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POLYMER SOUND SPEEDS AND ELASTIC
CONSTANTS

Bruce Hartmann, et al

Naval Ordnance Laboratory
White Oak, Maryland

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By
Bruce Hartmann
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13. ABSTRACT Sound speed measurements were made on 25 polymers at room temperature and on five of these polymers as a function of temperature. On 15 of the polymers, both longitudinal and shear sound speeds were measured. Using these sound speeds and measured densities, the elastic constants of the polymers were calculated.			

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POLYMER SOUND SPEEDS AND ELASTIC CONSTANTS

This report describes experimental work done in measuring longitudinal and shear sound speeds in polymers and using these measurements to calculate the elastic constants of the polymers. These measurements are needed for acoustic design purposes and for determining elastic constants for equation of state calculations.

This work was conducted in part under Task NOL 278/ONR and in part under Task ORD 333 004/092-1/UF 51-543-301. The materials used in this report were obtained from commercial sources. Their evaluation by the Laboratory in no way implies Navy endorsement of these materials.

ROBERT WILLIAMSON II
Captain, USN
Commander

Albert Lightbody
ALBERT LIGHTBODY
By direction

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II	Longitudinal Sound Speed for Rubbers
III	Temperature Dependence of Sound Speeds and Elastic Constants
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INTRODUCTION

This report presents the results of sound speed measurements on 25 polymers. This data is needed not only for various acoustic applications, where the sound speeds are used directly, but also for equation of state calculations, where sound speed measurements are used to determine elastic constants.

All the measurements reported here were made at a frequency of 0.6 MHz using the immersion apparatus previously described.¹ Both longitudinal and shear sound speed measurements were made on most of the polymers. On five of the polymers, measurements were made as a function of temperature. For the sake of completeness, all of the data obtained in the immersion apparatus is reported here, including the results previously reported in checking out the equipment.¹

The principal conclusions of this work are that sound speed measurements are relatively easy to make in the immersion apparatus, are of sufficient accuracy for most applications, and are useful both in acoustics and equation of state calculations.

CALCULATION OF ELASTIC CONSTANTS

One of the uses of sound speed measurements is to determine elastic constants. This determination requires both longitudinal sound speed:

$$v_1 = \sqrt{(B + 4G/3)/\rho} \quad (1)$$

and shear sound speed:

$$v_s = \sqrt{G/\rho} \quad (2)$$

where B = bulk modulus, G = shear modulus, and ρ = density. The shear modulus can be calculated from Equation (2), knowing v_s and ρ . The bulk modulus can then be calculated from Equation (1) knowing v_1 , G, and ρ .

For an isotropic solid, such as the polymers studied here, there are only two independent elastic constants.² These two can be taken to be G and B, but it is sometimes convenient to use other elastic constants, such as Young's modulus, Y, and Poisson's ratio, σ .

These constants can be calculated using the standard relations²

$$Y = \frac{3G}{1 + G/3B} \quad (3)$$

$$\sigma = \frac{1}{2} - \frac{Y}{6B} \quad (4)$$

The four constants G , B , Y , and σ are referred to as engineering constants. Other constants are also used, and they can be calculated from the engineering constants. For example the Lamé constants μ and λ are given by

$$\mu = G \quad (5)$$

$$\lambda = B - \frac{2}{3}G \quad (6)$$

The elastic constants can also be expressed using the elastic stiffness matrix. In generalized form, Hooke's law is given² by

$$\sigma_i = \sum_{j=1}^6 c_{ij} \epsilon_j \quad (7)$$

where the σ_i are the stress components, the ϵ_i are the strain components, and the c_{ij} are the isothermal elastic stiffness coefficients. For an isotropic solid

$$c_{44} = c_{55} = c_{66} = G \quad (8)$$

$$c_{11} = c_{22} = c_{33} = B + 4G/3 \quad (9)$$

$$c_{12} = c_{13} = c_{23} = c_{21} = c_{31} = c_{32} = B - 2G/3 \quad (10)$$

All other coefficients are zero.

In this report, all the engineering elastic constants will be calculated. If any other elastic constants are desired, they can be calculated using Equations (5) to (10).

EXPERIMENTAL RESULTS

All of the experimental results will be given in this section. A description of the materials used is given in the appendix.

In Table I are a list of measured sound speeds and densities at room temperature for various rigid polymers. They are listed in order of decreasing longitudinal sound speed. About half of these results were given in the previous report¹ and compared with literature values. The sound speeds were found to be accurate to about $\pm 2\%$. In some cases, no shear wave measurements were possible because the absorption was too high.

In Table II are a list of measured longitudinal sound speeds at room temperature for various compounded rubbers. The values for butyl and natural rubber are in reasonable agreement with literature values.³ In no case was it possible to measure a shear sound speed.

Sound speed measurements as a function of temperature were made on five polymers. Results for polymethylmethacrylate, polyethylene, and polypropylene were reported previously.¹ Measurements on polyethylene oxide (longitudinal sound speed only) have also been published elsewhere.⁴ In addition, measurements were made on polyacrylonitrile-butadiene-styrene. The temperature derivatives of the sound speeds are given in the first two columns of Table III.

For those polymers on which both longitudinal and sheer sound speed measurements are available, the engineering elastic constants at room temperature have been calculated and are given in Table IV, using data from Table I.

Since the sound speeds are accurate to about $\pm 2\%$ and the elastic constants depend on the square of the sound speed, the elastic constants are expected to be accurate to about $\pm 4\%$. In comparing these results with other values, two points need to be considered. First, high frequency measurements (such as those reported here) yield higher modulus values than low frequency measurements because of relaxation effects. Pastine⁵ has pointed out that the frequency dependence of B is small but the frequency dependence of G and Y can be considerable. For example, recent measurements of the low frequency elastic constants of high density polyethylene⁶ gave $B = 4.5 \times 10^{10}$ dyne/cm² compared with our value of 4.54×10^{10} dyne/cm² and $Y = 0.7 \times 10^{10}$ dyne/cm² compared with our value of 2.55×10^{10} dyne/cm². Schuyer⁷ has pointed out that the Young's modulus of polyethylene can vary by a factor of ten depending on the frequency.

There is another source of difference between high frequency and low frequency measurements of elastic constants. Low frequency measurements are, generally, isothermal while high frequency measurements are adiabatic. For rigid polymers at room temperature, the adiabatic bulk modulus is about 10% greater than the isothermal bulk modulus⁸ while the adiabatic and isothermal shear moduli are identical.⁹ For many purposes, the difference between adiabatic and isothermal elastic constants can be ignored, especially when compared with relaxation effects.

Having both sound speeds as functions of temperature, the elastic constants can be calculated as a function of temperature. Illustrative results for polypropylene are shown in Figure 1. The temperature dependence of the bulk modulus is an important parameter for the Gruneisen equation of state, which is widely used for reentry calculations. In particular, the Anderson-Gruneisen

parameter, δ , is given by¹⁰

$$\delta = - \frac{1}{\alpha} \frac{d \ln B}{dT} \quad (12)$$

where α is the cubic coefficient of thermal expansion and T is the absolute temperature. Values of $-\frac{d \ln B}{dT}$ are also given in Table III.

For polymethylmethacrylate, our value of 0.0020 deg^{-1} is in excellent agreement with the value of 0.0022 deg^{-1} found by Asay, Lamerson, and Guenther.¹¹ For high density polyethylene, our value of 0.0051 deg^{-1} is in good agreement with the value of 0.0041 deg^{-1} found by Asay, Urzendowski, and Guenther.¹²

There is an additional source of error in these calculations of elastic constants as a function of temperature. In these calculations, it was assumed that the density of the polymer is constant at its room temperature value. There are two ways in which this causes an error. First, the sound speeds are calculated using the room temperature thickness of the specimen. Second, the elastic constants are calculated using the room temperature density. These effects may add another 10% to the error in the temperature dependence of the elastic constants.

CONCLUSIONS AND RECOMMENDATIONS

The immersion apparatus gives a convenient way to determine the sound speeds and elastic constants of polymers. These values are of sufficient accuracy for the majority of cases in acoustics and equation of state calculations.

Further work should be done to make shear wave measurements on those polymers for which only longitudinal values are now available. Some improvement in the electronics will be required to accomplish this.

As a useful adjunct to the sound speed measurements, thermal expansion measurements should be made on all the polymers examined. The expansion coefficient is necessary not only in order to make accurate calculations of the elastic constants as a function of temperature, but also in determining the Anderson-Gruneisen parameter, δ .

Finally, more polymers should be examined in order to build up a sufficient amount of data to make possible the determination of relations between polymer structure and bulk properties.

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TABLE I. SOUND SPEEDS AND DENSITY FOR RIGID POLYMERS

Polymer	Density g/cm ³	Longitudinal speed*, m/sec	Shear speed*, m/sec
Polyepoxide + MPDA	1.205	2820	1230
Polyhexamethylene adipamide	1.147	2710	1120
Polycaprolactam	1.146	2700	1120
Polymethylmethacrylate	1.191	2690	1344
Polypropylene	0.913	2650	1300
Polyoxymethylene	1.425	2440	1000
Polyethylene, high density	0.957	2430	946
Polystyrene	1.052	2400	1150
Polyepoxide + glass spheres II	0.718	2400	1280
Polyvinylbutyral	1.107	2350	—
Polyethylene oxide	1.208	2250	—
Polyepoxide + glass spheres I	0.691	2220	1170
Polyacrylonitrile-butadiene-styrene I	1.041	2160	930
Polyepoxide + glass spheres III	0.793	2100	1020
Polyacrylonitrile-butadiene-styrene II	1.022	2020	810
Polyethylene, low density	0.922	1970	—
Polyvinylidene fluoride	1.779	1930	775
Polyester + water	1.042	1840	650
Polytetrafluoroethylene	2.177	1380	—

*At room temperature and a frequency of 0.6 MHz

TABLE II. LONGITUDINAL SOUND SPEED FOR RUBBERS

<u>Rubber</u>	<u>Longitudinal speed*, m/sec</u>
Butyl	1990
Neoprene	130
Polybutadiene	1570
Natural rubber	1550
Polycarboranesiloxane	1450
Polydimethylsiloxane	1020

*At room temperature and a frequency of 0.6 MHz

TABLE III. TEMPERATURE DEPENDENCE OF SOUND SPEEDS AND ELASTIC CONSTANTS

Polymer	$-\frac{dv_l}{dT}$ m/sec deg	$-\frac{dv_s}{dT}$ m/sec deg	$-\frac{d \ln B}{dT}$ 1/deg
Polymethylmethacrylate	2.5	2.0	0.0020
Polypropylene	15.	6.7	0.0101
Polyethylene, high density	9.6	6.8	0.0051
Polyethylene oxide	7.2	—	—
Polyacrylonitrile-butadiene-styrene	3.5	0.7	0.0039

TABLE IV. ELASTIC CONSTANTS OF RIGID POLYMERS

Polymer	Poisson's Ratio	Shear Modulus	Bulk Modulus	Young's Modulus
Polyepoxide + MPDA	0.38	1.83	7.13	5.05
Polyhexamethylene adipamide	0.40	1.43	6.53	3.99
Polycaprolactam	0.40	1.43	6.45	4.00
Polymethylmethacrylate	0.34	2.33	6.49	6.24
Polypropylene	0.34	1.54	4.37	4.13
Polyoxymethylene	0.40	1.43	6.59	4.01
Polyethylene, high density	0.41	0.91	4.54	2.55
Polystyrene	0.35	1.39	4.21	3.76
Polyepoxide + glass spheres II	0.30	1.18	2.56	3.07
Polyepoxide + glass spheres I	0.31	0.94	2.15	2.46
Polyacrylonitrile-butadiene-styrene I	0.39	0.90	3.64	2.49
Polyepoxide + glass spheres III	0.35	0.83	2.39	2.23
Polyacrylonitrile-butadiene-styrene II	0.40	0.67	3.23	1.89
Polyvinylidene fluoride	0.40	1.07	5.18	3.00
Polyester + water	0.43	0.44	2.94	1.25

All moduli in 10¹⁰ dyne/cm²

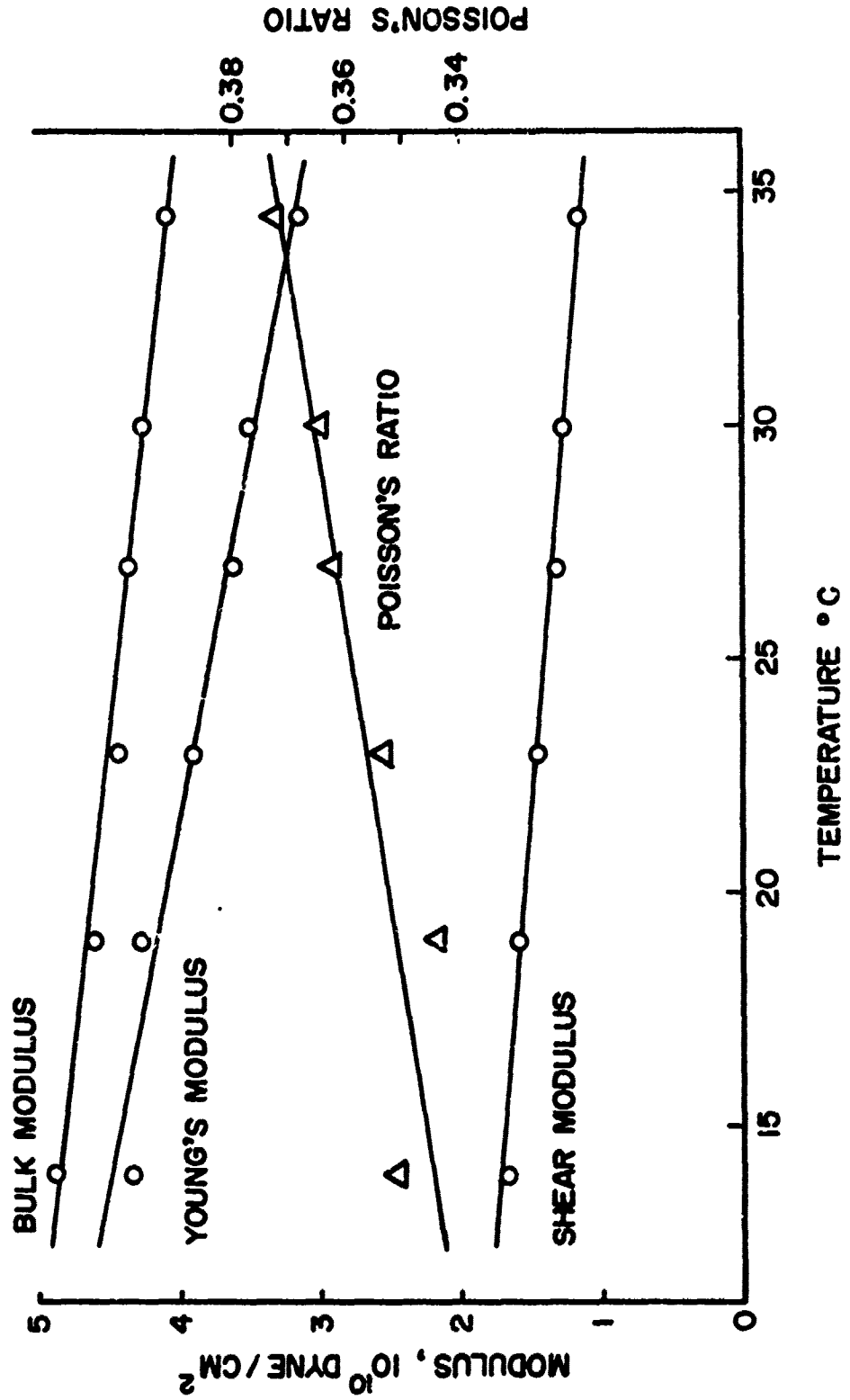


FIG. 1 ELASTIC CONSTANTS VS TEMPERATURE FOR POLYPROPYLENE

APPENDIX A

MATERIALS

All of the materials used in this work will be described in this section. Trade names are given for identification purposes only.

Polyepoxide: a reaction product of bisphenol-A with epichlorohydrin crosslinked with metaphenylene diamine. The resin was made by the Shell Chemical Company, New York, New York, under the trade name Epon 828.

Polyhexamethylene adipamide (Nylon 6-6): a highly crystalline polymer made by the Dupont Company, Wilmington, Delaware, under the trade name Zytel 101.

Polycaprolactam (Nylon 6): a highly crystalline polymer made by the Allied Chemical Corporation, Morristown, New Jersey, under the trade name Plaskon 8200.

Polymethylmethacrylate: an amorphous polymer made by the Rohm and Haas Company, Philadelphia, Pennsylvania, under the trade name Plexiglas II UVA.

Polypropylene: a highly crystalline polymer made by the Avisun Corporation, Marcus Hook, Pennsylvania, under the trade name Avisun 1010.

Polyethylene, high density: a highly crystalline polymer made by the Allied Chemical Corporation, Morristown, New Jersey, under the trade name FF-001.

Polyoxymethylene: a highly crystalline polymer made by the Dupont Company, Wilmington, Delaware, under the trade name Delrin.

Polystyrene: an amorphous polymer made by the Dow Chemical Company, Midland, Michigan, under the trade name Styron 666.

Polyepoxide + glass spheres II: a syntactic foam made of hollow glass spheres in an epoxy resin made by the Hysol Corporation, Olean, New York, under the trade name C8-5388 with H2-3551 hardener.

Polyvinylbutyral: an amorphous polymer made by the Dupont Company, Wilmington, Delaware, under the trade name Butacite.

Polyethylene oxide: a highly crystalline polymer supplied in powder form by the Union Carbide Corporation, New York, New York, under the trade name WSR-301. 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.

Polyepoxide + glass spheres I: a syntactic foam made of hollow glass spheres in an epoxy resin made by the 3M Company, St. Paul, Minnesota, under the trade name Scotchcast XR-5090.

Polyacrylonitrile-butadiene-styrene I: a terpolymer made by the Marbon Chemical Company, Washington, West Virginia, under the trade name Cycolac T-1000.

Polyepoxide + glass spheres III: a syntactic foam made of hollow glass spheres in an epoxy resin made by the Hysol Corporation, Olean, New York, under the trade name C8-5388 with H-3737 hardener.

Polyacrylonitrile-butadiene-styrene II: a terpolymer made by the Marbon Chemical Company, Washington, West Virginia, under the trade name Cycolac H-1000.

Polyethylene, low density: a highly crystalline polymer made by the Columbian Carbon Company, New York, New York, under the trade name EF403.

Polyvinylidene fluoride: a highly crystalline polymer made by the Pennsalt Chemicals Corporation, Philadelphia, Pennsylvania, under the trade name Kynar.

Polyester + water: an unsaturated polyester (from isophthalic and maleic acids with propyl and dipropyl glycol) and styrene which has been emulsified with water, trapping the encapsulated water. The polymer used here was 50% water and was made by the Ashland Chemical Company, Columbus, Ohio, under the trade name WEP661P.

Polytetrafluoroethylene: a highly crystalline polymer made by the Dupont Company, Wilmington, Delaware, under the trade name Teflon.

The next six materials are rubbers. Except as noted, these materials were all compounded with carbon black and various other fillers, and were obtained as a commercial product. Only the rubber itself will be described below.

Butyl rubber: a copolymer of isobutylene with a small amount of isoprene added in order to make it vulcanizable.

Neoprene: generic name denoting rubberlike polymers of chloroprene (2 chloro-1,3 butadiene).

Polybutadiene: a research sample with a 1,2 polybutadiene content of 65% kindly supplied by the Firestone Tire and Rubber Company, Akron, Ohio.

Natural rubber: a high molecular weight polymer of isoprene, in which essentially all the isoprenes have the cis-1,4 configuration.

Polycarboranesiloxane: a cross-linked siloxane polymer with metacarborane incorporated into the backbone after every two siloxane groups. Supplied by the Olin Company, Stamford, Connecticut, under the trade name Dexsil 200.

Polydimethylsiloxane: an unfilled silicone rubber.