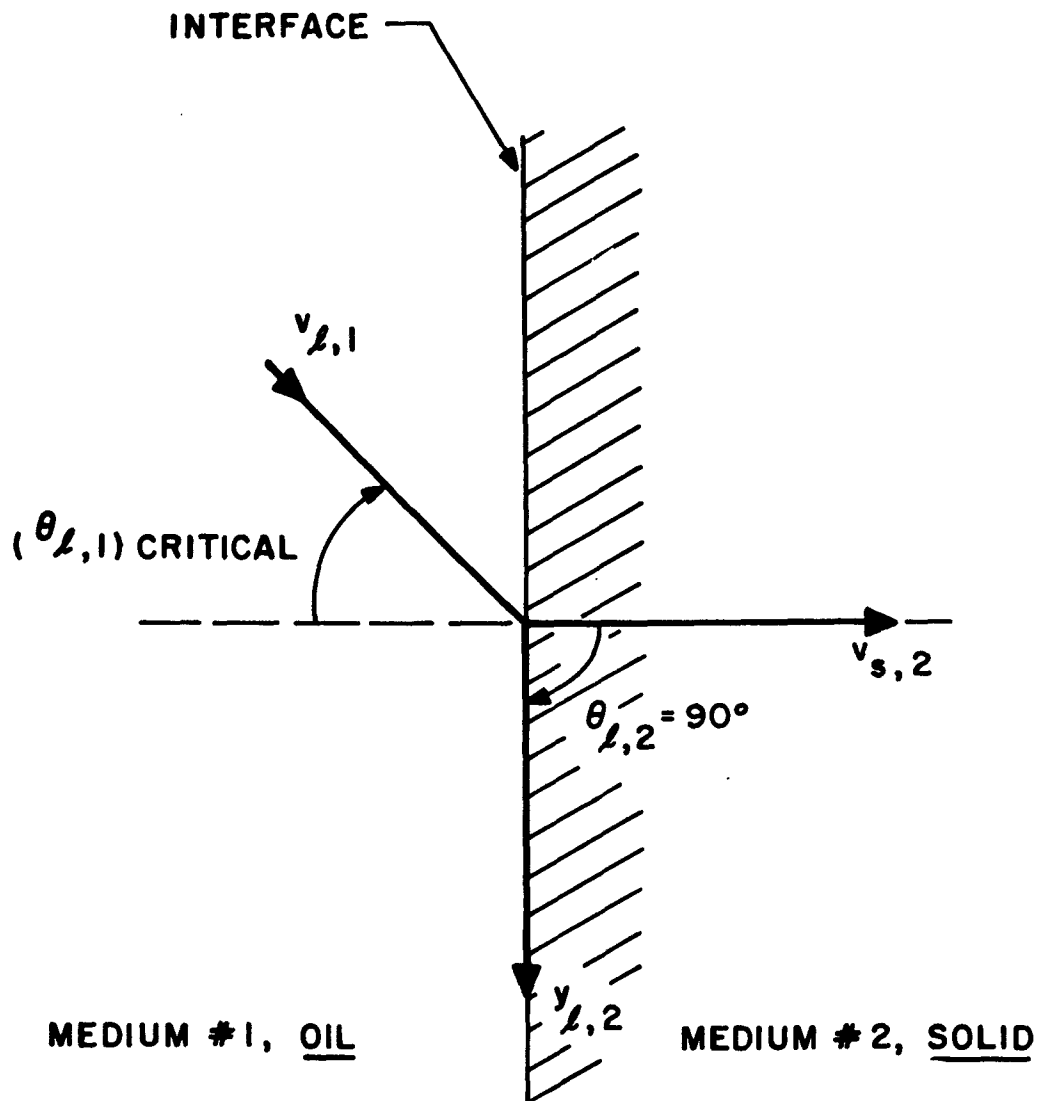


Figure 2. A Plane Compressional Wavefront Incident Upon a Flat Surface at the Critical Angle.

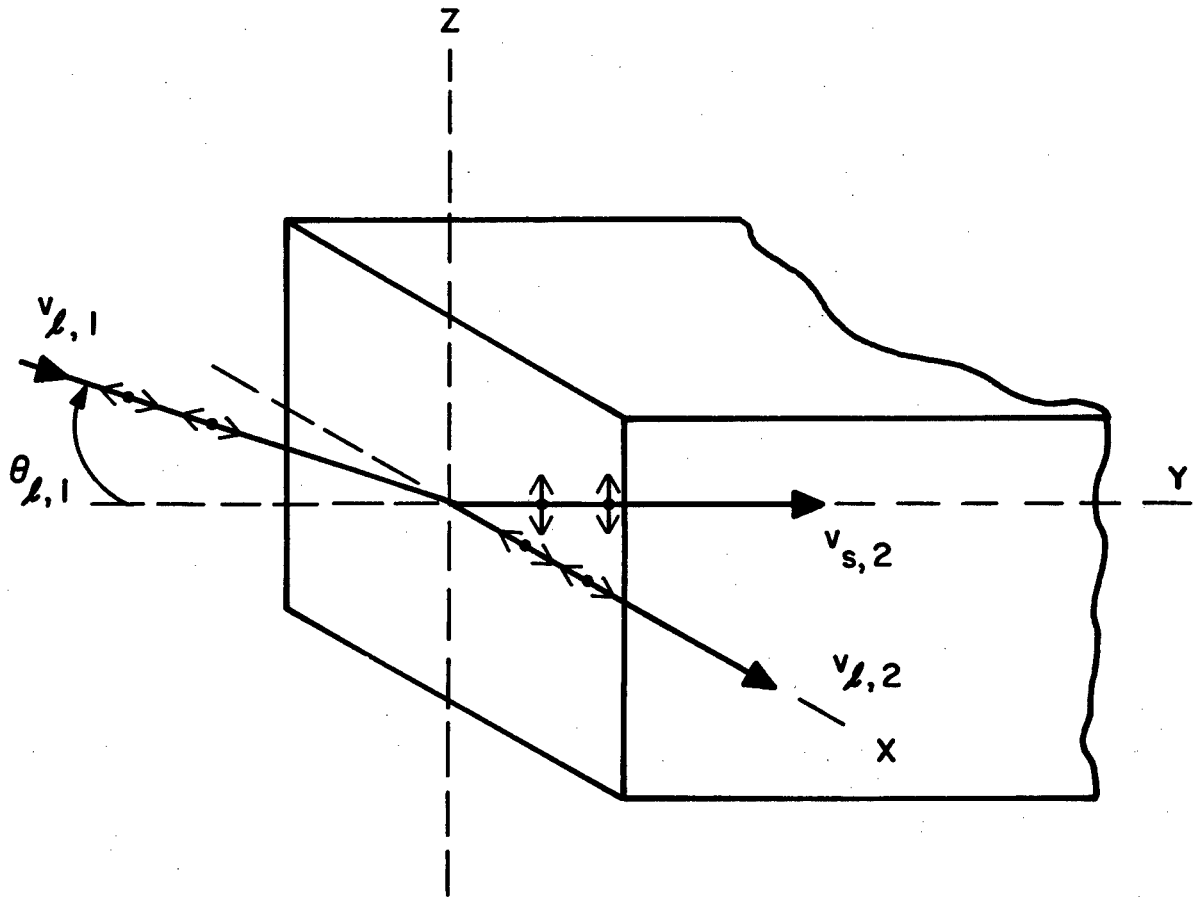


Figure 3. Illustration of the Directions of Particle Motion in the Incident, Refracted and Surface Waves.

where B = bulk modulus and G = shear modulus. The shear modulus can be calculated, knowing v_s and ρ . The bulk modulus can also be calculated from equation 6 knowing v_l , G and ρ .

For an isotropic solid, such as the polymers studied here, there are only two independent elastic constants (B and G) (Reference 12). It is sometimes convenient to use Young's modulus E and Poisson's ratio σ (see equations 3 and 4). In addition to these elastic constants, Lamé coefficients are sometimes used where

$$\mu = G \quad (8)$$

and

$$\lambda = B - \frac{2}{3}G \quad (9)$$

For anisotropic materials, the elastic properties may be presented by a constitutive relation, the most general linear relation being between six components of stress and the six components of strain,

$$\sigma_{ij} = C_{ijkl} \epsilon_{kl} \quad (10)$$

where C_{ijkl} is a fourth-order tensor. The quantities C_{ijkl} are known as elastic stiffness coefficients (Reference 12). An alternative way of expressing the generalized Hooke's Law (equation 10) is to write the stress and strains as six dimensional vectors related by a 6×6 matrix of stiffness (the stiffness matrix)

$$\sigma_i = \sum_{j=1}^6 C_{kj} \epsilon_j \quad (11)$$

The stress $\underline{\sigma}$ and strain $\underline{\epsilon}$ are treated simply as vectors and the stiffness coefficients can be determined for anisotropic materials. Further, if one has an isotropic solid, then

$$\begin{aligned} C_{ii} &= B + 4G/3 & \text{for } i = 1, 2, 3 \\ C_{ii} &= G & \text{for } i = 4, 5, 6 \end{aligned}$$

and

$$\begin{aligned} C_{ij} &= B - 2G/3 && \text{for } i, j = 1, 2, 3 \\ i &\neq j && \\ C_{ij} &= 0 && \text{for } i, j = 4, 5, 6 \\ i &\neq j && \end{aligned} \tag{12}$$

Thus, the usual engineering parameters can be related directly to the elastic stiffness parameters.

SECTION III

DESCRIPTION OF APPARATUS

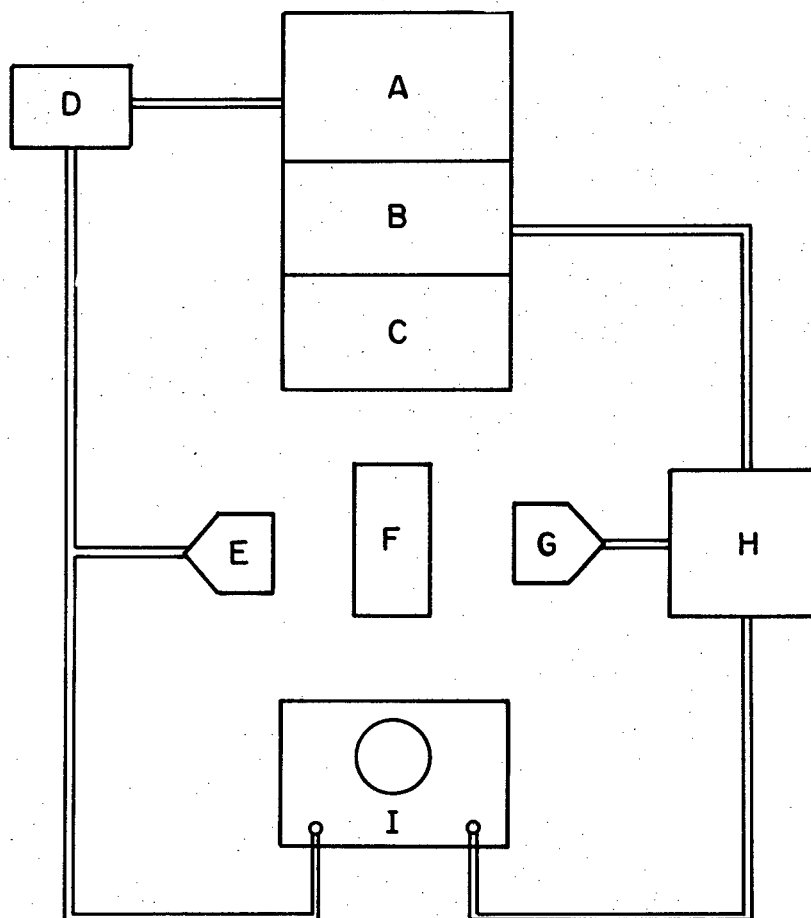
Figure 4 is a flow chart of the scheme used to interconnect the various electronic components. The following is a brief description of the major individual items in this apparatus.

TRANSDUCERS (see Figure 4)

Ceramic transducers produced by Panametrics Inc. were used for all the measurements. These were the Videoscan Immersion Transducers, model V308SU, diameter 0.5 inch, with their peak output frequency 5MHz, and having UHF connectors. Their useful frequency bandwidth was from 3 to 7 MHz. Identical transducers were used for transmitting and receiving. Each transducer was connected to a right-angle immersible type connector which, in turn, was connected to a 12-inch long immersion rod (see Figure 4), thus allowing the transducers to be submerged in silicone oil. These transducers with immersion connectors were securely fixed in a specially designed specimen mount.

TRANSDUCER SPECIMEN MOUNT (see Figures 5 and 6)

A specially designed transducer and specimen holder made of black anodized aluminum was fabricated. It permitted independent sidewise translational movements of either transducer. This translation was controlled by a screw-thread drive permitting 0.05 inch translation per full rotation of the threaded rod. Each transducer was rigidly secured to a movable piece which, in turn, was dove-tailed into a machined channel. In addition to the sidewise translation, one of the transducer mounts had a translational motion along the axial line connecting the two cylindrical transducers and perpendicular to the above sidewise motion. This translational motion permitted very precise changes in transducer separation, i. e. 0.001 inch increments. A rotatable holder for cylindrical specimens of thickness 0.125 to 2 inches and diameter



- A = ULTRASONIC OSCILLATOR
- B = WIDE BAND AMPLIFIER
- C = POWER SUPPLY
- D = ATTENUATOR
- E = TRANSMITTING TRANSDUCER
- F = SAMPLE SPECIMEN
- G = RECEIVING TRANSDUCER
- H = PREAMPLIFIER
- I = CATHODE RAY OSCILLOSCOPE

Figure 4. Schematic of Ultrasonics Apparatus.

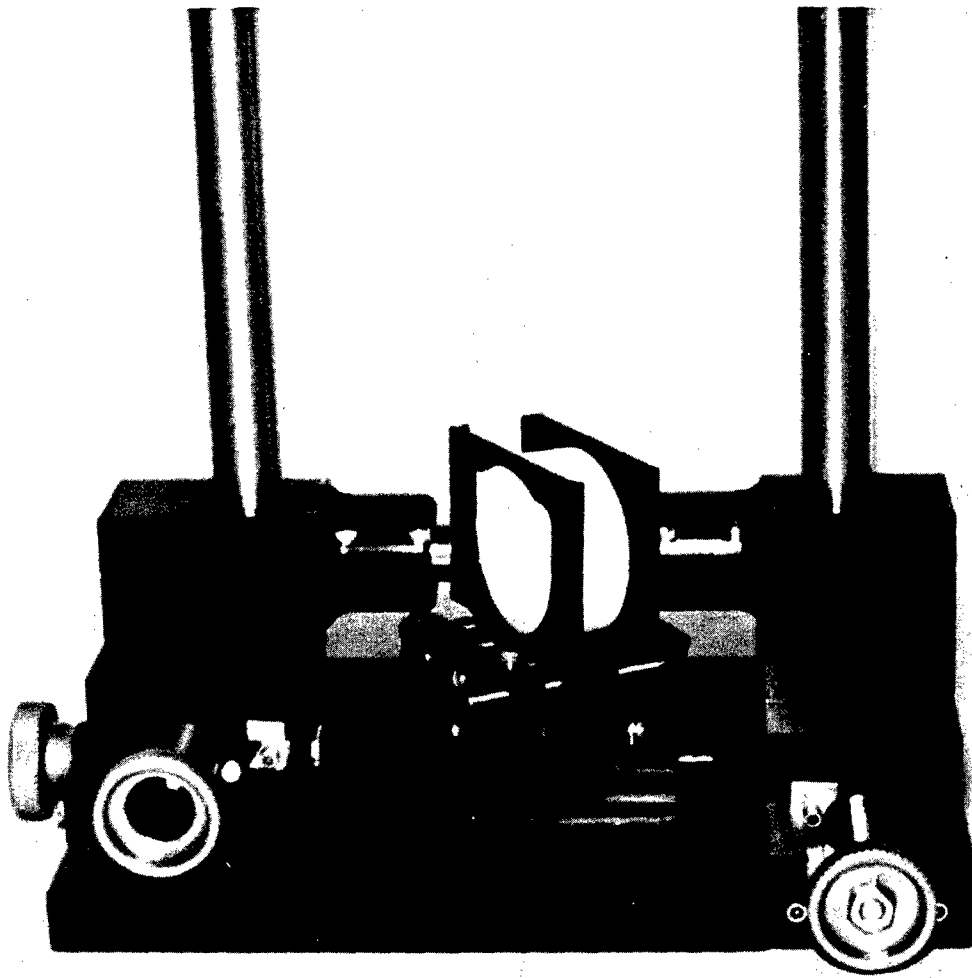


Figure 5. Transducer Specimen Mount Assembled.

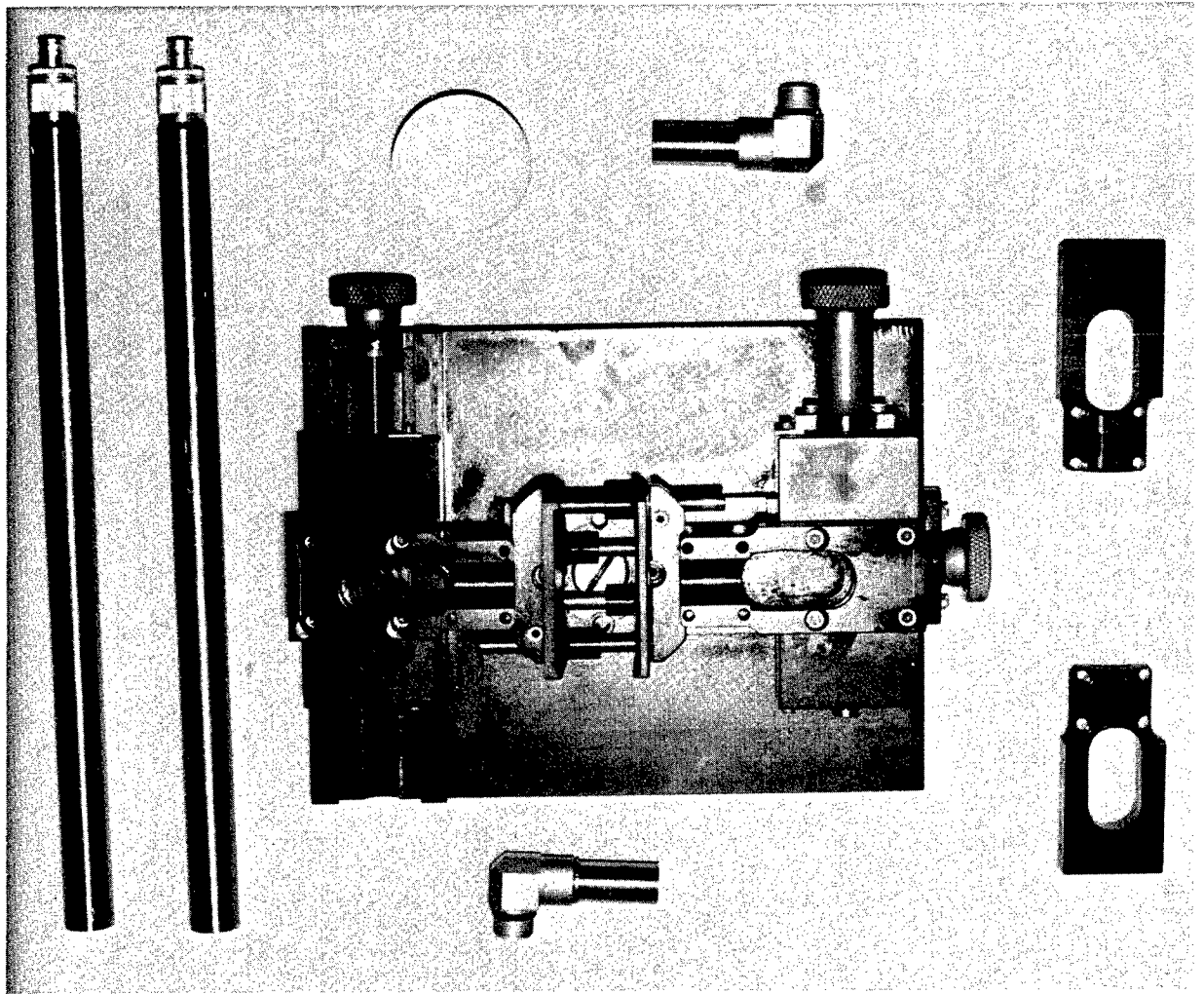


Figure 6. Transducer Specimen Mount Disassembled.

of about 1.5 inches was located at the center of the mount. With a specially designed adapter, this specimen holder was capable of supporting polymer films 0.001 inch thick. The specimen holder could also be rotated either clockwise or counter-clockwise in one degree increments from 0° to 40°, where a zero degree reading indicates that a normal to plane of specimen is parallel with the axis of the aligned transducers.

IMMERSION BATH (see Figure 7)

The assembled apparatus with transducers, connectors, and specimen was placed in a fiberglass insulated, aluminum box measuring one foot on each edge. This box was lined with a 1/8 inch thick polyethylene insert, which was used to eliminate any possible echo reflections. Dow Corning 200 silicone oil (viscosity 100 CS at ambient temperatures) was placed in the box to a depth of about 9 inches. A Blue M, Model Th-2006 laboratory immersion heater was inserted into the bath to regulate the temperature of the oil for temperatures above ambient. A mechanical stirrer with three propeller blades mounted on a shaft was used to circulate the oil. Ice water was circulated through a loop of copper tubing set along the inside perimeter of the box to cool the oil and specimens below ambient.

DETECTION LOOP

The shielded cable attached to the receiving transducer was connected to a narrow band, tunable Arulab preamplifier, Model PA-620. Its output connector was then connected directly to the Tektronix Model 556 oscilloscope via one of the oscilloscope preamplifiers, Tektronix Model 1A1 or 1A2.

TRANSMITTER LOOP

The complete pulser package was composed of three Arulab components. These were a Model PG-650C oscillator, a Model WA-600-E wideband amplifier, and a Model PS-666 high voltage power supply. The wideband amplifier (1-60 Hz) was also used as a power source for the preamplifier of

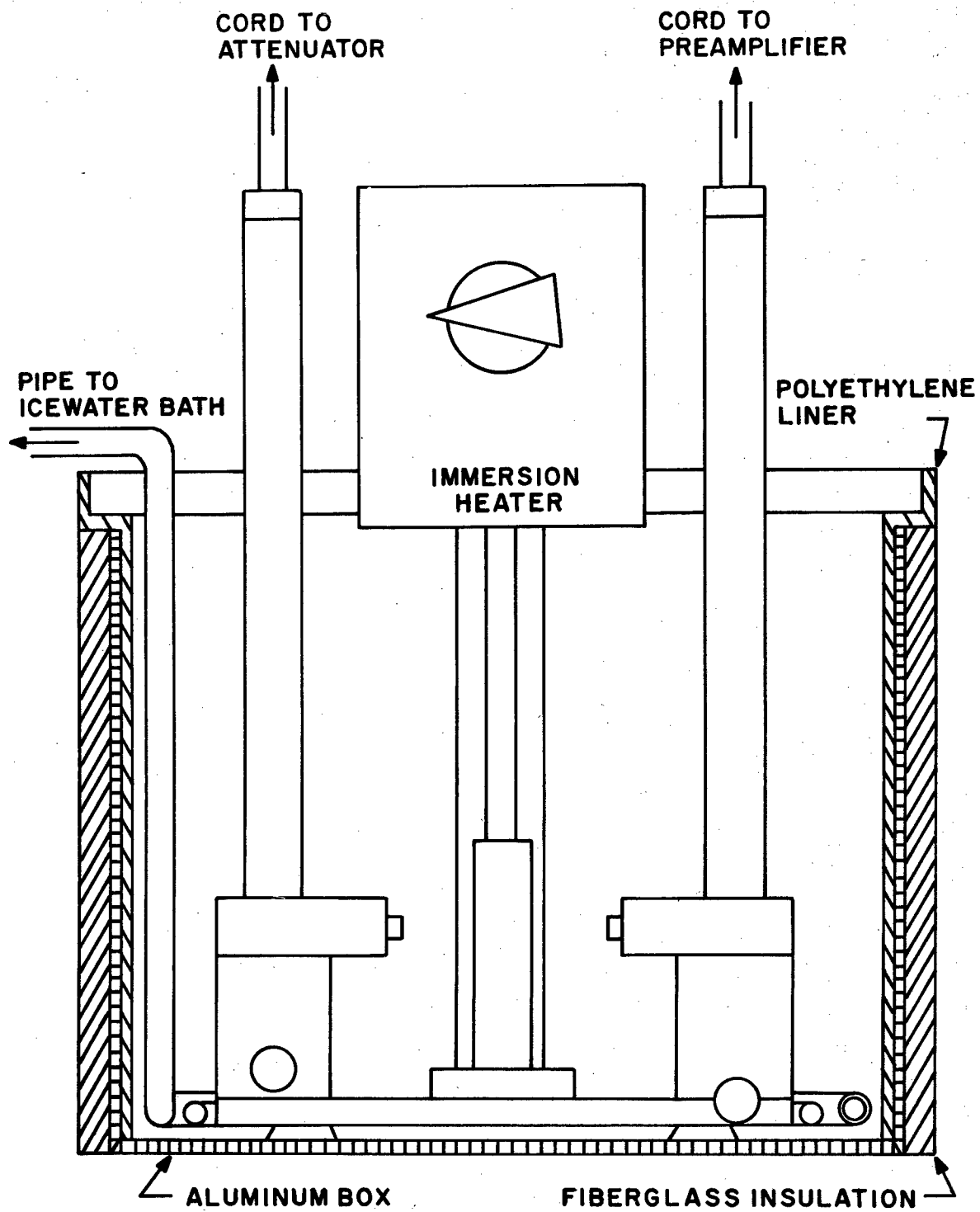


Figure 7. Immersion Tank Showing Location of Transducer Mount and Heating Coil.

the Detection Loop. A tuning coil with a range of 3.923 to 7.132 MHz was used to provide oscillations at 4.4 MHz. The oscillator is capable of continuous wave or pulsed wave mode operation. The the output of the oscillator was connected a 93 ohm, 20 watt Arulab attenuator. The transmitting transducer was then connected to this attenuator.

SECTION IV

MEASUREMENT TECHNIQUE

For accurate, dependable measurements of the sound speeds in oil, it was necessary to out-gas the oil because air-saturated silicone oil exhibited a marked decrease in the speed of sound. This degassing was achieved by removing the transducers (which could be damaged by temperatures exceeding 50°C) and heating the oil to 75°C while constantly stirring. After several hours at 75°C, the oil was allowed to cool to room temperature. Before submersion of the completely assembled transducer mount, the transducer front surfaces were placed 0.750 ± 0.001 inches apart by adjusting the screw rods on the mounting apparatus. The transducer central axes were precisely positioned coaxially by the transverse screw adjustment existing on the one transducer holder. The complete assembly was then lowered into the oil bath where the ultrasonic measurements were performed (see Figure 7). With the trailing edge of the transmitted and received pulses displayed on the oscilloscope, the time of travel of one ultrasonic pulse was measured using the oscilloscope delayed sweep capability. Knowing the separation between transducers and the time of travel, the speed of sound in the oil ($v_{l,1}$) was calculated.

The heater was then turned on, warming the oil to a higher temperature. After the temperature of the oil stabilized, the above procedure was repeated, i. e. the new time of travel was measured. Speeds at several temperature settings were determined (see Figure 8 and Table 1).

At each temperature, a specimen having parallel surfaces and thickness "d" was placed between the transducers. Care was taken so that the normal to the specimen surfaces was parallel to the axis of symmetry of the transducers (see Figure 9).

The time of travel t' was then measured by the above technique, i. e. comparing the trailing edges of the transmitted and received pulses. If the

SPEED OF SOUND IN SILICONE OIL

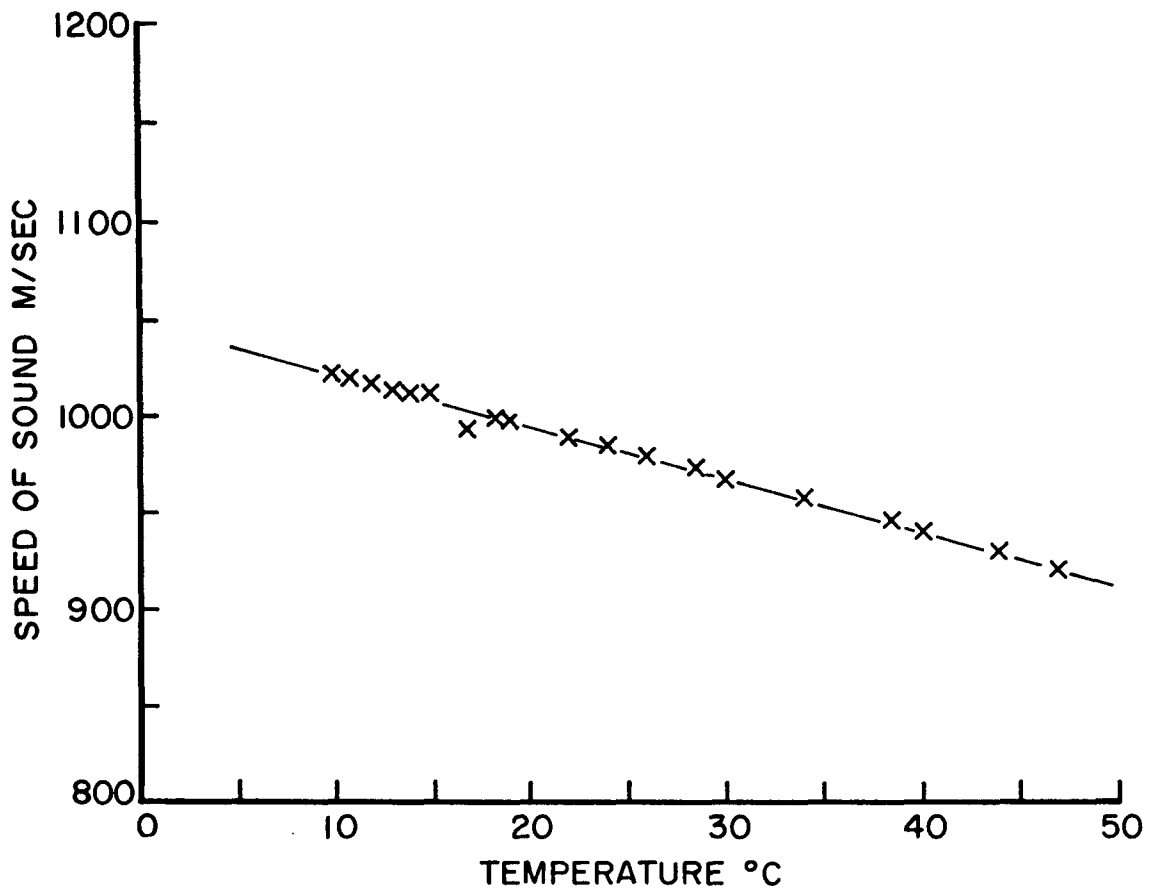


Figure 8. Speed of Sound in Silicone Oil as Function of the Temperature.

TABLE I
LONGITUDINAL SPEEDS* VS. TEMPERATURE

| <u>Temp. °C</u> | <u>Silicone Oil</u> | <u>Polymethyl Methacrylate</u> | <u>Polyhexamethylene Adipamide</u> |
|-----------------|---------------------|------------------------------------|--|
| 10 | 1021 | — | — |
| 11 | 1019 | — | 2236 |
| 12 | 1016 | — | — |
| 13 | 1013 | — | — |
| 14 | 1011 | — | — |
| 15 | 1011 | — | — |
| 17 | 992 | 2582 | — |
| 18 | 997 | — | — |
| 19 | 995 | — | — |
| 20 | — | 2561 | — |
| 22 | 987 | — | — |
| 24 | 982 | 2561 | — |
| 26 | 977 | — | — |
| 28 | 969 | 2561 | 2252 |
| 30 | 965 | — | — |
| 32 | — | 2541 | 2261 |
| 34 | 955 | — | — |
| 36 | — | 2521 | 2245 |
| 38 | 943 | — | — |
| 40 | 938 | — | 2220 |
| 41 | — | 2521 | — |
| 44 | 927 | — | — |
| 45 | — | 2501 | — |
| 46 | — | — | 2181 |
| 47 | 918 | 2502 | — |

* Speeds were measured in meters per second.

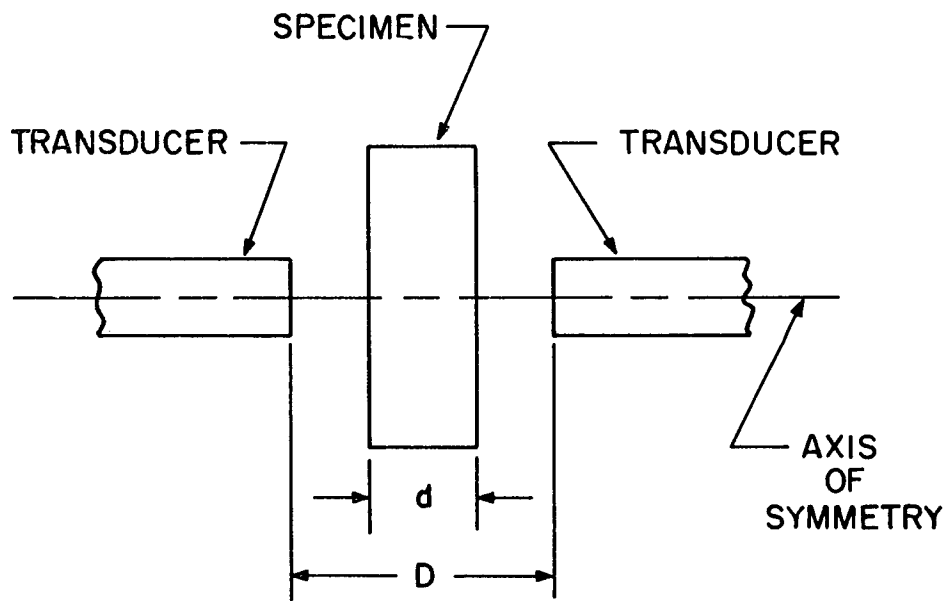


Figure 9. Alignment of Transducers.

time of travel without the specimen in place (i. e. only oil) is ($t_1 = d/v_{l,1}$), then

$$\Delta t = t_1 - t' = d \left(\frac{1}{v_{l,1}} - \frac{1}{v_{l,2}} \right) \quad (13)$$

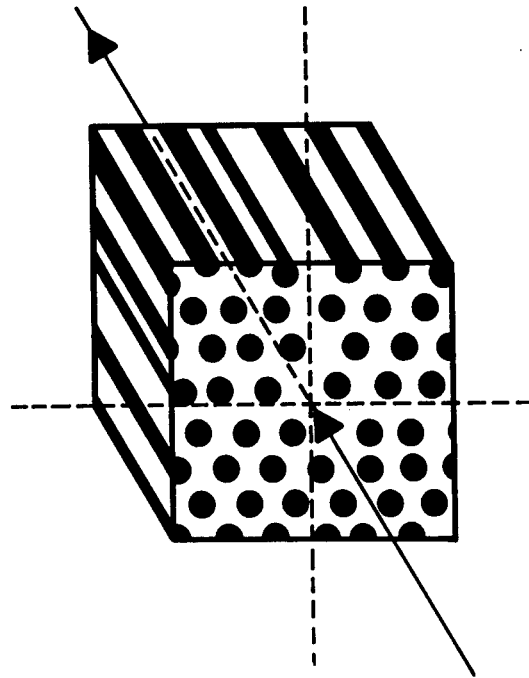
where $d/v_{l,2}$ is the time for the longitudinal wave to traverse the specimen and ($d/v_{l,1}$) is the time required to traverse the oil displaced by the specimen. It is desirable to find t_2 which can then be used to calculate the longitudinal speed in the specimen ($v_{l,2}$) by

$$v_{l,2} = \frac{d}{t_2} \quad (14)$$

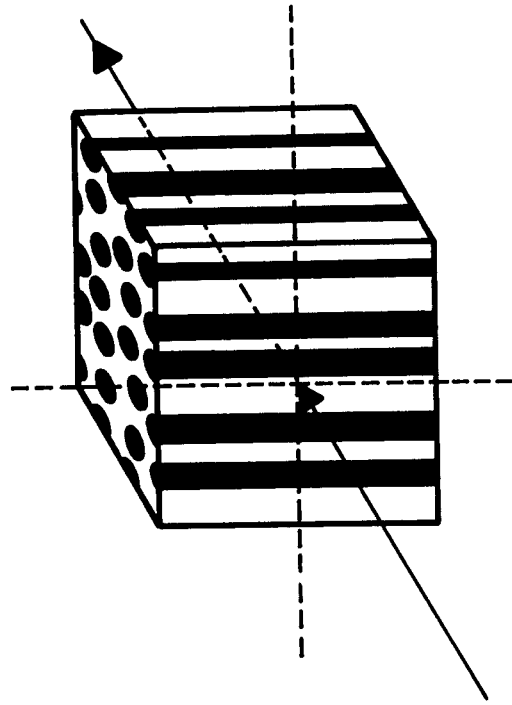
For isotropic specimens, this would be the only longitudinal speed measurement required. If the specimen is anisotropic, it would have to be reoriented such that the direction of interest in the specimen coalesces with the transducer axis of symmetry (see Figure 10).

Having measured the longitudinal speed ($v_{l,2}$) at the desired temperature, the corresponding critical angle can be calculated (see equation 5 and Figure 2). Once the critical angle is determined, the specimen can be rotated by this amount and locked securely into place. This now allows only the shear wave with speed $v_{s,2}$ to be transmitted through the isotropic specimen (Reference 15). When the composite time t' is then measured, it is sum of the times for the longitudinal wave to travel through the oil and for the shear wave to transverse the specimen. The longitudinal wave in the material is reflected back into the silicone oil by definition of the critical angle ($\theta_{l,1}$)^{critical}. One might "a priori" assume that the shear wave is traversing the shortest path in the specimen (thickness) but this condition is not mandatory (Reference 16).

At the boundary (oil and specimen) Snell's Law can still be applied using the longitudinal speed in the oil and shear speed in the specimen (see Figure 11). The time lapse between the pulse leaving the transmitting transducer and arriving at the receiving transducer is measured as t' . Therefore,



ULTRASOUND TRAVELING PARALLEL
TO THE DIRECTION OF HIGHEST
MOLECULAR ORIENTATION



ULTRASOUND TRAVELING PERPENDICULAR
TO THE DIRECTION OF HIGHEST
MOLECULAR ORIENTATION

Figure 10. Measuring the Anisotropy of a Material.

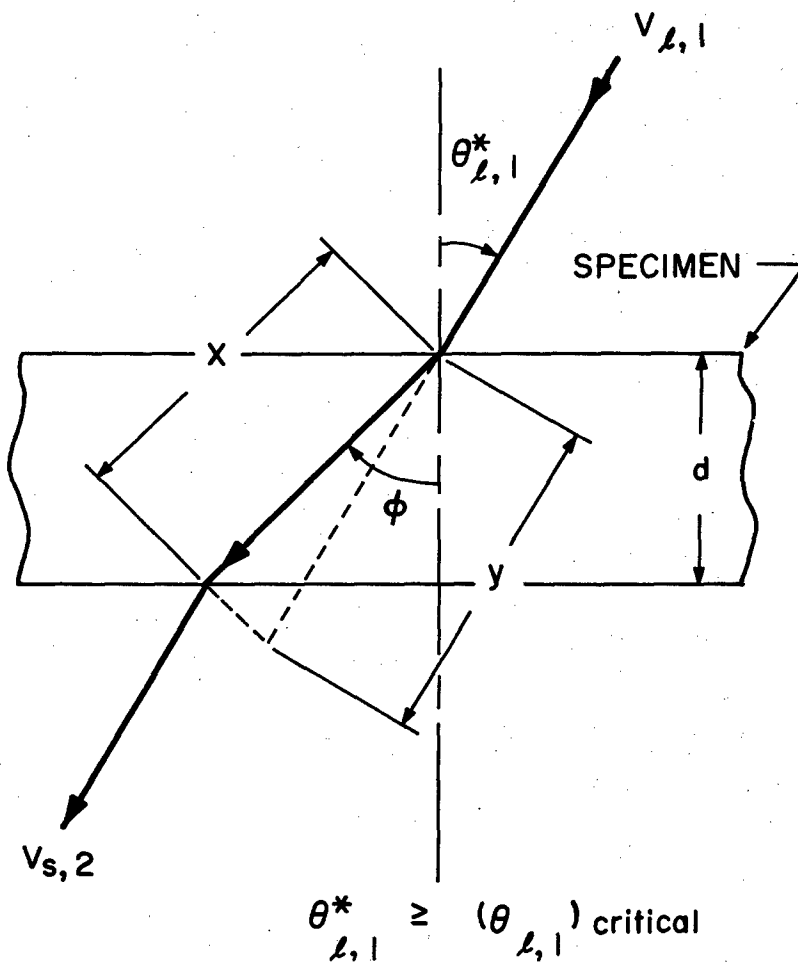


Figure 11. Shear Wave Being Refracted through a Piece of Material with Parallel Sides.

$$\frac{\sin \theta_{l,1}^*}{\sin \phi} = \frac{v_{l,1}}{v_{s,2}} \quad (15)$$

if as in equation 13, t_1 is the time lapse with only oil between the transducers, then the time difference is

$$\Delta t = t_1 - t' = \frac{y}{v_{l,1}} - \frac{x}{v_{s,2}} \quad (16)$$

where from Figure 11 we see that the time $(y/v_{l,1})$ is the time as if oil filled the volume of the specimen and the time $(x/v_{s,2})$ is the actual time required to traverse the specimen. Equation 16 can be rewritten as:

$$\frac{(\Delta t) v_{l,1}}{x} = \frac{y}{x} - \frac{v_{l,1}}{v_{s,2}} \quad (17)$$

Referring to Figure 11,

$$\cos \phi = \frac{d_2}{x} = \sqrt{1 - \frac{v_{s,2}^2}{v_{l,1}^2} \sin^2 \theta_{l,1}^*} \quad (18)$$

$$\cos [\theta_{l,1}^* - \phi] = \frac{y}{x} = \frac{(\Delta t) v_{l,1}}{x} + \frac{v_{l,1}}{v_{s,2}} \quad (19)$$

Using a standard trigonometric identity and equations 15 and 18, equation 19 becomes:

$$\cos \phi \cos \theta_{l,1}^* + \frac{v_{s,2}}{v_{l,1}} \sin^2 \theta_{l,1}^* = \frac{(\Delta t) v_{l,1}}{d_2} \cos \phi + \frac{v_{l,1}}{v_{s,2}} \quad (20)$$

Rearranging terms

$$\left\{ \cos \theta_{l,1}^* - \frac{(\Delta t) v_{l,1}}{d_2} \right\} \cos \phi = \frac{v_{l,1}}{v_{s,2}} - \frac{v_{s,2}}{v_{l,1}} \sin^2 \theta_{l,1}^* \quad (21)$$

Using equation 18 we have

$$\cos \theta_{l,1}^* - \frac{(\Delta t) v_{l,1}}{d_2} = \frac{v_{l,1}}{v_{s,2}} \sqrt{1 - \frac{v_{s,2}^2}{v_{l,1}^2} \sin^2 \theta_{l,1}^*} \quad (22)$$

Squaring and collecting terms

$$\frac{v_{l,1}^2}{v_{s,2}^2} = \left[\cos \theta_{l,1}^* - \frac{(\Delta t) v_{l,1}}{d_2} \right]^2 + \sin^2 \theta_{l,1}^* \quad (23)$$

Finally, taking the square root of each side and solving for the shear velocity, $v_{s,2}$

$$v_{s,2} = v_{l,1} \sqrt{\left[\cos \theta_{l,1}^* - \frac{(\Delta t) v_{l,1}}{d_2} \right]^2 + \sin^2 \theta_{l,1}^*} \quad (24)$$

See Reference 16.

SECTION V
APPLICATION AND COMPARISON

Longitudinal and shear velocity measurements, at 4.4 MHz and ambient temperatures, were made on seven commercially available thermoplastics. Six of these were procured through a DuPont Company distributor, Cadillac Plastics & Chemical Co., Cincinnati, Ohio. These six materials were:

- 1) Polyhexamethylene adipamide (nylon 6-6), a highly crystalline polymer. DuPont's trade name for this material is Zytel 101. Its measured density was 1.139 g/cm^3 .
- 2) Polypropylene (PP), a highly crystalline polymer. Its measured density was 0.903 g/cm^3 .
- 3) Polyoxymethylene (POM), a highly crystalline polymer purchased under the trade name Delrin. Its measured density was 1.426 g/cm^3 .
- 4) Polyethylene (PE), a highly crystalline polymer. Its measured density was 0.921 g/cm^3 .
- 5) Polystyrene (PS), an amorphous polymer. Its measured density was 1.047 g/cm^3 .
- 6) Polytetrafluoroethylene (PTFE), a highly crystalline polymer purchased under the trade name Teflon. Its measured density was 2.183 g/cm^3 .

All of these materials were received in the form of rods having diameters of about two inches. From these rods, discs with smooth parallel surfaces were machined. Five thicknesses (nominally 1, 3/4, 1/2, 1/4 and 1/8 inch) of each type were prepared. The seventh type material was:

- 7) Polymethylmethacrylate (PMMA), generally an amorphous polymer. It was made by Rohm and Haus Co. and purchased

in the form of sheets under the trade name Plexiglas. Its measured density was 1.173 g/cm^3 .

The PMMA samples used were of nominal thicknesses $3/4$, $1/2$, $3/8$, $1/4$ and $1/8$ inch. For all samples studied, the maximum error in density determinations was estimated to be $\pm 0.003 \text{ g/cm}^3$.

Using equations 13 and 14, the longitudinal speeds for each of these materials were determined (see Tables 1, 2, and 3 and Figure 12). The estimated accuracy in determining $v_{l,2}$ was about $\pm 2\%$. The major obstacle of experimentation was the limited input power capability of the transducers. If a particular specimen absorbed most of the signal, the trailing edge of the transmitted pulse vanished. The results obtained for $v_{l,2}$ in the present investigation were compared with other published results in Table 3. In all cases, these measurements were taken at about 5 MHz and at 19°C . For those cases where we had sufficient signal to detect the shear wave, the shear wave velocity $v_{s,2}$ was determined with the aid of equation 24. These and comparative results are presented in Table 3. Using the results presented in Tables 3 and 4, the measured densities, and equations 6 and 7, the bulk modulus, B, and shear modulus, G, were determined. These determined values along with comparisons from the published literature are presented in Table 5. Again, for comparison purposes, Figures 13 and 14 present the measured and other published longitudinal and shear speeds of polymethylmethacrylate and polyoxymethylene as a function of temperature. Even though the various independent measurements (not identical specimens) give somewhat different magnitudes of velocities, they all produce linear plots over the temperature range investigated.

TABLE 2
SPEED OF SOUND AS A FUNCTION OF SAMPLE ROTATION
FOR POLYMETHYLMETHACRYLATE

| <u>Angle °</u> | <u>Speed of Sound M/Sec</u> |
|----------------|-----------------------------|
| 0 | 2528 |
| 2 | 2528 |
| 4 | 2588 |
| 6 | 2588 |
| 8 | 2650 |
| 10 | 2715 |
| 12 | 2856 |
| 14 | 2932 |
| 16 | 3281 |
| 17 | 3381 |
| 18 | 3602 |
| 19 | 3381 |
| 20 | 1351 |
| 22 | 1351 |
| 24 | 1368 |
| 26 | 1402 |
| 28 | 1420 |
| 30 | 1439 |
| 32 | 1458 |
| 34 | 1478 |
| 36 | 1518 |

TABLE 3

SPEEDS OF SOUND FOR VARIOUS MATERIALS AT 19° C

| <u>Material</u> | <u>Experimental Shear Speed*</u> | <u>Published Shear Speed*</u> | <u>Experimental Longitudinal Speed*</u> | <u>Published+ Longitudinal*</u> |
|-----------------------------|----------------------------------|-------------------------------|---|---------------------------------|
| Polymethylmethacrylate | 1351 | 1340 | 2528 | 2690 |
| Polytetrafluoroethylene | — | — | 1453 | 1380 |
| Polystyrene | 1147 | 1150 | 2268 | 2400 |
| Polyhexamethylene Adipamide | 1126 | 1120 | 2516 | 2710 |
| Polyoxymethylene | 1043 | 1000 | 2367 | 2440 |
| Polypropylene | 1303 | 1300 | 2388 | 2650 |

*Speeds were measured in Meters per second.

†Hartman & Jarzynski (Reference 16.)

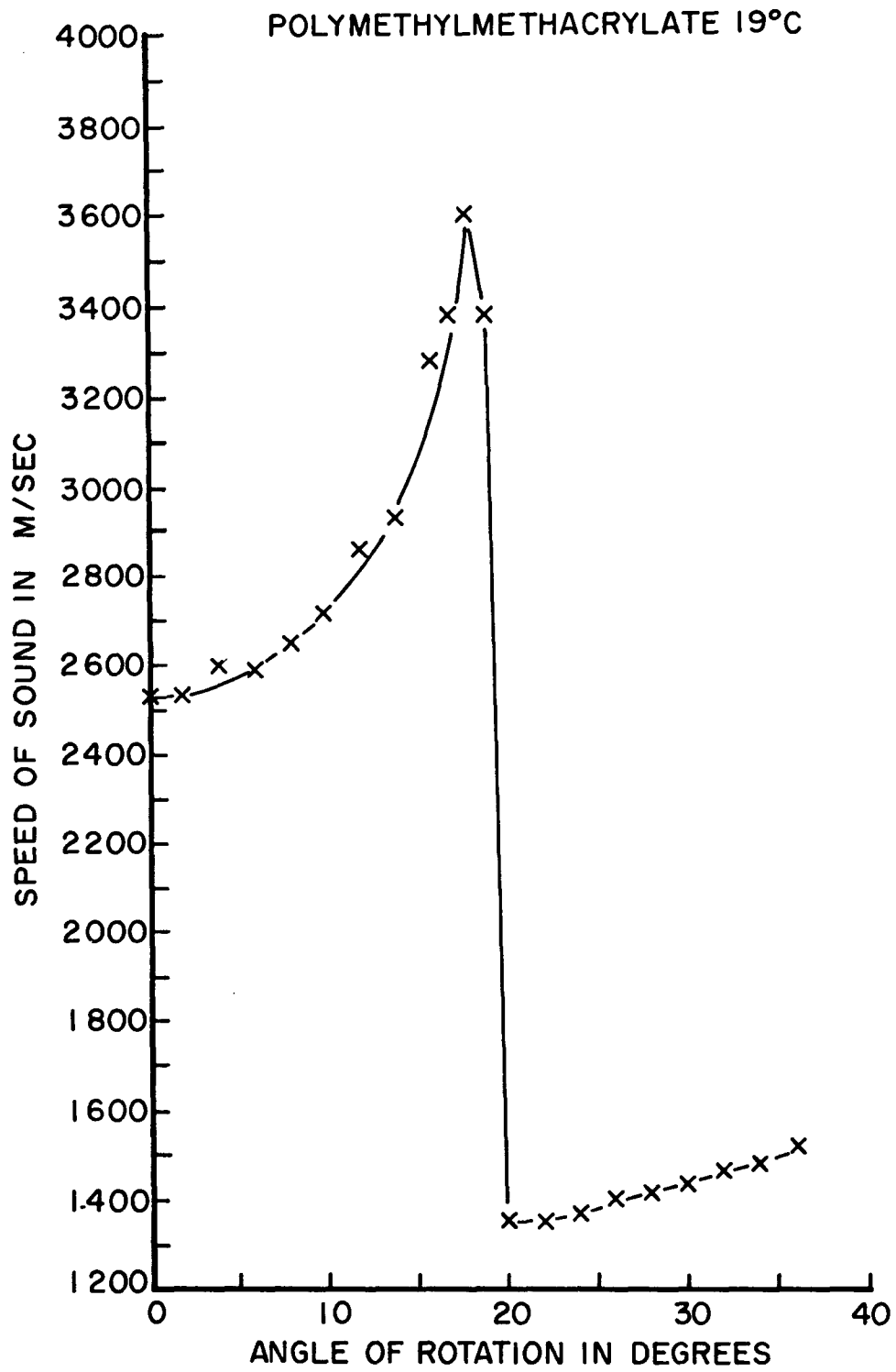


Figure 12. Sound Speeds as Function of Angle of Incidence for PMMA at 19°C.

TABLE 4
SHEAR SPEEDS vs. TEMPERATURE

| <u>Temperature °C</u> | <u>Polymethylmethacrylate*</u> | <u>Polyhexamethylene * Adipamide</u> |
|-----------------------|--------------------------------|--|
| 10 | 1408 | — |
| 11 | 1403 | — |
| 14 | 1387 | 1046 |
| 18 | 1391 | 1067 |
| 22 | 1400 | 1028 |
| 24 | 1389 | — |
| 26 | 1379 | — |
| 27 | — | 1029 |
| 28 | 1390 | — |
| 30 | — | 1020 |
| 32 | 1380 | — |
| 34 | 1362 | 1019 |
| 38 | 1367 | 1041 |
| 40 | 1356 | — |
| 42 | — | 1027 |
| 44 | 1390 | — |
| 46 | — | 1016 |
| 47 | 1340 | — |
| 50 | — | 991 |

*Speeds were measured in meters per second.

TABLE 5
COMPUTED ELASTIC PARAMETERS OF A VARIETY OF SEMICRYSTALLINE POLYMERS

| <u>Material</u> | <u>Density g/cm³</u> | <u>G</u> | <u>B</u> | <u>M</u> | <u>A</u> |
|-----------------------------|---------------------------------|----------|----------|----------|----------|
| Polyethylmethacrylate | 1.173 | 2.14E10 | 4.64E10 | 2.14E10 | 3.21E10 |
| Polytetrafluoroethylene | 2.183 | --- | --- | --- | --- |
| Polystyrene | 1.047 | 1.377E10 | 3.55E10 | 1.38E10 | 2.63E10 |
| Polyhexamethylene Adipamide | 1.139 | 1.44E10 | 5.28E10 | 1.49E10 | 4.32E10 |
| Polyoxymethylene | 1.426 | 1.55E10 | 5.92E10 | 1.55E10 | 4.89E10 |
| Polypropylene | 0.903 | 1.53E10 | 3.11E10 | 1.53E10 | 2.09E10 |

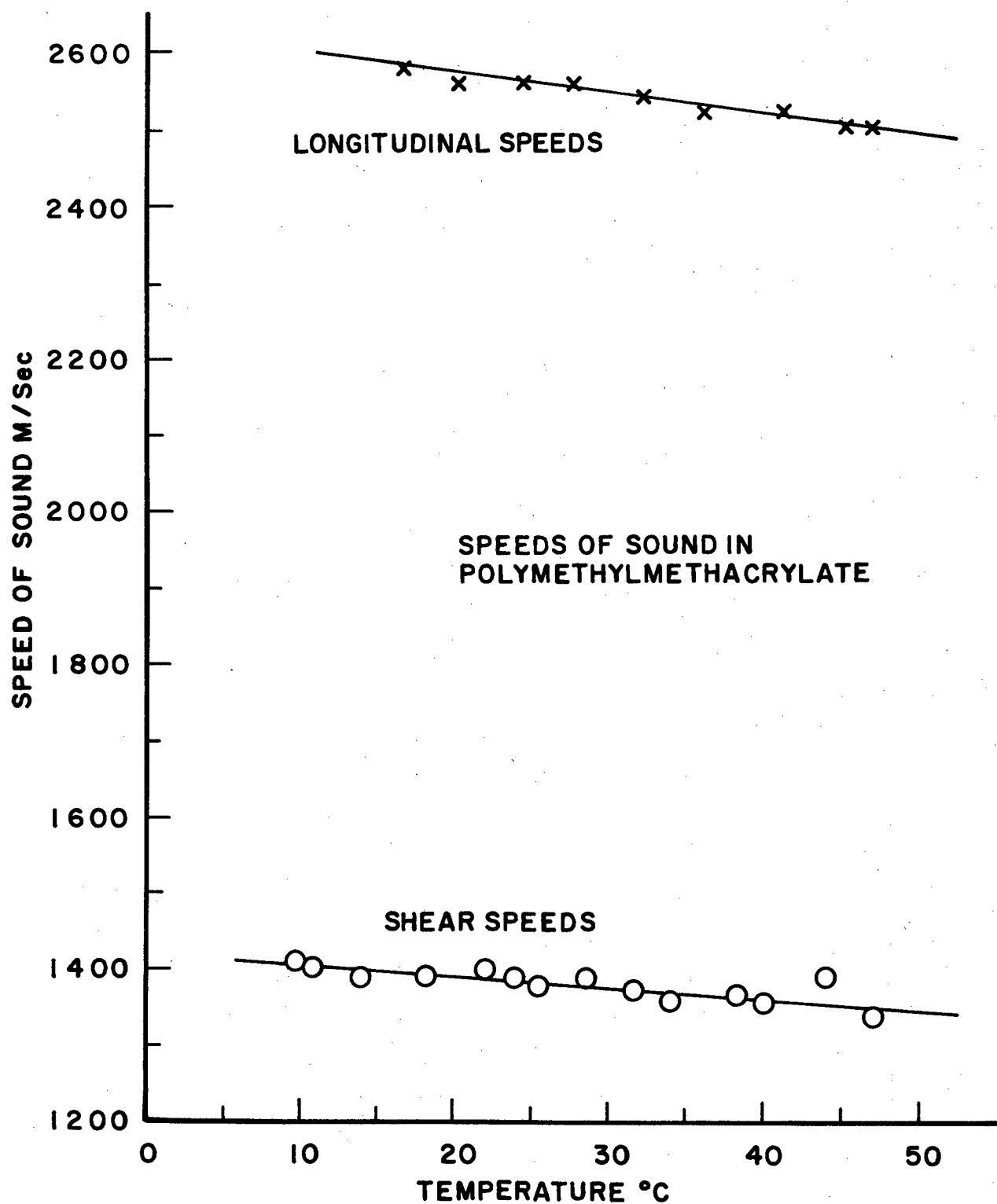


Figure 13. Sound Speeds as Function of Temperature for PMMA.

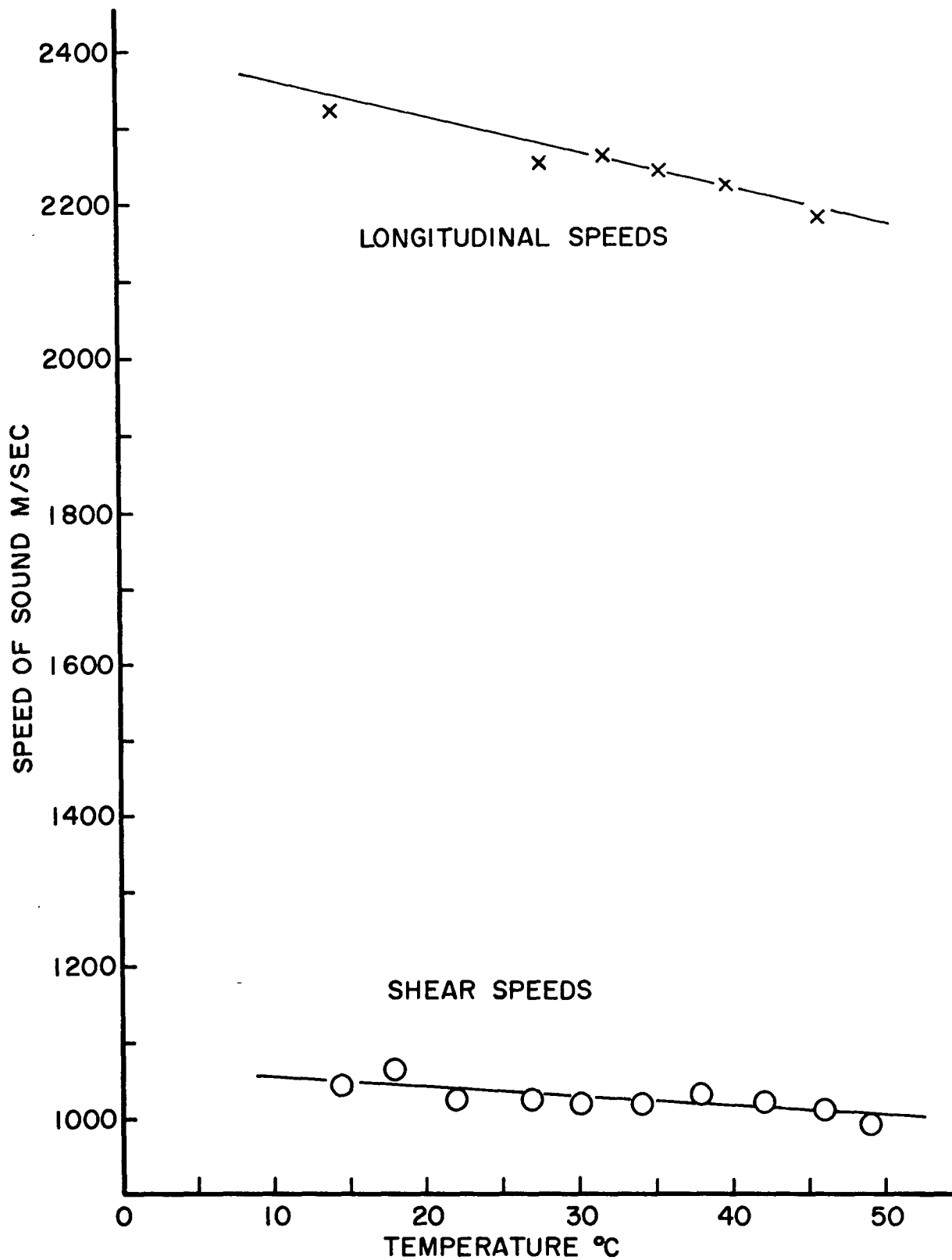


Figure 14. Sound Speeds as Function of Temperature for Nylon.

SECTION VI

CONCLUSIONS

The described ultrasonics experiments to determine the longitudinal and shear speeds in plastic materials have the required precision and ease of operation to determine elastic mechanical properties in a nondestructive fashion. In any application where nondestructive techniques are of prime importance, the ultrasonics measurements will serve as an important contribution. Especially, this technique should be applicable in the study of composites. The matrix, resin, and their regions of surface interaction can have separable responses in the measured response ultrasonic signal.

The present apparatus does not have a programmed temperature capability or a wide temperature range capability. With these modifications, it could become a useful tool for detecting first and second order phase transitions in a mechanical property-temperature spectrum. However, this technique will not displace well established commercially available equipment used for this type measurement, e. g. TMA (Thermal Mechanical Analyzer) or Rheovibron Viscoelastometer.

Most industrial laboratories are interested in property-phenomenon correlations such as in quality control and even in engineering applications. For this type of correlation, a standard "number" measurement which varies with the phenomenon being tracked is sufficient. That is, usually people are not interested in relating mechanical properties correlatable with molecular and microstructural characteristics. If one is interested in such correlations, then the bulk modulus, shear modulus, and Poisson's ratio (easily derivable from ultrasonics measurements), are important.

The basic question seems to be whether one is performing a measurement to sell a material or in order to gain more insight into the material's morphological character. If the reason is for the sale of an isolated item, a correlatable number suffices. If the reason is to correlate the properties

to either the molecular (or mechanical model) structure, the ultrasonics technique will contribute significantly in its own frequency range. As a non-destructive technique, ultrasonics will contribute in both of these areas simultaneously, but its uniqueness will be the nondestructive capability.

SECTION VII
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