Experimental Determination of Ultrasonic Wave Velocities in Plastics as Functions of Temperature. IV. Shear Velocities in Common Plastics

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Synopsis

The temperature dependence of acoustic shear velocities are reported for Poly-Penco nylon, type G Plexiglass [poly(methyl methacrylate], TFE Teflon (tetrafluoroethylene), low- and high-density polyethylene, Lexan (polycarbonate), and Delrin Acetal (nylon). Most of the data were obtained at a frequency of 1 Mc./sec. over the temperature range of 25–100°C. In addition, previously unreported longitudinal velocities to ~125°C. are reported for Lexan and Delrin Acetal.

INTRODUCTION

The determination of the shear velocities in the materials reported herein is part of a continuing materials research program being conducted by this laboratory. These data are used in conjunction with other equation-of-state parameters to predict the behavior of these plastics under various high pressure impulsive loading conditions.

The longitudinal velocities in all of these materials except Delrin Acetal (E. I. du Pont de Nemours) and Lexan (General Electric) have been reported in an earlier publication.[1] The combination of the longitudinal and shear velocities, in combination with a knowledge of material thermal properties, permits a calculation of the Grüneisen number[2] as well as an estimation of the pressure–volume relationship at high pressure (few hundred kilobars).[3]

EXPERIMENTAL METHOD

The details of the experimental technique used here have been reported elsewhere.[4] Basically, however, the technique consists of applying a pulsed signal of the desired carrier frequency to a piezoelectric transducer bonded to the specimen. The generated acoustic signal traverses the specimen and is detected by a second transducer. The velocity is obtained by measuring the elapsed acoustic delay time for various sample thicknesses and performing a least-square analysis for specimen thickness versus sample transit time. The resulting technique yields uncertainties of ~1–2% in the longitudinal and shear velocities for sample thicknesses employed

(1–10 mm.). Considering inherent sample variations and inhomogeneities, this magnitude of uncertainty is sufficient.

The transducers used for the determination of shear velocities were AC-cut quartz and were operated at the fundamental frequency of 1 Mc./sec. or at the third harmonic of 3 Mc./sec. The crystals were bonded to the specimen with an epoxy resin (Eastman 910 adhesive) for the shear measurements. Lead zirconate titanate transducers were used for the longitudinal measurements and were bonded to the specimen with a low viscosity silicone oil (DC-220, manufactured by Dow-Corning, Midland, Mich.). The samples were machined flat and parallel to within a few microns and were large enough that a semi-infinite medium could be assumed as the boundary condition for one-dimensional wave propagation at these frequencies.

RESULTS

Delrin Acetal

This material is one of the more recently developed plastics which possess material properties comparable with many of those common to metals. It is a highly crystalline, stable form of polymerized formaldehyde (super polyoxymethylene), which exhibits high tensile strength, rigidity, and creep resistance over a wide temperature range. The material used in the present experiments exhibited a mean density of 1.434 g./cc.

The variations of the longitudinal and shear velocity with temperature in Delrin Acetal are shown in Figures 1 and 2, respectively. The velocities were corrected for thermal expansion, Warringer's[5] value of $8.1 \times 10^{-5}/°C.$ being used for the linear coefficient of expansion. The data for the longitudinal mode of propagation indicate negligible dispersion in the frequency range of 1.5–3.0 Mc./sec. The data for the shear velocity are limited to 1 Mc./sec. in the present experiments, due to the fact that the attenuation of the third harmonic was too great to allow accurate velocity measurements at this frequency.

The least-squares fit of the data corresponding to the graphs of Figures 1 and 2 are as follows.

Longitudinal velocity: $c_{l(25-125°C.)} = 2.58 - (4.21 \times 10^{-3})T - (1.25 \times 10^{-5})T^2$

Shear velocity: $c_{t(25-100°C.)} = 1.19 - (3.69 \times 10^{-3})T - (1.39 \times 10^{-5})T^2$

The velocity units are millimeters per microsecond, and the temperature is in degrees Centigrade.

The application of the velocity data to the calculations of the elastic moduli is largely limited by the acoustic attenuation arising from internal friction. The dissipation processes which are applicable in the present case are those associated with velocity gradients induced by the acoustic vibrations. These losses may be grouped into two general classes, depending upon whether the mechanical behavior of the specimen corresponds to the Maxwell or Voigt model.[6]
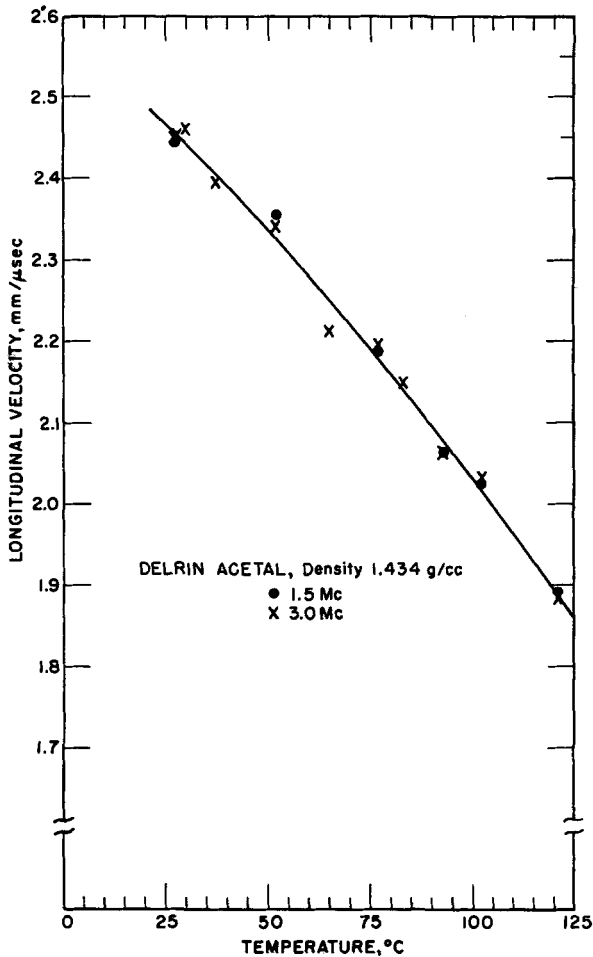
Fig. 1. Longitudinal velocity in Delrin Acetal as a function of temperature.

Based upon the appropriate model, the present data could be used to calculate the frequency dependent moduli in Delrin Acetal. However, the presented data would have to be supplemented with measurements showing the dependence of velocity and attenuation with frequency in order to verify the applicable model.

Assuming that the viscous terms are small enough that the mechanical behavior is essentially elastic, the elastic moduli can be derived from the two sets of reported velocities. In terms of the velocities, Young's modulus E, the shear modulus G, and the bulk modulus B are given as

$$E = \rho \left[c_l^2 \left(3c_l^2 - 4c_t^2 \right) / \left(c_l^2 - c_t^2 \right) \right]$$

$$G = \rho c_t^2$$

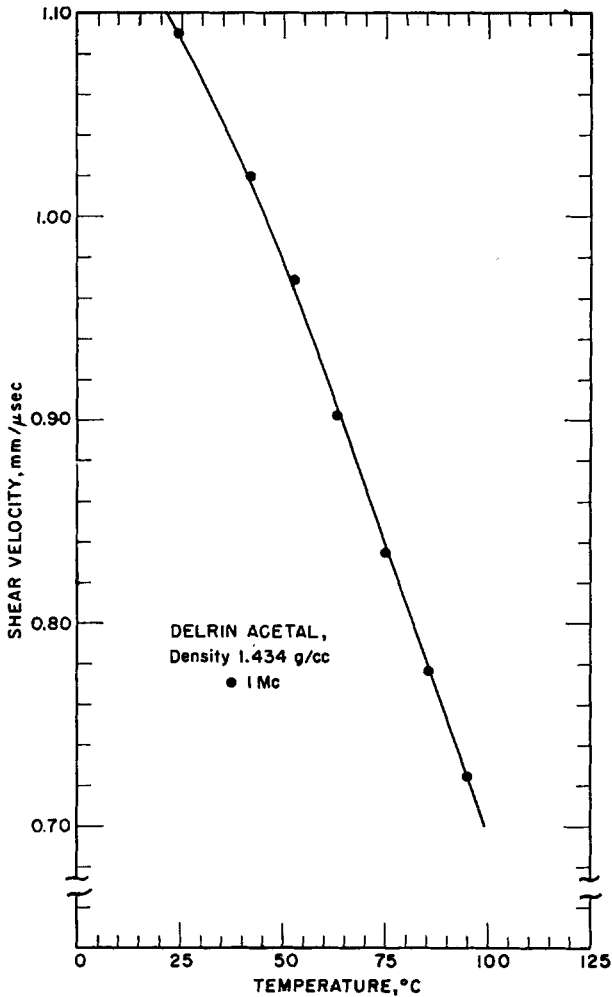$$B = \rho \left(c_l^2 - {}^4\!/_3 c_t^2 \right)$$

Fig. 2. Shear velocity in Delrin Acetal as a function of temperature.

where ρ is the density. In units of dynes/square centimeters and as a function of temperature (Centigrade) the adiabatic moduli are

$$E_{(25-100°C.)} = 5.81 \times 10^{10} - (4.57 \times 10^8)T - (6.25 \times 10^5)T^2$$

$$B_{(25-100°C.)} = 6.86 \times 10^{10} - (1.44 \times 10^8)T - (4.44 \times 10^5)T^2$$

$$G_{(25-100°C.)} = 2.13 \times 10^{10} - (1.76 \times 10^8)T - (2.84 \times 10^5)T^2$$

Of particular interest is the variation of the adiabatic bulk modulus with temperature. This parameter, which is essentially constant in metals, plays a fundamental role in many equations of state calculations. One such application relates to the determination of the Grüneisen parameter, which indicates the change in thermal energy corresponding to a pressure change

TABLE I
Shear Velocities vs. Temperature[a]

| | Shear velocity, mm./μsec. | | | | | | |
| | Polyethylene | | | Type G | | | |
Tempera-ture, °C.	0.922 g./cc.	0.967 g./cc.	TFE Teflon	Plexi-glass	Nylon	Delrin Acetal	Lexan
25.0	0.534	1.11	0.501	1.391	1.12	1.090	0.908
30.0	0.529	1.07	0.486	1.388	1.11	1.067	0.899
40.0	0.521	0.999	0.459	1.377	1.07	1.026	0.883
50.0	0.512	0.928	0.434	1.362	1.03	0.975	0.868
60.0	0.503	0.857	0.410	1.343	0.979	0.924	0.854
70.0	0.494	0.787	0.389	1.319	0.919	0.864	0.841
80.0	0.485	0.718	0.370	1.290	0.849	0.808	0.829
90.0	0.475	0.650	0.352	1.256	0.771	0.752	0.818
100.0	0.466	0.583	0.337	1.218	0.683	0.688	0.808
110.0	0.456	0.516	0.324	1.176	0.586	0.616	0.799
120.0	0.447	0.451	0.313	1.128	0.481	0.546	0.791

[a] All velocities reported in this table correspond to a frequency of 1.0 Mc./sec.

TABLE II
Longitudinal Velocities vs. Temperature[a]

| | Longitudinal velocity, mm./μsec. | | | | | | |
| | Polyethylene | | | Type G | | | |
Tempera-ture, °C.	0.916 g./cc.	0.964 g./cc.	TFE Teflon	Plexi-glass	Nylon	Delrin Acetal	Lexan
25.0	1.99	2.56	1.40	2.71	2.72	2.47	2.22
30.0	1.96	2.52	1.36	2.70	2.70	2.44	2.20
40.0	1.88	2.44	1.32	2.68	2.65	2.39	2.17
50.0	1.77	2.35	1.29	2.65	2.61	2.34	2.14
60.0	1.67	2.28	1.26	2.61	2.56	2.28	2.11
70.0		2.20	1.24	2.58	2.51	2.22	2.08
80.0		2.11	1.22	2.54	2.45	2.16	2.06
90.0		2.04	1.20	2.50	2.38	2.10	2.03
100.0		1.96	1.17	2.47	2.30	2.03	2.01
110.0			1.15		2.23	1.97	1.99
120.0			1.12			1.90	1.97

[a] The data in this table were taken from the previous paper,[1] with the exception of Delrin Acetal and Lexan, and represent average values over the frequency range 1.5–3.0 Mc./sec.

in a solid. Dorr and Guenther[7] show that this quantity which is formally defined as $\gamma = V (\partial P/\partial E)_V$ can be expressed thermodynamically in an isotropic medium as

$$\gamma = 3\alpha\beta/\rho c_p$$

where α is the linear coefficient of expansion and c_p is the specific heat at constant pressure. By using Warringer's[5] values of α and c_p (0.35 cal./g.-°C.), γ is calculated as 0.75 (at 25°C.) from the present experimental data.

Anderson[8] indicates that this ratio should be essentially independent of temperature. To ensure this constancy, the present data suggest that the ratio α/c_p increases markedly with temperature, in contrast to the behavior of this ratio in metals. The thermal behavior of the reported materials is currently being investigated in order to verify whether the Grüneisen ratio is indeed constant with temperature in common plastics.

Poly-Penco Nylon

Figure 3 shows the dependence of shear velocity on temperature in Poly-Penco nylon (density 1.14 g./cc.). The data were obtained over the
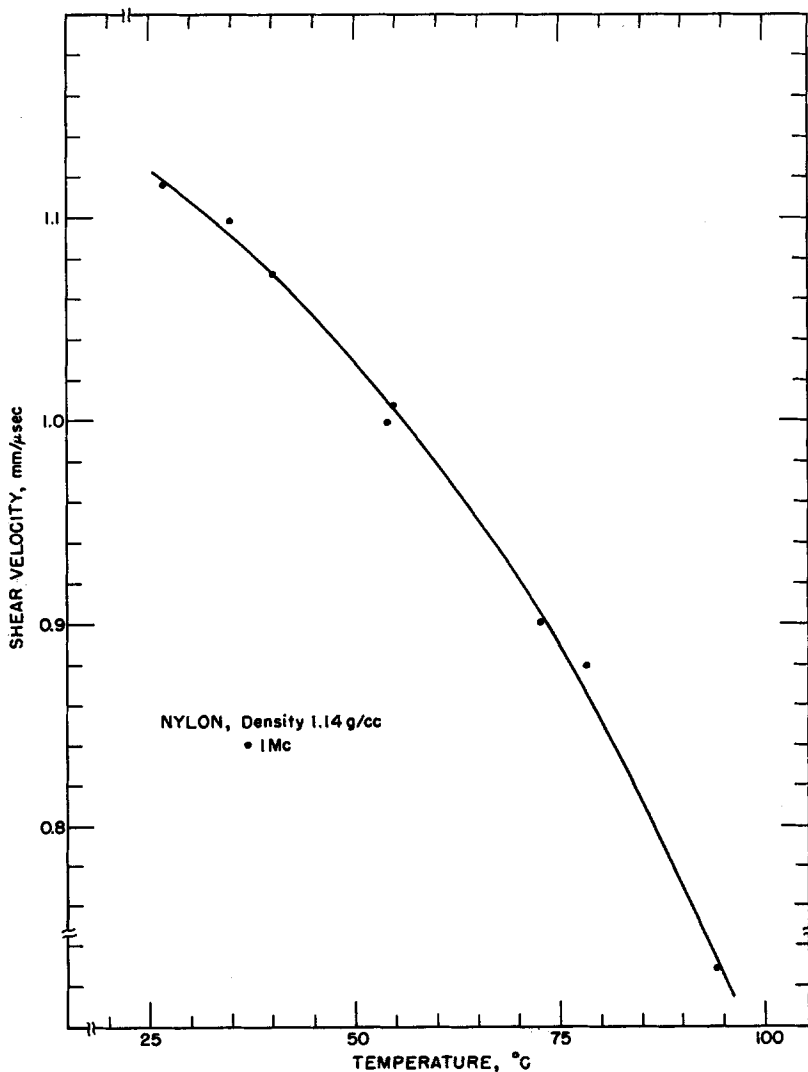
Fig. 3. Shear velocity in Poly-Penco nylon as a function of temperature.

temperature range of 25–100°C. and are corrected for thermal expansion by using Carswell's[9] value of 8.1×10^{-5}/°C. for the linear coefficient of expansion. The attenuation of the 3 Mc./sec. harmonic was too great to allow a reliable determination at that frequency. The least-squares fit for the data represented in Figure 3 is

$$c_{t(25-100°C.)} = 1.15 - (2.35 \times 10^{-4})T - (4.48 \times 10^{-5})T^2$$

Tetrafluoroethylene

The shear velocity in TFE tetrafluoroethylene (density, 2.19 g./cc.) is shown in Figure 4. Again, the experimental technique was not sensitive enough to allow a determination of the velocity of the 3 Mc./sec. acoustic wave. The expansion coefficient used to correct the data was 13.5×10^{-5}/°C. Because of the low-friction surface of Teflon, some difficulty was experienced in maintaining a good bond between the specimen and transducer. The data therefore show more variation than that experienced in the previous two materials, due to nonreproducibility of bonding.
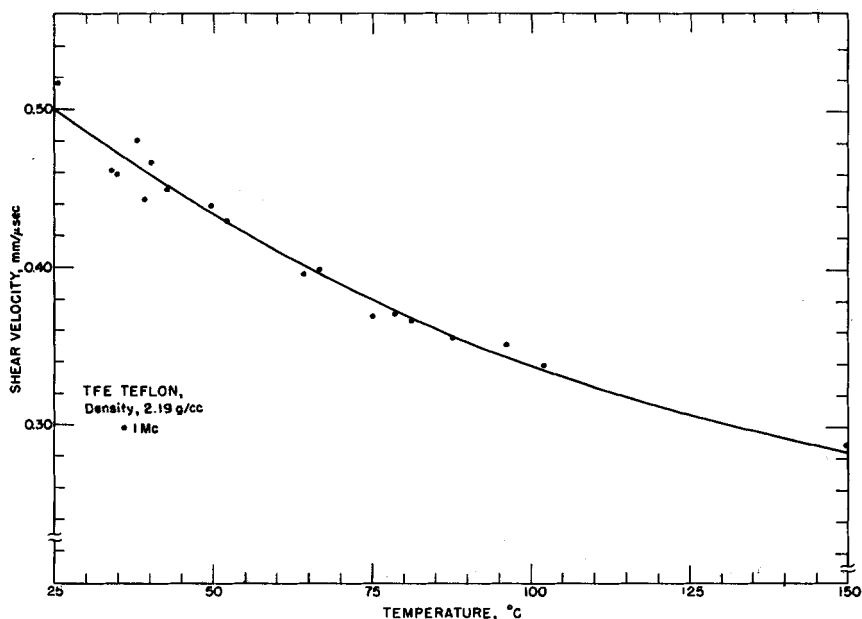

Fig. 4. Shear velocity in TFE Teflon as a function of temperature.

The variation of the shear velocity near room temperature was too great to allow a reliable observation of the second-order transition as observed by Arnold and Guenther[1] in the longitudinal velocity. The data corresponding to the temperature range of 25–150°C. were therefore fitted to the following polynomial

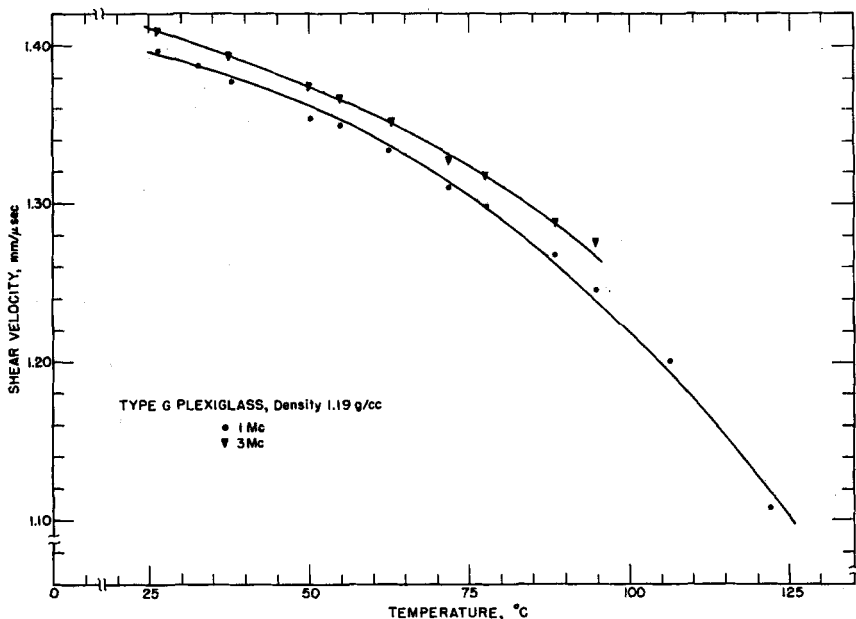$$c_{t(25-150°C.)} = 0.581 - (0.345 \times 10^{-2})T + (0.10 \times 10^{-4})T^2$$

Fig. 5. Shear velocity in type G Plexiglass as a function of temperature.

Type G Plexiglass

Figure 5 shows the shear velocity as a function of temperature in Type G Plexiglass. This material, which is a methyl methacrylate polymer, exhibited a mean density of 1.19 g./cc. and a linear coefficient of expansion of 6.48 × 10⁻⁵/°C.[11] As indicated in Figure 5, there is a difference of ~1% in the velocity at 1.0 and 3.0 Mc./sec. Although this uncertainty approaches the limitations of the technique, both curves were fitted to separate polynomials.

At 1 Mc./sec.: $c_{t(25-125°C.)} = 1.39 + (5.99 \times 10^{-4})T - (2.32 \times 10^{-5})T^2$
At 3 Mc./sec.: $c_{t(25-125°C.)} = 1.43 - (6.47 \times 10^{-4})T - (1.10 \times 10^{-5})T^2$

It is also noted that the separation in the velocities at ~100°C. appears to be ~2%. This effect could be due to a frequency-dependent relaxation mechanism, since increasing the temperature of a viscoelastic material is equivalent to lowering the frequency.

Polyethylene

Figures 6 and 7 illustrate the variation of shear velocity in different densities of polyethylene and the dependence of the velocity on temperature. Again, some dispersion in the high-density polyethylene was noted between 1 and 3 Mc./sec. (Fig. 7), so that separate curves were plotted for the two frequencies.

Of particular interest is the large difference in velocity (ca. a factor of two) corresponding to a density change of ~5%. Arnold and Guenther[1]

have measured the longitudinal velocity corresponding to the two dif-
ferent densities of polyethylene and obtained the results of 1.99 and 2.55
mm./μsec. at room temperature for the densities of 0.916 and 0.964 g./cc.,
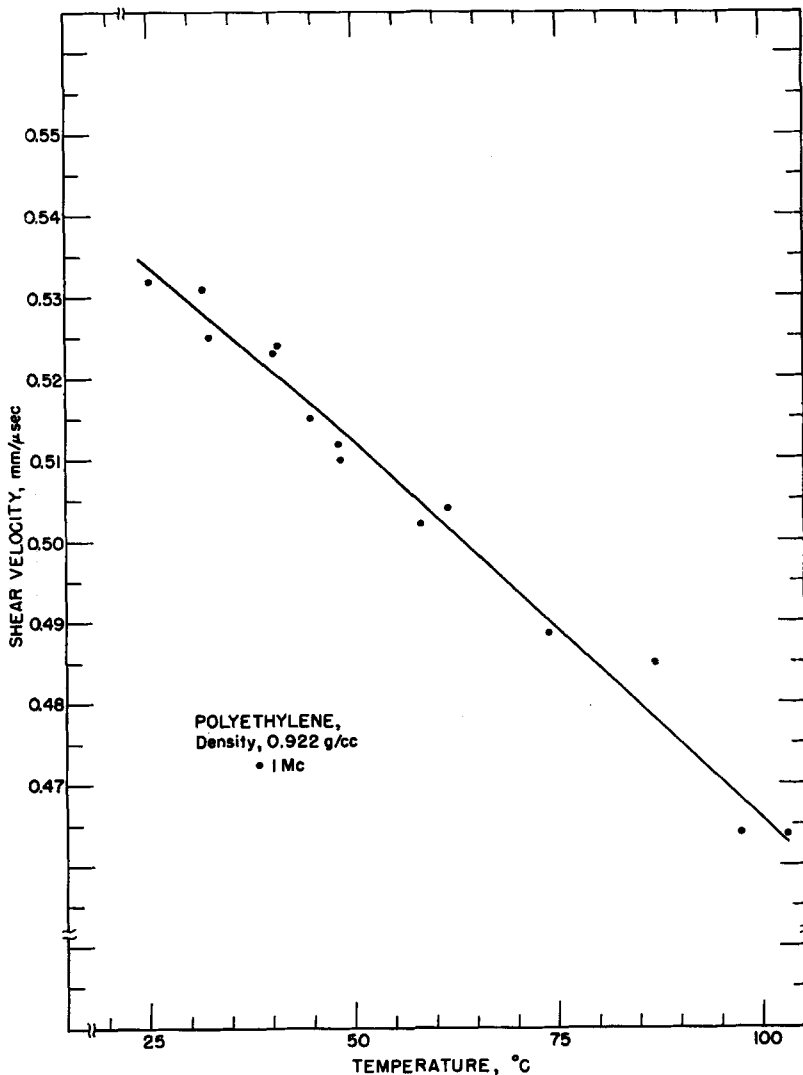respectively.   The change in the longitudinal velocity is therefore only

Fig. 6. Shear velocity in low-density polyethylene as a function of temperature.

$\sim$25% for this change of density.   However, the longitudinal velocity
is a function of two independent elastic constants in an isotropic medium
(the Lamé constants, λ and μ), whereas the shear velocity depends only
on the shear modulus, or Lamé constant μ (G as used earlier is identical with
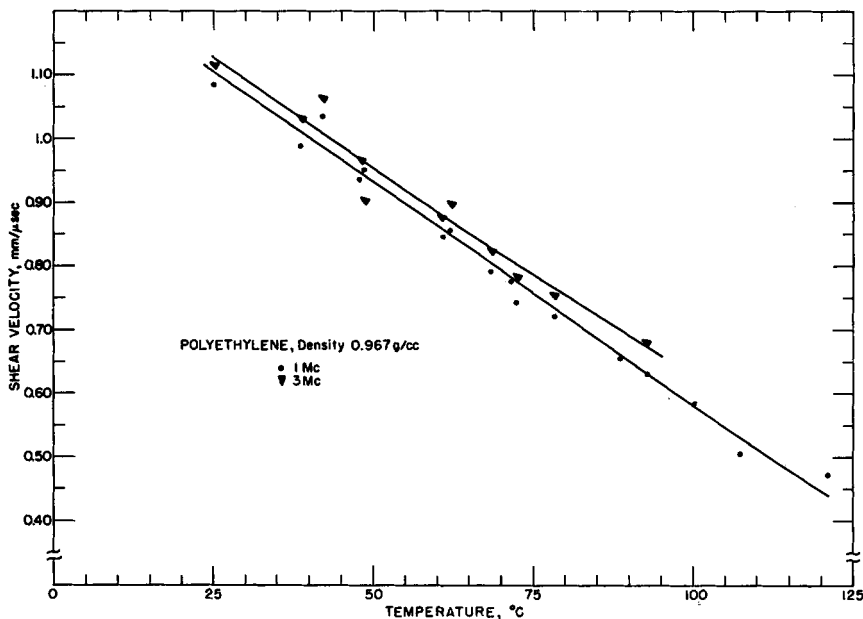the constant μ).

Fig. 7. Shear velocity in high-density polyethylene as a function of temperature.

The magnitude of variation in the shear velocities observed in the present experiments can be verified through correlation with other elastic properties of the material. Estes[12] states that for polyethylene the elastic modulus in tension varies by approximately an order of magnitude for the two densities of polyethylene used here. This modulus cannot be directly related to any dynamically determined modulus, such as the Young's modulus, because of creep and stress relaxation which are present in static tests. However, the effective modulus as reported by Estes is a function of both Lamé constants and hence would be influenced significantly by the variation of the shear modulus with density.

More direct support of the reported difference in shear velocities can be obtained by considering Young's modulus in the two materials. Using the previous results[1] for the longitudinal velocities and applying the elastic relations presented earlier, we obtained for the reported data the values of 3.2×10^{10} and 0.78×10^{10} dyne/cm.[2] for Young's modulus in the high- and low-density specimens, respectively. Young's modulus can also be related to the extensional or thin rod velocity V_{ext} as $E = \rho V_{ext}^2$. These velocities are calculated from the present data to be 1.8 and 0.91 mm./μsec. for the high- and low-density polyethylene, respectively. The above calculations are in good agreement with Davidse's[13] direct measurements of 1.9 and 0.9 mm./μsec. for the extensional velocities corresponding to the respective densities of 0.967 and 0.922 g./cc. The least-squares fit of the shear velocities for the densities of polyethylene in the temperature range 25–100°C. are as follows:

Density 0.922 g./cc., 1 Mc./sec.:
$$c_t = 0.554 - (0.816 \times 10^{-4})T - (0.685 \times 10^{-7})T^2$$

Density 0.967 g./cc., 1 Mc./sec.:
$$c_t = 1.29 - (7.56 \times 10^{-3})T + (4.36 \times 10^{-6})T^2$$

Density 0.967 g./cc., 3 Mc./sec.:
$$c_t = 1.32 - (7.85 \times 10^{-3})T + (9.71 \times 10^{-6})T^2$$

Lexan

Figures 8 and 9 illustrate the variation of the longitudinal and shear velocities with temperature in Lexan (a polycarbonate, density 1.20 g./cc.).
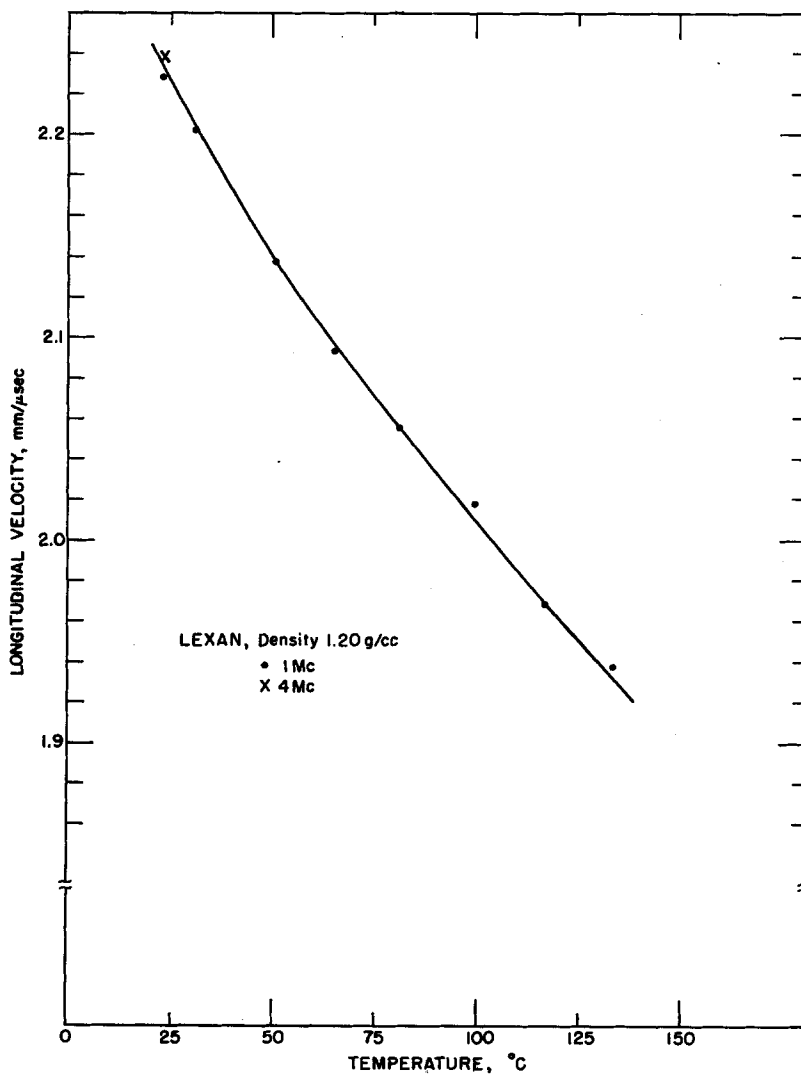

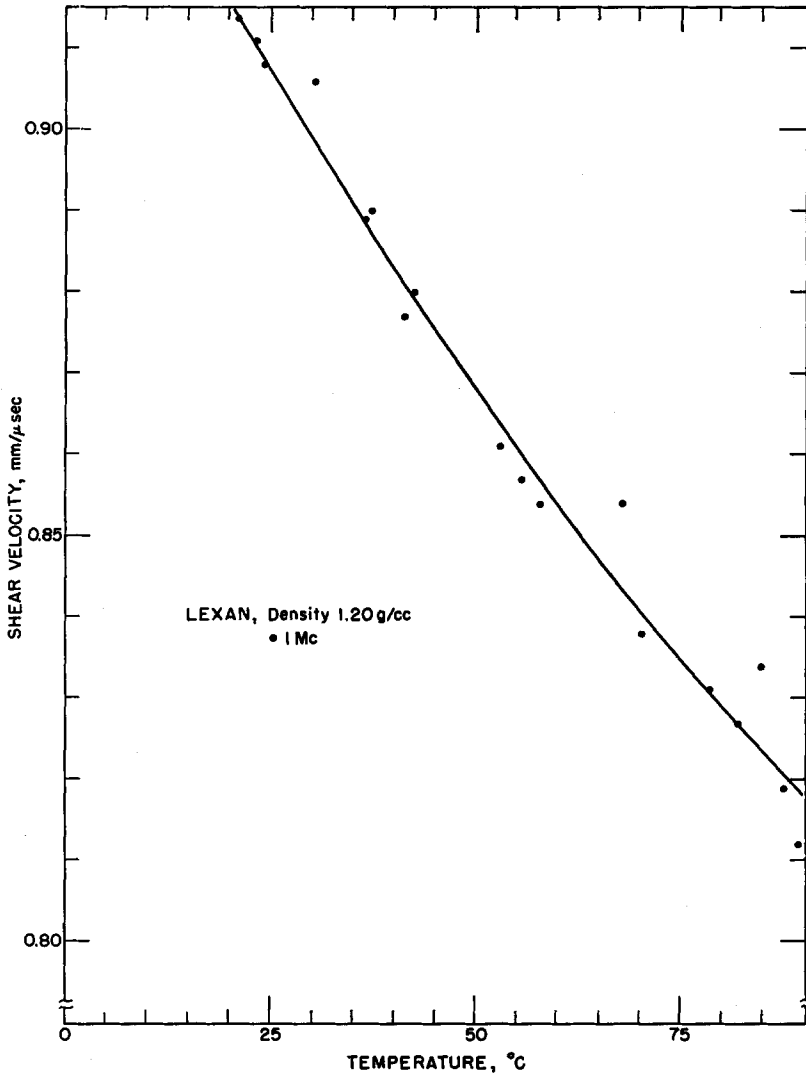Fig. 8. Longitudinal velocities in Lexan as a function of temperature.

Fig. 9. Shear velocity in Lexan as a function of temperature.

Both curves were corrected for thermal expansion by using the manufacturer's value of $6.75 \times 10^{-5}/°C.$ for the linear coefficient of thermal expansion. Kunze[14] has reported typical compressive and rigidity moduli for polycarbonates as obtained in static tests. His values for the modulus of elasticity and the shear modulus are 3.40×10^5 and 1.16×10^5 psi, respectively. By use of the appropriate equations of elasticity, the present data on the longitudinal and shear velocities yield 3.73×10^5 and 1.45×10^5 psi for Young's modulus and the shear modulus at 25°C., respectively. This agreement is fair considering the nature of both tests. Kunze[14] does not report the uncertainty of his values nor a specific poly-

carbonate. Furthermore, static tests, as mentioned earlier, are generally influenced by creep and stress relaxation so that a direct comparison cannot be made with the present data. Since the uncertainties for velocities in the present experiments are approximately 1–2%, the uncertainties in the elastic moduli as calculated above are on the order of 2–5%. The longitudinal and shear velocities are given in terms of temperature for Lexan as

$$c_{l(25-125°C.)} = 2.31 - (3.69 \times 10^{-3})T + (6.90 \times 10^{-6})T^2$$

$$c_{l(25-90°C.)} = 0.954 - (0.199 \times 10^{-2})T + (0.528 \times 10^{-5})T^2$$

Mylar

The longitudinal velocity in Mylar (E. I. du Pont de Nemours & Co.) was also obtained with an immersion technique. This approach was necessary, since the buffer technique does not yield good accuracy with thin samples (e.g. 10–14 mil in the case of Mylar) because of the reproducibility of bonding the buffers to the specimen. However, with the immersion technique, reproducibility errors become insignificant, since the fluid (water was used in the present experiments) acts as a buffer, and transit times corresponding to different insertions can be reproduced to within a few nanoseconds.

The velocity in Mylar was obtained for the frequencies of 2.0, 4.0, and 12.0 Mc./sec. The acoustic wavelengths ranged from ∼1 mm. to ∼0.2 mm. for these frequencies, with the lowest wavelength corresponding to approximately the sample thickness. For this range of frequencies, a trend in the velocity data was not observed within the limitations of the technique so that the results were averaged together. The average longitudinal velocity in 10-mil Mylar at 21.0°C. as obtained in the present experiment is 2.64 ± 0.09 mm./μsec. The velocity in 14-mil Mylar is 2.29 ± 0.06 mm./μsec. for the corresponding experimental conditions.

SUMMARY

The experimental technique used here has been found to yield shear velocities in plastics with uncertainties of 1–2%. The agreement with moduli values obtained by other methods such as tensile and compression tests, is good considering (1) the applicability of the appropriate equations of elasticity, (2) the difficulty of obtaining reliable results in the static tests, and (3) wide variation of sample uniformity.

For all of the materials investigated here, the decrease in both the longitudinal and the shear velocity with temperature is large. However, the behavior of the velocity as the melting point is approached is not the same for each material. That is, the curvature of the velocity curve is positive in some cases and negative in others. However, the sign of curvature is generally the same for the longitudinal and shear velocity in a given material.

References

1. N. D. Arnold and A. H. Guenther, *J. Appl. Polymer Sci.*, **10**, 731 (1966).

2. J. R. Asay, A. J. Dorr, N. D. Arnold, and A.H. Guenther, Air Force Weapons Laboratory, Technical Report No. AFWL-TR-65-188, Kirtland AFB, New Mexico.

3. J. R. Asay and A. H. Guenther, *J. Phys. Chem. Solids*, in press.

4. J. R. Asay and A. H. Guenther, *J. Appl. Polymer Sci.*, **10**, 753 (1966).

5. W. C. Warringer, *Mech. Eng.*, **60**, 60 (1959).

6. H. Kolsky, *Stress Waves in Solids*, Dover, New York, 1963.

7. A. J. Dorr and A. H. Guenther, *J. Appl. Polymer Sci.*, **10**, 745 (1966).

8. O. L. Anderson, *J. Appl. Phys.*, in press.

9. D. D. Carswell, *Machine Design*, **38**, 68 (1966).

10. R. T. Lovell, W. H. Holstein, and T. F. Jordan, *Machine Design*, **38**, 60 (1966).

11. O. L. Pierson, *Machine Design*, **38**, 49 (1966).

12. P. H. Estes, *Machine Design*, **38**, 77 (1966).

13. P. D. Davidse, H. I. Waterman, and J. B. Westerdijk, *J. Polymer Sci.*, **59**, 389 (1962).

14. R. J. Kunze, *Machine Design*, **38**, 75 (1966).

Résumé

La dépendance thermique des vitesses de cisaillement acoustique sont rapportées pour le Poly-Penco-nylon, le plexiglass type-G (polyméthacrylate de méthyle), le Teflon TFE, le polyéthylène à faible et haute densité, le Lexane (polycarbonate) et le Delrin-acetal (nylon). La plupart des résultats sont obtenus à une fréquence d'un Mc. dans un domaine de température de 25 à 100°C. En outre, des vitesses longitudinales rapportées antérieurement jusque 125° sont rapportées pour le Lexane et l'acétal-Delrin.

Zusammenfassung

Die Temperaturabhängigkeit akustischer Schergeschwindigkeiten wird für Poly-Penco-Nylon, Typ G Plexiglas (Polymethylmethacrylat), TFE Teflon, Polyäthylen niedriger und hoher Dichte, Lexan (Polycarbonat) und Delrin-Acetal (Nylon) bestimmt. Die Mehrzahl der Daten wurde bei einer Frequenz von 1 MHz im Temperaturbereich von 25 bis ~100°C erhalten. Ausserdem werden bis jetzt noch nicht bekannte Longitudinalgeschwindigkeiten bis ~125°C für Lexan und Delrin-Acetal angegeben.