

AD 686 388

**SINGLE SPECIMEN DETERMINATION OF YOUNG'S AND
BULK MODULI OF POLYMERS**

Robert W. Warfield, et al

**Naval Ordnance Laboratory
White Oak, Maryland**

February 1969

UNCLASSIFIED
NOLTR 68-212

SINGLE SPECIMEN DETERMINATION OF YOUNG'S AND BULK MODULI OF POLYMERS

Prepared by:
Robert W. Warfield
Joseph E. Cuevas
F. Robert Barnet

ABSTRACT: A new method is presented for the rapid and consecutive determination of the Young's and bulk moduli of polymeric solids in compression loading. Usually these properties are determined by separate measurements. However, by using an undersized specimen in a standard bulk compressibility tester it is possible to determine both moduli on the same specimen in a single test procedure. Initial loading of the undersized specimen results in a decrease in length and an increase in diameter. From these changes Young's modulus may be calculated. Once the bore of the tester is filled, the application of additional pressure results in a decrease in the volume of the polymer from which the bulk modulus may be calculated. Both determinations may be made within minutes. The moduli values are in general agreement with published values and the calculated values for Poisson's ratio fall into the expected range.

APPROVED BY:

F. Robert Barnet
Chief, Non-Metallic Materials Division

CHEMISTRY RESEARCH DEPARTMENT
U. S. NAVAL ORDNANCE LABORATORY
WHITE OAK, MARYLAND

UNCLASSIFIED

NOLTR 68-212

13 February 1969

SINGLE SPECIMEN DETERMINATION OF YOUNG'S AND BULK MODULI OF POLYMERS

The data presented in this report are of a research nature. A new and unique multi-modulus method is given whereby Young's and bulk moduli of polymeric materials can be readily determined. Because of the compatibility of these data, a more reasonable value for Poisson's ratio may be calculated.

It is expected that this technique will become most useful. In particular it permits basic property determinations towards an increased understanding of materials performance. Much use of this method should also be found in the selection and specification of materials for ordnance applications involving compression loading. In theory, the concept should be applicable to any material. But, in practice, there are obvious technical difficulties in working with materials having very low Poisson's ratios. The data presented herein are estimated to be accurate to within $\pm 5\%$.

This work was performed under Task FR-76 as part of an investigation of the solid state properties of polymers. It was accomplished during the period from December 1966 to March 1968.

E. F. SCHREITER
Captain, USN
Commander

Albert V. Lightbody
ALBERT LIGHTBODY
By direction

UNCLASSIFIED
NOLTR 68-212

CONTENTS

	Page
INTRODUCTION	1
YOUNG'S MODULI, BULK MODULI, AND POISSON'S RATIOS OF SOLID POLYMERS.....	1
EXPERIMENTAL.....	3
MATERIALS.....	4
RESULTS AND DISCUSSION.....	4
CONCLUSIONS.....	9
RECOMMENDATIONS.....	9
ACKNOWLEDGEMENT.....	10
APPENDIX A - DESCRIPTION OF MATERIALS USED.....	A-1

ILLUSTRATIONS

Figure	Title
1	Compressibility Tester
2	Stress-Strain Plot for Polystyrene
3	Stress-Strain Plot for A Polyepoxide Polymer
4	Stress-Strain Plots for A Grooved Sample of Polystyrene

TABLES

Table	Title
1	Polymers Studied
2	Young's Modulus, E, Bulk Modulus B, and Poisson's Ratio, μ , for Polymers
3	Young's Modulus, E, Bulk Modulus, B, and Poisson's Ratio, μ , for Polystyrene and Polyethylene

UNCLASSIFIED

NOLTR 68-212

REFERENCES

1. See for example, Wostl, W. J., Buehler, R. J., and Dresser, T., *Rev. Sci. Inst.*, 37, No. 12, 1665(1966).
2. Bondi, A., *J. Phy. Chem.*, 70, 530(1966).
3. Leonard, R. W., *The Journal of the Acoustical Soc. of America*, Vol. 40, No. 1, 160 (1966).
4. Koster, W., and Franz, W., "Poisson's Ratio for Metal and Alloys," *Metallurgical Reviews*, Vol 6, No. 21, (1961) p 1.
5. Matsuoka, S., and Maxwell, B., *J. Polymer Sci.*, 32, 131 (1958).
6. Nielsen, L. E., *Mechanical Properties of Polymers*, Reinhold, New York, N. Y., 1962, pp 3-4.
7. Mason, W. P., *Physical Acoustics*, Vol. II, Academic Press, Inc., New York, N. Y., 1964, 1965.
8. Roark, Raymond J., *Formulas for Stress and Strain*, McGraw-Hill Book Co., Inc., 1954, p 10.
9. Seely, F., and Smith, J., *Advanced Mechanics of Materials*, John Wiley and Sons, 1959, p 69.
10. Warfield, R. W., *Polymer Eng. and Sci.*, 6, No. 2, 176 (1966); *J. Applied Chem.*, 17, 263 (1967).
11. Warfield, R. W., Cuevas, J. E., and Barnett, F. Robert, *J. Applied Polymer Sci.*, 12, 1147 (1968).
12. Zemansky, M. W., *Heat and Thermodynamics*, McGraw-Hill, New York, N. Y., 1957, p 133.
13. Ferry, J. O., *Viscoelastic Properties of Polymers*, Wiley, New York, N. Y., 1961, p 101.
14. Warfield, R. W., Pastine, J. D., and Petree, M. C., to be published.
15. O'Reilly, J. M., *J. Polymer Sci.*, 57, 429 (1962).
16. Ishai, O., and Cohen, L. J., *J. Composite Materials*, Vol 2 No. 3 (July 1968), p 302-315.
17. Vincent, P. I., in *Physics of Plastics*, Ritchie, P. C., Ed., Van Nostrand, Princeton, N. J., 1965, p III.
18. Anand, J. N., *J. Macromol. Sci. -Phys.*, B1, No. 3, 445 (1967).
19. Weir, C. B., *J. Res. Natl. Bur. Stand*; 46, 207 (1951).
20. Schuyer, J., *J. Polymer Sci.*, 36, 475 (1959).
21. Tobolsky, A. V., *Properties and Structure of Polymers*, John Wiley, New York, N. Y., 1960, p 4.
22. Du Pont Technical Literature on Polyimide Plastic (1967).
23. Novak, R. C., and Bert, C. W., *J. Composite Materials*, Vol. 2 No. 4 (Oct 1968) p 506-8.
24. Resnick, I., *Modern Plastics*, 43, 144 (1965).

INTRODUCTION

Recently, techniques^{1,2} have been developed for the isothermal determination of moduli characteristics. But these and previous methods require different specimens, different apparatus, and different procedures for each measurement. As a result, when such moduli data are used in calculating Poisson's ratio (μ) values, uncertainties may be introduced. In particular, these uncertainties may result from variations between specimens and because of differences in the rates of loading between tests. Such uncertainties may well be one reason for some of the unusual Poisson's ratio data to be found in the literature.³ Thus, there is a need for a method of determining multiple moduli on a single specimen in the same apparatus under given conditions. Then more realistic values of μ would become obtainable. These same arguments are also stated by Koster and Franz⁴.

Based upon compression loading in a Matsuoka-Maxwell type apparatus⁵, we have developed a new static isothermal technique for rapidly determining Young's modulus (E) and bulk modulus (B) on solid polymers. Values for E and B on a series of representative materials all check well with the limited amount of data available in the literature which is suitable for comparison purposes. The Poisson's ratios calculated from these moduli are all in the expected range. Preliminary tests also indicate that this method will be useful in measuring moduli for composites having μ 's near 0.3. The various ramifications of this new concept are discussed below.

YOUNG'S MODULI, BULK MODULI, AND POISSON'S RATIOS OF SOLID POLYMERS

All polymers belong to the class of solids whose stress-strain behavior may be broadly described as visco-elastic. That is, in addition to having some of the characteristics of viscous liquids, they also have some of the characteristics of elastic solids. Thus at very low stress and strain levels, such materials have stress-strain behaviors very closely described in equation (1)⁶:

$$\sigma = K\dot{\epsilon} \left(1 - e^{-\frac{E\epsilon}{K\dot{\epsilon}}} \right) \quad (1)$$

where σ is the stress, K is the rate of strain, η is the viscosity of the polymer, E is the modulus, and ϵ is the strain. If we expand the exponential of equation (1) we obtain:

$$\sigma = K\dot{\epsilon} \left(\frac{E\epsilon}{K\dot{\epsilon}} + \frac{E^2\epsilon^2}{2K^2\dot{\epsilon}^2} - \frac{E^3\epsilon^3}{6K^3\dot{\epsilon}^3} + \dots \right) \quad (2)$$

Then, ignoring terms higher than first order, equation (2) reduces to the well-known relationship:

$$\sigma = E\epsilon \quad (3)$$

UNCLASSIFIED
NOLTR 68-212

Essentially we can now say that for a linear visco-elastic material, mechanical performance is describable to the first approximation by Hooke's law.

For Hookean solids, Young's modulus is defined as the ratio of tensile stress to tensile strain:

$$E = \frac{\text{Tensile Stress, } (\sigma)}{\text{Tensile Strain, } (\epsilon)} = \frac{\text{Force per unit Area}}{\text{Stretch per unit Length}}$$

or

$$E = \frac{F/A}{\Delta l/l} \quad (4)$$

where F is the tensile force, A is the cross sectional area, and Δl is the change in length per unit length, l , due to F . Although E is usually determined in tension it may also be determined in compression⁶ and the same general modulus equation holds for this latter case.

The second modulus of present interest is the bulk modulus, B . It is defined as the ratio of the hydrostatic pressure, P , to the volume strain as follows:

$$B = \frac{\text{Hydrostatic Pressure, } (P)}{\text{Volume Strain}} = \frac{\text{Hydrostatic Pressure}}{\text{Volume Change per Unit Volume}}$$

or

$$B = \frac{P}{\Delta V/V_0} = \frac{PV_0}{\Delta V} \quad (5)$$

where P is the hydrostatic pressure, V_0 is the original volume of the solid and ΔV is the change in volume caused by P . Generally B is determined by a hydrostatic measurement although it can be also determined by sound velocity techniques.⁷ A mathematical approach has also been developed by Bondi.² Using corresponding states correlations, it allows one to estimate B of liquids and polymer melts to within $\pm 10\%$. Lack of good experimental data in the past has necessitated the development of methods such as this latter one.

Once E and B are obtained it is then possible to calculate Poisson's ratio (μ) from the values of the two moduli. Poisson's ratio is defined as "the ratio of lateral unit strain to longitudinal unit strain, under the condition of uniform and uniaxial longitudinal stress within the proportional limit."⁸

$$\mu = \frac{\text{Change in Width per unit Width}}{\text{Change in Length per unit of Length}} = \frac{\Delta C/C_0}{\Delta l/l_0} \quad (6)$$

where C_0 and ΔC are the original width and the change in width, and l_0 and Δl are the original length and the change in length. To calculate μ , the classical relationship⁴ involving μ , E , and B is used in the following form:

$$\mu = \frac{1}{2} - \frac{E}{6B} \quad (7)$$

It can be demonstrated mathematically that μ may only take values between the limits of -1.0 and 0.5.⁹ For liquids with very little change in volume upon compression, μ equals 0.50. And in general, most polymers have values of μ in the range of 0.35 to 0.49. There are no known real elastic materials with negative values of Poisson's ratio.

EXPERIMENTAL

For some time we have been measuring the compressibility of polymers¹⁰ using a modified Matsuoka-Maxwell apparatus.⁵ Recently, we noted that under certain conditions, this apparatus could be used to consecutively determine both E and B on the same specimen in a single experiment.¹¹

The Matsuoka-Maxwell apparatus, shown in Figure 1, is of the piston displacement type. Briefly, it consists of an outside steel casing fitted with a hardened steel inner bushing, the inner surface of which is lapped and polished to 0.635 cm in diameter.

In preparation for an experimental run, a specimen 7.62 cm long and about 0.630 cm in diameter is inserted into the bore of the tester. Care is taken to insure that the specimen has adequate but not excessive clearance in the bore. Then conditions are maintained within the limits of Hooke's law and equations (4) and (5) are applicable to this experimental arrangement. (In our case, a clearance of 0.005 cm was found suitable for the visco-elastic materials while lesser clearances were needed for the stiffer and more brittle materials.) Then two case-hardened steel plungers 4.128 cm long and 0.635 cm in diameter are inserted into the open ends of the bore. The entire assembly is next placed in a testing machine and the specimen is loaded in compression by pressing down on the steel plungers. By measuring the plunger travel and the load, a stress-strain chart is automatically plotted. The normal loading rate is 0.064 cm per minute. Since we are chiefly interested in obtaining E and B at low pressures and under elastic conditions, we seldom apply loads in excess of 1000 kilograms.

It should be noted that all the present measurements were made at room temperature (approximately 25°C). At this temperature the amorphous polymers reported herein are well below their glass transition temperatures and are in the glassy state. However, when it is desired to obtain data at elevated temperatures, heating coils may be placed around the apparatus.

In the stress-strain plot for a polymer (Fig. 2), three stages will be noted. From the first stage, Young's modulus is calculated. This is done by drawing a tangent, T_1 , to the first stage of the plot. A normal, N_1 , is then dropped from a point of T_1 to the abscissa. The distance between its intersection and that of T_1 describes a characteristic specimen deformation Δl , for stage 1, for a force, F_1 , equivalent to the height of N_1 . This phase describes that part of the loading cycle during which the sample is under axial compression and gradually

UNCLASSIFIED
NOLTR 68-212

expanding radially and elastically to fill the bore of the tester. E is calculated using the equivalent of equation (4):

$$E = \frac{F_1 l_0}{A \Delta l_1} \quad (8)$$

where l_0 is the original specimen length, and A is the area of the plunger which transmits the load to the specimen.

The second stage of the plot develops at that time when the specimen completely fills the tester and can no longer expand radially in an unrestricted fashion. Under these conditions, it is under bulk compression loading and the slope of stage 2 is the bulk modulus. To obtain B, tangent T_2 is drawn and normal N_2 is dropped to the abscissa to determine Δl_2 , the change in length while under the compression conditions. Then the following relationship, the equivalent of equation (5), is used to calculate B:

$$B = \frac{F_2 l_0}{A \Delta l_2} \quad (9)$$

where F_2 is the force associated with the change Δl_2 in the specimen length.

In analyzing the results, the intermediate stage generally may be ignored. As will be shown later, this stage develops because of lack of perfection in specimen size and shape which may lead to an undesirable flow condition or simply because of the "barrel" deformation typical of materials in compression. It represents that period between the time at which the first part of a specimen becomes bulk constrained and the time at which the entire specimen becomes so constrained. The change in slope across this stage is of course a function of the difference between the values of E and B.

MATERIALS

The polymers chosen for this study were representative of amorphous, partly crystalline, highly crystalline, and crosslinked systems. A list of these materials indicating their types and approximate crystalline contents is given in Table 1. They are further discussed in Appendix A.

Most of the specimens for these materials were prepared from rod stock obtained from commercial sources. They were machined on a lathe to the required size. In the case of the polyester polymer, however, the specimens were cast to the desired size.

RESULTS AND DISCUSSION

A new technique for determining multiple moduli on single specimens is presented. Its applicability has been demonstrated by tests on 14 polymeric materials. Figure 2 shows a typical stress-strain plot for polystyrene made under ideal conditions. Similar curves but with variations in the intermediate stage were obtained for the other linear materials. The crosslinked materials show stress-strain characteristics as in Figure 3. When there is a serious

variation in specimen shape and size, a stress-strain plot like that of Figure 4 is characteristically obtained.

Table 2 presents values for E, B, and μ . In general, E and B are in excellent agreement with the limited amount of published data suitable for comparison purposes. E ranges from 0.7 to 4.7×10^{10} dynes/cm² while B ranges from 2.1 to 8.1×10^{10} dynes/cm². Values of μ range from 0.39 to 0.47. These latter values are in reasonable agreement with the literature in the very few instances where comparable data are to be found. They also fall in the nominally accepted range.

The static technique for determining multiple moduli as described herein is essentially isothermal. That is, the rate at which loading is applied is sufficiently slow to allow ample time for molecular motions to take place. Hence thermal equilibrium within the specimen is continuously assured throughout the test. This contrasts with dynamic tests which are almost always adiabatic.^{7,12} Usually, dynamic load cycles are more rapid than molecular relaxation times and so the chain segment motion cannot be completed in the time period of the measurement. There is, of course, a critical frequency for an isothermal-adiabatic transition which is dependent upon the material and somewhat upon the specimen dimensions. According to Ferry,¹³ this frequency can be as low as 0.1 cycles per second. Very often this distinction between isothermal and adiabatic conditions is ignored on the assumption that the observed differences are very small and hence negligible. While in some cases such differences have been found to be small indeed, we have recently noted instances wherein they are of the order of 20%.¹⁴

For most of the polymers considered in this report, E and B were determined at temperatures well below their T_g's. Thus, at best, configurational equilibrium was only approximated because true equilibrium is rarely if ever obtained due to the extremely long relaxation times involved. The only solution to this problem is to conduct the test at such a slow rate that the polymer can approximately and continuously adjust itself to its ever changing boundary conditions.

Toward this end, we selected a standard loading rate of 0.064 cm/min. This rate gives excellent compressibility isotherms both above and below the pressure and temperature range of the glass transition and the isotherms are consistent with T_g determinations. Such a rate is equivalent to a frequency of the order of one half a cycle per 900 seconds. At slower rates of loading - 0.025 cm/min - the isotherms are superimposable on those obtained at 0.064 cm/min. At rates greater than 0.254 cm/min, the nature of these curves is changed markedly, particularly for the crosslinked polymers. Thus we conclude that the 0.064 cm/min loading rate is satisfactory in assuring practical attainment of thermal and configurational equilibrium conditions.

Furthermore, it is possible to consider these measurements against the theoretical value for the pressure dependence of the glass transition under bulk compression. Various investigators have established that amorphous solids have a value for the derivative dT_g/dP, of about 0.025°/atmosphere.^{13,15} Since the pressure derivative is a function of pressure and temperature, it is possible from a series of isotherms to determine dT_g/dP. For many polymers, loaded at 0.064 cm/min, it has been found that dT_g/dP is equal to 0.024 - 0.030°/atmosphere. Hence, we must conclude that a loading rate of 0.064 cm/min permits the polymer to attain a state closely approximating equilibrium throughout a typical E and B determination.

UNCLASSIFIED
NOLTR 68-212

In the ideal case, one would expect only stages 1 and 2 to be present in a typical stress-strain plot. However, an intermediate stage is typically encountered as shown in Figure 3 for polyepoxide polymer. This intermediate stage occurs in between the region from which E is calculated and the region from which B is obtained. We feel that this intermediate stage occurs between the time that the first portion of the specimen fills the bore of the tester and the time that the last portion fills the bore. Such is possible as the specimen undergoes unrestricted compression and develops the characteristic "barrel" shape as noted by Ishai and Cohen.¹⁶ If the specimen is perfect, this maximum deformation will take place at its center. If it is tapered, it is reasonable to assume that upon loading, that part of the specimen having the greatest diameter will be first to fill the bore of the tester. Other sections of the specimen having lesser diameters will then successively fill the bore at somewhat later times and if the differences are sufficiently great, material yielding can occur. During this interval the stress-strain plot will exhibit an intermediate or transition stage.

To test the above, the following experiment was conducted. A polystyrene rod 6.60 cm long and 0.063 cm in diameter was prepared. Grooves, approximately 0.159 cm in depth and width were cut in the specimen at distances of about 1.58 cm, 3.18 cm, and 4.60 cm from one end. The specimen was then loaded to 1000 Kg at the standard loading rate giving the results as shown by Plot I of Figure 4. By inspection it is evident that the grooves on the specimen significantly magnified the intermediate stage. It also appeared that the dimensions of the specimen had been permanently changed.

At the conclusion of the first run, and without removing the specimen from the tester, we immediately repeated the run. These results are shown as Plot II of Figure 4. This plot is outwardly similar to a typical stress-strain plot. Upon removal of the specimen from the tester, it was noted that the three grooves were almost completely filled, that the diameter was the same as before, but that the length was shortened to 6.29 cm. Thus, the specimen showed a decrease in length due to the partial filling of the grooves. This lack of filling the grooves accounts for the greater compressibility indicated by the upper part of Plot II. Normally, this particular polymer would show no permanent change in dimensions, at a loading of only 1000 Kg. In fact, polystyrene has been taken to at least 10,000 atmospheres in bulk compression with no measurable dimensional effects.¹⁰

The presence of an exaggerated intermediate stage during the first run on the grooved specimen and its minimization on the second run is evidence that the above hypothesis is correct. Therefore, we conclude that this intermediate stage will be at a minimum with a perfect specimen but that inexact machining of the polymer rods may lead to irreversible flow in the material. In either case the intermediate stage in no way detracts from the usefulness of the multiple modulus technique.

Comparison of the E, B, and μ values obtained by this technique with literature values is desirable but difficult simply because very few data of this type have been reported. Furthermore, in those cases where data are available, they are not classified as being adiabatic or isothermal. In any event the sparseness of data and the uncertainties in it serve to make comparison difficult.

UNCLASSIFIED
NOLTR 68-212

However, a few moduli comparisons are possible. Nielsen⁵ gives values of E for three polymers on which we also have data. He failed to mention just how the data were obtained, nevertheless the values are compared below in units of dynes/cm x 10¹⁰.

<u>Polymer</u>	<u>E, (Nielsen)</u>	<u>E, (NOL Method)</u>
Polystyrene	3.4	3.4
Polymethyl Methacrylate	3.7	3.2
Polyhexamethylene Adipamide	2	1.8

As can be seen, the agreement is good. Also, Vincent¹⁷ gives an E value of 4.14×10^9 dynes/cm² for polytetrafluoroethylene which compares favorably with our value of 4.66×10^9 dynes/cm². Anand¹⁸ has recently reported a value of E for highly crystalline bulk polyethylene of 6.9×10^9 dynes/cm² which is in excellent agreement with our value of 7×10^9 dynes/cm². We conclude that, considering the limited amount of data available and the uncertainties in the nature of the published data, our results are satisfactory.

The same situation occurs as above when we attempt to compare values of B. In a few cases static values of the compressibility have been presented and the values agree with our results. For example, Weir's¹⁹ data, in units of dynes/cm² x 10¹⁰, compare with ours as follows:

<u>Polymer</u>	<u>B, (Weir)</u>	<u>B, (NOL Method)</u>
Polyethylene	4.06	4.5
Polytetrafluoroethylene	2.8	2.1

In addition, the results of Schuyer²⁰ indicate a value of 4.35×10^{10} dynes/cm² for polyethylene of density 0.954 which is identical in density to that which we used.

Of more general interest is the table of bulk moduli of many substances given by Tobolsky.²¹ Tobolsky shows that B for many relatively soft substances is in the range of 2 to 8×10^{10} dynes/cm². In this range we find such liquids as glycerin and water, metals such as sodium and potassium, and most polymers. As will be seen by inspection of Table 2 most of the polymers studies in this investigation have values of B in this range.

Apart from the previously noted uncertainties, extreme caution must be exercised in comparing E and B. Many polymers, particularly highly crystalline ones, exhibit considerable differences in their properties depending upon their thermal and pressure history. This is particularly true for polyethylene but, unfortunately, few workers report even the density when presenting their results.

UNCLASSIFIED
NOLTR 68-212

Poisson's ratio was calculated by means of equation (7) and the calculated values are presented in Table 2. Again, we are unable to compare our values broadly with published data due to the lack of work in this area. In the case of the polyimide we found a literature value of 0.45²² which is in satisfactory agreement with our value of 0.42. All the values presented in Table 2 appear reasonable. And because of the similar conditions of thermal and configuration equilibrium for both the E and B determinations, we believe that the μ values given in Table 2 are inherently more correct than those estimated from any two separate determinations of E and B.

It may also be noted from Table 2 that the data appear to separate by polymer category. This is particularly true in regard to the Poisson's ratio values. Amorphous and crosslinked polymers act much alike while the highly crystalline polymers differ. Although the present data, as is, seems to support such an analysis, they are too few to be conclusive. Also one would anticipate that anomalous materials will be found which will have atypical properties.

The NOL multi-modulus compression technique appears to be particularly well suited for experiments on materials which undergo reversible changes under pressure. For polymers of this type, the results obtained are reproducible. With polymers, which undergo irreversible changes, the results are less satisfactory. In general, polymers which tend to flow readily under pressure should not be studied by this technique although we have had some success with such solids when the compressibility tester tolerances were kept extremely small. Close tolerances make it difficult for the polymer to extrude up the bore of the tester.

As a check on the above, five "identical" specimens were prepared from a large slab of crystalline polyethylene and five others from a block of amorphous polystyrene. Every effort was made to prepare each specimen in the same manner. Then the E and B determinations were made on the same day using the same equipment.

The results are presented in Table 3. For the polystyrene specimens the data reproducibility is excellent - within $\pm 1\%$ - while for the polyethylene data it is not. These later data were only reproducible to within $\pm 5\%$ for E and μ and to $\pm 25\%$ for B. We attribute the data variability noted on polyethylene to the extreme sensitivity of this polymer to minor changes in its thermal and pressure history. Such changes are usually reflected in considerable differences in crystallinity. This is apparent from inspection of the specific gravity data. For example, sample number 3 had a specific gravity of 0.9506 while sample number 4 exhibited a value of 0.9217. It is also possible that some recrystallization occurred during the application of pressure. On the other hand, amorphous polystyrene is not sensitive to minor changes in its thermal and pressure history and it is possible to obtain excellent data reproducibility from a series of specimens.

Further indications of the worth of the multi-modulus technique can be inferred from the remarks of Novak and Bart.²³ These investigators reiterate the fact that the elastic properties of unfilled polymers (polyepoxides) differ in tension and compression. Thus, use of classical formula to predict shear modulus using mixed tension and compression data fails to give good values. They also state that the best agreement with experiment is obtained

UNCLASSIFIED
NOLTR 68-212

when only compression data are utilized in the classical formula. Otherwise this formula must be modified to permit use of a mixture of tensile and compression data.

In an effort to extend the usefulness of these measurements to materials other than bulk polymers we investigated the properties of a composite. Our initial studies were conducted on a polyepoxide syntactic foam having a density of 0.72 gm/cc. This material, as described by Resnick,²⁴ contained approximately 20 to 40% of microscopic hollow glass spheres (microballoons). Knowing the relative ease with which this material can be compressed, we used a maximum load of 150 kilograms instead of the usual 1000 kilograms. Under these conditions, and with an undersized specimen of diameter = 0.622 cm, we were able to obtain good E and B plots from which values of $E = 2.9 \times 10^{10}$ dynes/cm² and $B = 3.2 \times 10^{10}$ dynes/cm² were calculated. From these moduli, μ was found to be 0.35. These values appear reasonable.

Thus it would appear that the general multi-modulus technique can be applied to various types of reinforced plastics. However, several technical points remain to be explored before such an application can be fully supported.

CONCLUSIONS

Consideration of the results presented in this report have led to the following conclusions:

- a. The NOL multi-modulus compression method can be readily employed to determine both Young's and bulk moduli consecutively on the same specimen.
- b. The values obtained for both moduli appear reasonable and, where comparison is possible, are in agreement with published data. They, in turn, permit calculation of Poisson's ratio values.
- c. With the values of E, B, and μ , shear modulus (G) can also be calculated. Thus, from one test, all the elastic constants for a material can be either measured directly or calculated.
- d. It appears that this technique is well suited for viscoelastic solids having values of Poisson's ratio between 0.30 and 0.50.
- e. The method can also be applied to syntactic foam plastics and, very probably, to certain reinforced plastics.
- f. With amorphous polymers the data reproducibility by this technique is excellent.

RECOMMENDATIONS

It is recommended that additional data be collected on E, B, and μ . These should be accumulated on many different types of polymers and composites. Both the pressure and temperature dependence of E, B, and μ should also be determined.

UNCLASSIFIED
NOLTR 68-212

ACKNOWLEDGEMENT

The authors would like to express their appreciation to Dr. John O. Outwater of the University of Vermont and a Consultant to NOL. He played a major role in the interpretation of some of the original experimental data which led to the multi-modulus concept described above.

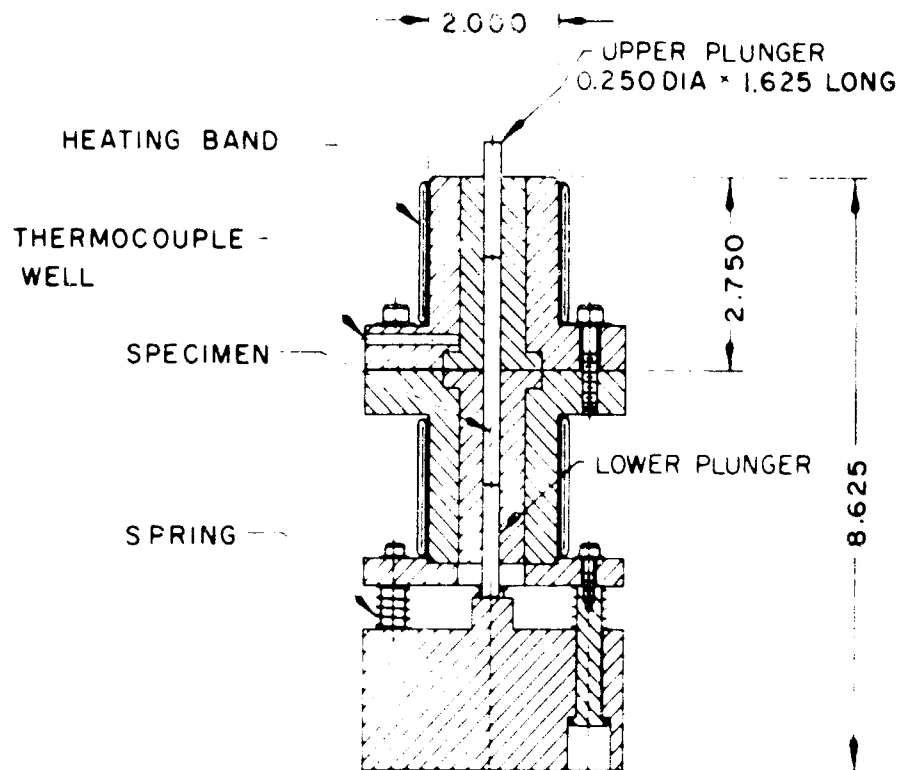


FIG.1 COMPRESSIBILITY TESTER

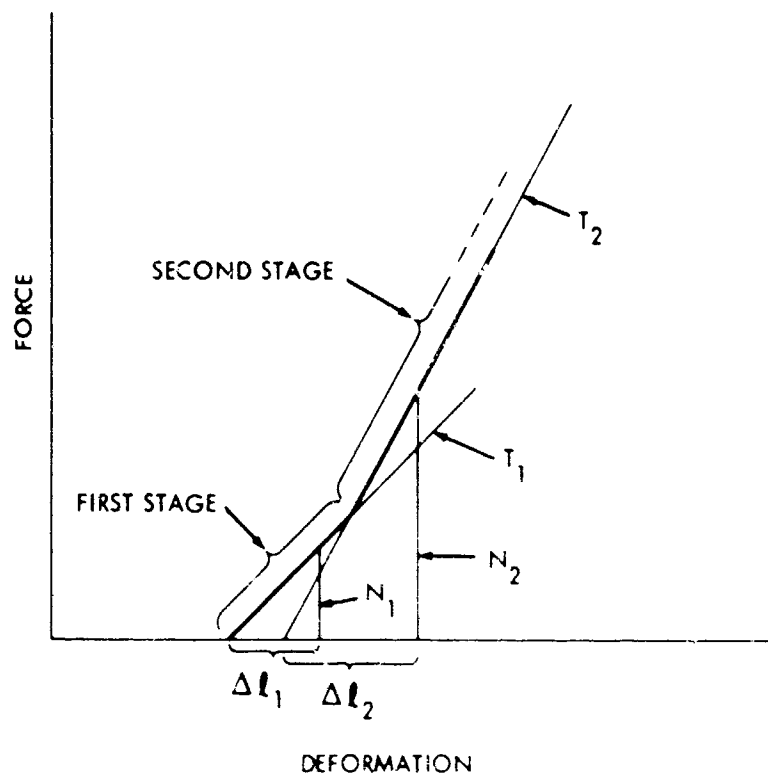


FIG.2 STRESS-STRAIN PLOT FOR POLYSTYRENE

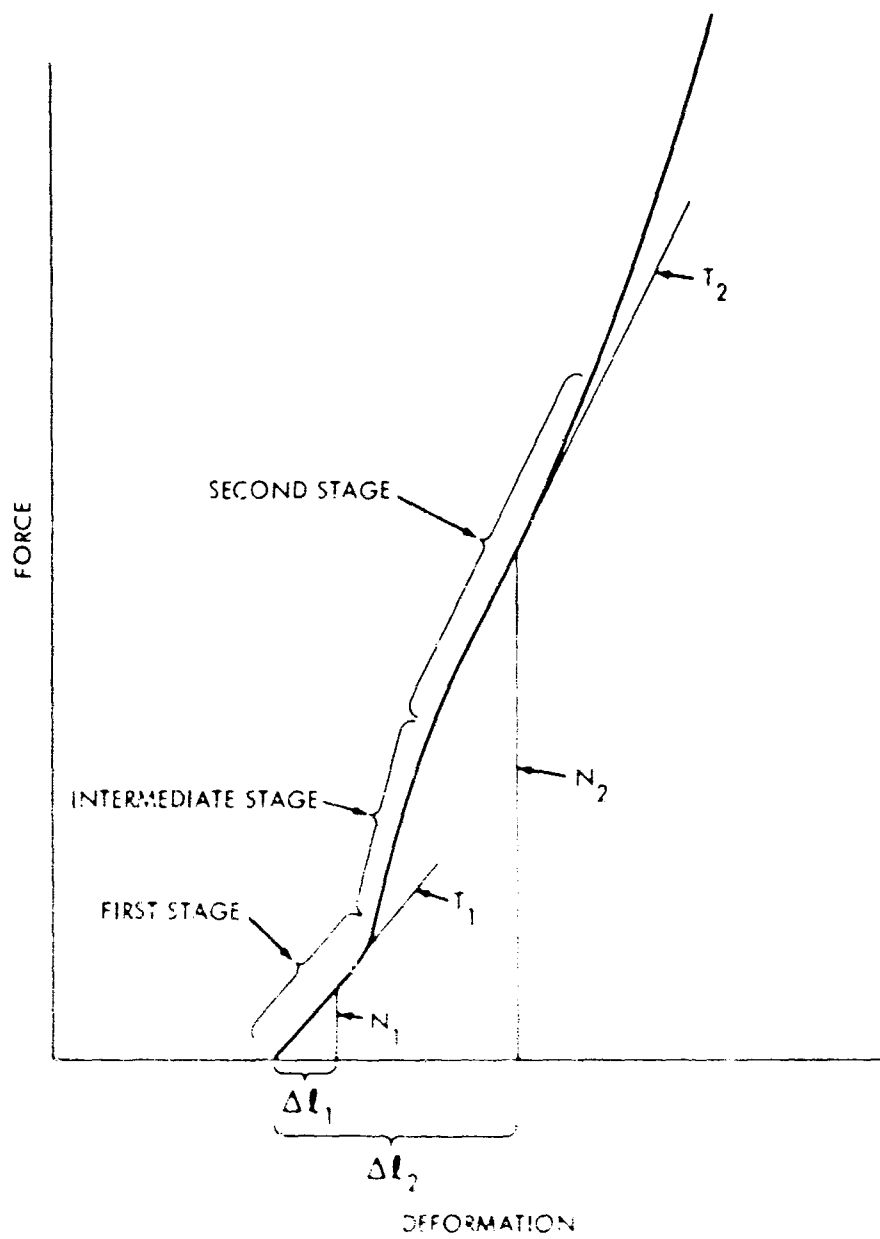


FIG. 3 STRESS-STRAIN PLOT FOR A POLYEPOXIDE POLYMER

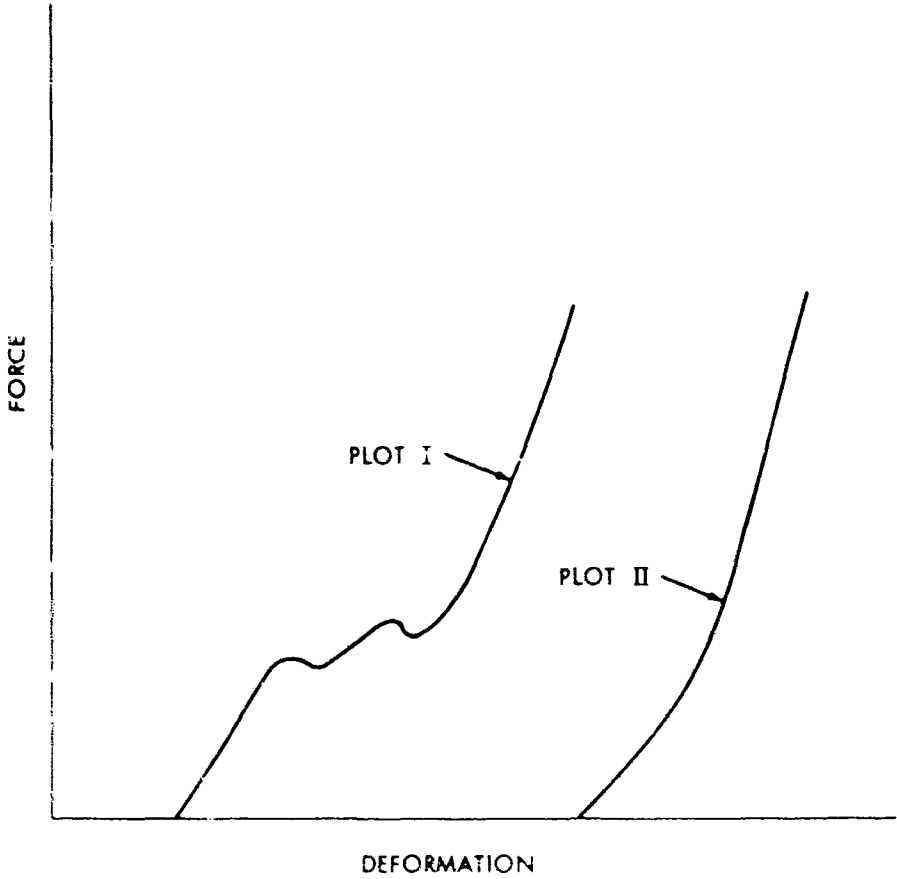


FIG. 4 STRESS - STRAIN PLOTS FOR A GROOVED SAMPLE OF POLYSTYRENE

TABLE 1

POLYMERS STUDIED

<u>Polymer</u>	<u>Type</u>	<u>Crystallinity</u>
Polystyrene	Linear, Amorphous	None
Polymethyl Methacrylate	Linear, Amorphous	None
Polyhexamethylene adipamide	Linear, Crystalline	~90%
Polychlorotrifluoroethylene	Linear, Crystalline	~90%
Polyethylene	Linear Crystalline	~ 60 to 90%
Polyimide	Amorphous	None
Polytetrafluoroethylene	Linear, Crystalline	~90%
Polyoxymethylene	Linear, Crystalline	~90%
Styron 475	Linear, Amorphous (contains a filler)	None
Polyepoxide + 12.6% of MPDA	Crosslinked, Amorphous	None
Polyepoxide ₁	Crosslinked, Amorphous	None
Polyepoxide ₂	Crosslinked, Amorphous	None
Polyepoxide + DDSA	Crosslinked, Amorphous	None
Polyester	Crosslinked, Amorphous	None

UNCLASSIFIED
NOLTR 68-212

TABLE 2

YOUNG'S MODULUS, E, BULK MODULUS B,
AND POISSON'S RATIO, μ , FOR POLYMERS

Polymer	E x 10 ⁻¹⁰ dynes/cm ²	B x 10 ⁻¹⁰ dynes/cm ²	μ
A. LINEAR AMORPHOUS MATERIALS			
Polystyrene	3.4	4.4	0.37
Polystyrene, Filled (Styron 475)	4.2	7.7	0.41
Polymethyl Methacrylate	3.2	5.1	0.40
Polyimide	3.0	6.0	0.42
B. LINEAR CRYSTALLINE MATERIALS			
Polyethylene	0.71	4.5	0.47
Polyhexamethylene Adipamide	1.8	8.1	0.46
Polychlorotrifluoroethylene	1.9	5.2	0.44
Polytetrafluoroethylene	0.47	2.1	0.46
Polyoxymethylene	2.7	6.9	0.44
C. CROSSLINKED MATERIALS			
Polyester	5.0	9.9	0.42
Polyepoxide ₁	3.5	6.4	0.41
Polyepoxide ₂	3.4	6.0	0.40
Polyepoxide + DDSA	3.1	4.4	0.38
Polyepoxide + MPDA	3.2	5.4	0.40

UNCLASSIFIED

UNCLASSIFIED
NOLTR 68-212

TABLE 3

YOUNG'S MODULUS, E, BULK MODULUS, B, AND POISSON'S RATIO, μ ,
FOR POLYSTYRENE AND POLYETHYLENE

<u>E X 10⁻¹⁰ dynes/cm²</u>	<u>POLYSTYRENE</u>	<u>POLYETHYLENE</u>
1	3.45	0.74
2	3.46	0.68
3	3.45	0.72
4	3.44	0.88
5	3.34	0.76
Average	3.43	0.76
C _v	0.0138	0.10
<u>B X 10⁻¹⁰ dynes/cm²</u>		
1	4.48	1.66
2	4.45	1.74
3	4.42	3.13
4	4.44	4.42
5	4.32	2.02
Average	4.42	2.59
C _v	0.0142	0.45
<u>μ</u>		
1	0.372	0.426
2	0.371	0.435
3	0.370	0.461
4	0.371	0.467
5	0.371	0.437
Average	0.371	0.445
C _v	0.0016	0.039
<u>Specific Gravity*</u>		
1	1.0522	0.9286
2	1.0523	0.9253
3	1.0525	0.9506
4	1.0521	0.9217
5	1.0520	0.9449
Average	1.0522	0.9343

* Measured after the compression tests had been run.

APPENDIX A

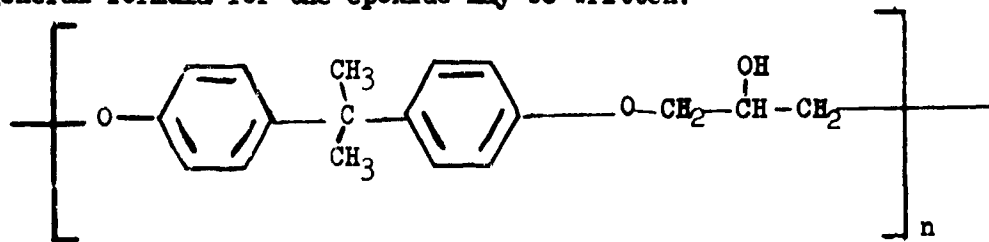
DESCRIPTION OF MATERIALS USED

Since the values of E, B, and μ are fundamental properties of polymers it is important that the polymers themselves be identified as closely as possible. Unfortunately many polymers, because of their complex structure, do not lend themselves to an exact description. For example, several different types of polyethylene exist and as a result wide differences are noted in such fundamental properties as density, crystallinity, melting point, etc. Almost all of the different types of polyethylene consist of long chains of methylene groups $[-CH_2-]$ yet with very minor changes in the chemistry, for example in the CH_2/CH_3 ratio, major differences in properties may occur. For the linear systems, a very brief description is given below. The crosslinked systems are more difficult to describe and when possible we have given a general formula for the monomer and such other information as are available.

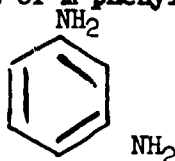
LINEAR POLYMERS

1. Polystyrene: an amorphous solid (Styron 666, Dow Chemical Corp.) having the repeating unit $[-CH(C_6H_5)CH_2-]_n$.
2. Polymethyl methacrylate: an amorphous solid (Rohm and Haas Corp.) having the repeating unit $[-CH(CH_3)(COOCH_3)CH_2-]_n$.
3. Polyhexamethylene adipamide: a crystalline solid having a high melting point ($>200^\circ C$) (Nylon 66, duPont Co.) with a repeating unit $[-NH(CH_2)_6-NHCO(CH_2)_4CO-]_n$ and a density of 1.156 gms/cc.
4. Polychlorotrifluoroethylene: a crystalline high melting solid (Kel-F, Minnesota, Mining and Manufacturing Co.) having a density of 2.148 gm/cc and the repeating unit $[-CF_2-CClF-]_n$.
5. Polyethylene: a highly crystalline solid which melts at about $127^\circ C$ and with a density of 0.954 gms/cm² (Marlex 5003, Phillips Chemical Co.). The repeating unit is $[-CH_2-]_n$.
6. Polyimide: a new amorphous polymer (duPont Co. SP-1).
7. Polytetrafluoroethylene: a highly crystalline polymer having a high melting point (Teflon, duPont Co.) having the repeating unit $[-CF_2-]_n$.
8. Polyoxymethylene: a crystalline polymer which melts at about $180^\circ C$ which has a repeating unit $[-CH_2-O-]_n$ (Delrin, duPont Co.).
9. Styron 475: a butadiene modified styrene polymer containing a filler (Dow Chemical Corp.).
10. Polyeepoxide + MPDA: an amorphous solid having a glass transition temperature of about $190^\circ C$. The epoxide (Epon 828, Shell Chemical Co.) is a diglycidyl

ether of bisphenol A with an epoxide equivalent within the range 185 to 205. The general formula for the epoxide may be written:

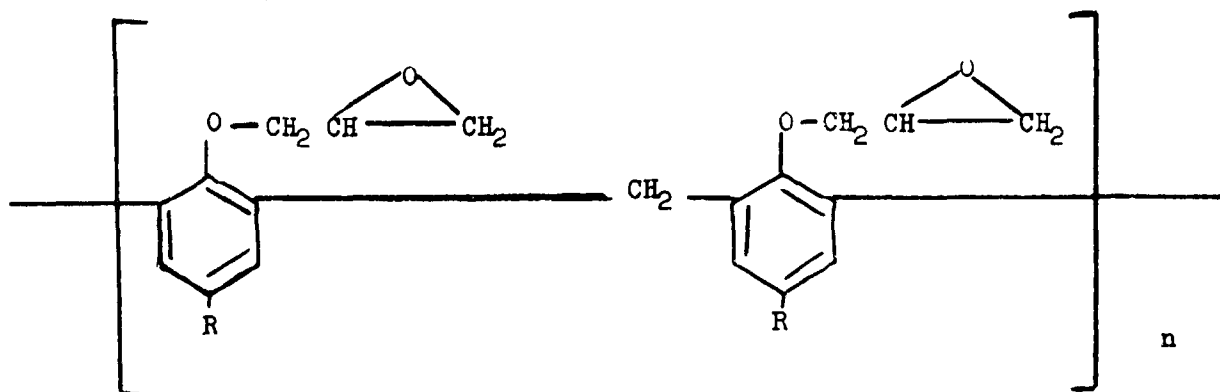


The epoxide was polymerized with 12.6% of m-phenylenediamine (MPDA).



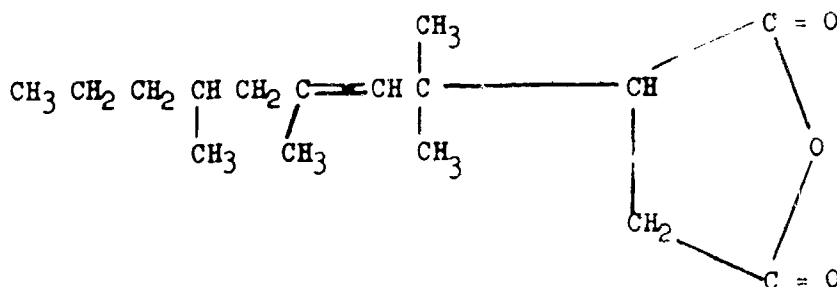
11. Polyepoxide₁: an amorphous solid, similar to the previous polyepoxide.

12. Polyepoxide₂: an amorphous copolymer which consists of an epoxylated Novolac resin (DEN 438, Dow Chem. Co.) having the general structure



and an epoxide (Epon 828). These two resins were copolymerized using $\text{BF}_3 \cdot \text{NH}_2\text{CH}_2\text{CH}_3$ as a catalyst.

13. Polyepoxide + DDSA: an amorphous polymer which is, in effect, a copolymer consisting of 40.5% of an epoxide (Epon 828) and 59.5% of dodecenylsuccinic anhydride (DDSA). DDSA has the structure



UNCLASSIFIED
NOLTR 68-212

14. Polyester: an amorphous solid which consists of 70% of an unsaturated linear polyester dissolved in 30% of styrene. The polyester component consists of a linear reaction product of the condensation of phthalic and maleic acids with propylene glycol. Crosslinking by the styrene was initiated by 1% of methyl ethyl ketone peroxide.

UNCLASSIFIED

Security Classification

DOCUMENT CONTROL DATA - R & D		
<i>Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified</i>		
1. ORIGINATING ACTIVITY (Corporate author) U. S. Naval Ordnance Laboratory White Oak, Silver Spring, Maryland		2a. REPORT SECURITY CLASSIFICATION Unclassified
		2b. GROUP
3. REPORT TITLE SINGLE SPECIMEN DETERMINATION OF YOUNG'S AND BULK MODULI OF POLYMERS		
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) Summary		
5. AUTHOR(S) (First name, middle initial, last name) Robert W. Warfield, Joseph E. Cuevas, F. Robert Barnett		
6. REPORT DATE 13 February 1969	7a. TOTAL NO. OF PAGES 19	7b. NO. OF REFS 22
8a. CONTRACT OR GRANT NO. MAT 03L 000/ROLL-01-01, Prob. 076	9a. ORIGINATOR'S REPORT NUMBER(S) NOLTR 68-212	
b. PROJECT NO.		
c.	10. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)	
d.	None	
10. DISTRIBUTION STATEMENT Distribution of this document is unlimited.		
11. SUPPLEMENTARY NOTES		12. SPONSORING MILITARY ACTIVITY Department of the Navy Bureau of Naval Weapons Washington, D. C.
13. ABSTRACT A new method is presented for the rapid and consecutive determination of the Young's and bulk moduli of polymeric solids in compression loading. Usually these properties are determined by separate measurements. However, by using an undersized specimen in a standard bulk compressibility tester it is possible to determine both moduli on the same specimen in a single test procedure. Initial loading of the undersized specimen results in a decrease in length and an increase in diameter. From these changes Young's modulus may be calculated. Once the bore of the tester is filled, the application of additional pressure results in a decrease in the volume of the polymer from which the bulk modulus may be calculated. Both determinations may be made within minutes. The moduli values are in general agreement with published values and the calculated values for Poisson's ratio fall into the expected range.		

DD FORM 1473

5 N. 0101-101-101-101

UNCLASSIFIED

Security Classification

UNCLASSIFIED

Security Classification

14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Elastic Constants, Young's Modulus, Bulk Modulus and Poisson's Ratio, Polymers, Solid State, Compressibility, Thermodynamic Properties, Amorphous Polymers, Crystalline Polymers, Crosslinked Polymers, Linear Polymers						

DD FORM 1473 (PAGE 2)

UNCLASSIFIED

Security Classification