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ELASTIC CONSTANTS OF BULK POLYMERS

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Elastic Constants of Bulk Polymers

The results presented in this report are of a research nature. It is expected that they will lead to a better understanding of polymer physics and aid materially in the selection and specification of polymeric materials for ordnance applications involving compression loading. The data presented herein are estimated to be accurate to within $\pm 5\%$ and as such, are practical for engineering use.

This work was performed under Independent Research Project MAT 03L-000-176-23-ZR011-01-01 as part of an investigation of the solid state properties of polymers. It is an extension of the work previously reported in references 1, 2, and 3.

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INTRODUCTION

Previously a "Multi-Modulus" technique was described for determining the Young's modulus (E) and the bulk modulus (B) of polymeric materials on a single specimen in a single compressibility experiment^{1,2,3}. Data on linear amorphous, linear crystalline, and cross-linked systems were reported and it was shown that Poisson's ratio ν , could be readily calculated from the two elastic constants. These data were then compared with other experimental data from the literature. It was concluded that the "Multi-Modulus" technique provides a novel and expeditious means for determining fundamental static elastic property data on a wide range of polymeric substances. The method eliminates the interspecimen variability problem, subsequently decried by Bonnin, et al⁴, and the data compare favorably with other data determined under similar isothermal conditions.

This report extends our previous work. Much of the past data is repeated for clarity of discussion and new data on polymers have been added. Extended discussions of these data and of the literature, further support the reliability of this experimental approach to the measurement of static elastic constants of polymers.

EXPERIMENTAL

The E and B data presented herein was determined on a Matsuoka-Maxwell compression-type apparatus⁵ and Poisson's ratio was calculated therefrom, as previously described^{1,2,3}. The new polymeric materials evaluated are indicated on Table 1.

RESULTS AND DISCUSSION

Values of E, B, and density for a series of polymers, determined at 25°C, are shown in Table 1. It was previously demonstrated^{2,3} that the precision in statically determining E and B for polystyrene was within $\pm 1\%$. However, for polyethylene this precision was no better than $\pm 5\%$ which may be attributed to the extreme sensitivity of this polymer to minor changes in its thermal and pressure history. Thus, the error in the Multi-Modulus technique is due primarily to polymer variability.

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TABLE 1

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

Polymer	Density gms/cc	E x 10 ⁻¹⁰ dynes/cm ²	B x 10 ⁻¹⁰ dynes/cm ²	μ
Polystyrene*	1.05	3.43	4.42	0.37
Polymethyl Methacrylate*	1.19	3.01	5.37	0.40
Polyisobutyl Methacrylate*	1.04	1.49	2.89	0.41
Poly(4,4'-dioxydiphenyl- 2,2-propane) carbonate	1.20	2.47	4.94	0.42
Poly(2,6-dimethyl-1,4- phenyleneoxide)	1.07	2.29	4.13	0.41
Polychlorotrifluoroethylene*	2.15	1.94	5.24	0.44
Poly-4-methyl Pentene-1	0.84	1.59	4.03	0.43
Polybutene-1	0.91	0.75	3.84	0.47
Polysulfone	1.24	2.62	5.30	0.42
Polytetrafluoroethylene*	2.22	0.47	2.11	0.46
Polyepoxide + MPDA**	1.21	3.21	5.40	0.40
Polyvinyl Butyral	1.11	2.66	4.22	0.40
Polyvinylidene Fluoride	1.77	1.72	5.36	0.45
Polycaprolactam	1.14	1.94	5.05	0.44
Polyethylene*	0.95	0.76	2.59	0.45
Polypropylene (Tisotactic)	0.91	1.42	3.48	0.43
Polypyromellitimide*	1.43	2.99	6.02	0.42
Polyoxymethylene*	1.43	2.70	5.90	0.44
Polyethylene Oxide	1.21	0.29	5.68	0.49
Polyethylene***	0.948	0.88	4.53	0.47
Poly-m-carboranylenedisiloxane	1.04	3.03	2.81	0.48
Polyethylene	0.921	0.20	3.39	0.49
<u>Polyurethane (Crosslinked)</u>	1.03	2.64	8.86	0.45

* Previously reported in references 1, 2, and 3

** Epon 828 (Shell Chemical Co.) Crosslinked with 12.6% of
 m-phenylene diamine.

*** Marlex 5003 (Philips Petroleum Co.) a very slightly branched
 polyethylene.

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Comparison of our experimental elastic data with those of other workers is impractical because of the dearth of such data and because of the difficulty in comparing static data with that obtained at various frequencies. Standard relationships⁶ are available for converting adiabatic E and B data to the corresponding isothermal data. However, the frequency dependence of E, and to a lesser extent of B, cannot be predicted. For example, this frequency dependence is seen in the data of Schuyer,⁷ who reported that the statically determined E for polyethylene is an order of magnitude lower than that found by sound velocity measurements at 2 MHz. Likewise, Davidse, et al,⁸ demonstrated that the dynamic E for polyethylene, determined by sound velocity measurements of 8 KHz, is three to four times greater than when obtained by static, tensile methods. Pastine⁹ has recently pointed out that shear relaxation effects cause the high frequency values of shear modulus (G_{Hf}) to differ appreciably for the low frequency values (G_{Lf}). The same would be expected to be true for E_{Hf} and E_{Lf} . However, this is not the case for the bulk modulus property as the B_{Hf}/B_{Lf} ratio does not differ appreciably from unity. Thus, while we cannot directly compare static values of E with those determined at high frequencies, we can, to a first approximation, compare static and dynamic B data.

In Table 2, values of E as determined by the Multi-Modulus technique are compared with values obtained by tensile creep and other very low frequency (static) measurements. Only in the case of polyethylene is there a significant difference between the various data and this may well be explained by the extreme sensitivity of this polymer to changes in its thermal and pressure history. From these comparisons we conclude that values of E determined by the Multi-Modulus technique are in satisfactory agreement with other reliable static values.

In the case of the bulk modulus, since B is not highly frequency dependent, it is possible to make first approximation comparisons of our static data with high frequency data, as suggested above. Table 3 shows that this comparison is reasonable and that our bulk modulus values agree with other published values. The B_{Hf} values cited in Table 3 are all adiabatic and can be easily converted to the corresponding isothermal values by standard relationships¹⁰. Thus, comparisons of B, can be made without serious regard to the value of the relaxation time of the polymer or the exact rate of loading used in making the measurements.

TABLE 2
 YOUNG'S MODULUS, E, OF BULK POLYMERS

Polymer	E x 10 ⁻¹⁰ , dynes/cm ²		
	By Multi-Modulus Techniques	By Tensile Creep Methods	By Other Methods
Polymethyl Methacrylate	3.01	3.08 (5)	--
Polypropylene	1.42	1.43 (5)	--
Poly-4-methyl pentene-1	1.59	1.59 (5)	--
Polyoxymethylene	2.70	3.04 (5)	--
Polyethylene	0.76	1.05 (5)	--
Polyethylene	0.76	--	0.98 (8)
Polyethylene	0.76	--	0.69 (14)
Polyethylene Oxide	0.29	--	0.28 (19)

Numbers in brackets are reference citations

TABLE 3
 BULK MODULUS, B, OF POLYMERS

Polymer	B x 10 ⁻¹⁰ , dynes/cm ²		References for High Freq. Methods
	By Multi-Modulus Technique	By High Frequency Methods (Hz)	
Polystyrene	4.42	4.0 (2.5 MHz)	16
Polyisobutyl Methacrylate	2.89	3.3 (2.5 MHz)	16
Polychlorotri- fluoroethylene	5.6	5.6 (2.5 MHz)	16
Polymethyl Methacrylate	5.37	6.1 (2.5 MHz)	16
Polymethyl Methacrylate	5.37	5.9 (6 MHz)	17
Poly(4,4'-dioxydi- phenyl-2,2-propane carbonate)	4.94	4.83 (6 MHz)	17
Polyoxmethylene	6.90	7.96 (6 MHz)	17
Polytetrafluoro- ethylene	2.11	2.11 --	18
Polycaprolactam	5.05	5.27 --	18

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Since both E and B are determined on the same specimen under the same experimental conditions in the Multi-Modulus technique, these two constants may be readily employed to calculate Poisson's ratio, μ . Use of the formula $\mu = \frac{1}{2} - \frac{E}{6B}$ is justified for this purpose as the same specimen is used in measuring both E and B, analogous conditions prevail, and the specimen is in a quasi-isotropic state, thus meeting the criteria set forth by Koster and Franz¹¹. The values of μ are then also free of inter-specimen variability and frequency dependence. Unfortunately, such is not the case for much of the published data. One often finds μ 's calculated from frequency dependent values of E_{Hf} and G_{Hf} or from values of B with only small frequency dependency combined with values of E with high frequency dependency. Also, different samples are frequently employed to determine each modulus. As Bonnin, et al,⁴ has recently pointed out this has had the effect of creating considerable confusion as to the true values of μ for polymers.

Shamov¹² recently considered this problem and pointed out the importance of considering the time dependence of μ . Measurements made at very high frequencies yield values of μ of about 1/3 whereas data obtained at very low frequencies yield values of μ asymptotically approaching $\frac{1}{2}$. Thus, depending upon the frequency at which the experimental values of the moduli were obtained, the value of μ for a polymer ranges from that of an elastic solid to that of a liquid. Shamov illustrates this point with a plot of the time-variation of μ for polyethylene (density = 0.955 gms/cc) and shows that after 100 minutes μ attains a value of about 0.45. Likewise, we have found the μ of polyethylene to be 0.45 at a density of 0.95 gms/cc.

Additional arguments for the validity of determining E by compression measurements have been presented by Novak and Bert¹³. These workers considered the variations in Young's modulus between samples of crosslinked polyepoxide when measured in tension and compression. They concluded that compression measurements gave the better results and they calculated a μ of 0.39. This value compares favorably with our value of 0.40 for a similar crosslinked polyepoxide.

CONCLUSIONS

The results presented in this report lead to the following conclusions:

- a. E and B values obtained using the Multi-Modulus technique closely agree with values determined by other techniques using a similar rate of loading.
- b. Since the bulk modulus exhibits little frequency dependence, static B data can be compared with dynamic B data as a first approximation. When this comparison is made, our results are in good agreement with other published data.

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c. Since the value of μ for a polymer is a function of the rate of loading and the measurements reported herein were all made over a much longer time period than the relaxation times of the polymers, it follows that in general the calculated values of μ should approach $\frac{1}{2}$. Since this is observed, our results may be said to exhibit Shamov's generalization.

RECOMMENDATIONS

The work should be broadened to include data on the elastic constants of rubbery polymers. Also, the pressure and temperature dependence of E, B and μ should be further explored.

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