Compressibility of Elastomers with Crystalline Fillers and Microvoid Inhomogeneities Related to Various Empirical Equations of State for Liquids and Solids

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Synopsis

Modified classical compressibility techniques are described which measure both the adiabatic and isothermal bulk moduli of polymers. These differ from familiar methods principally in the utilization of sensitive electronic deformation sensors (differential transformers) to assess volume changes, the autographic recording of pressure and volume changes during an essentially quasi-static pressurization cycle. The uniaxial and volumetric methods both characterize the compressibility behavior of polymers in the relatively low pressure region (0–100 atm.). Compressibility data for several well-known liquids and solids are reported. The nonlinear nature of the PV behavior of liquids are shown to be adequately characterized by a simple equation of state which is applicable to rubbery polymerics as well. Equations of state for polymers and filled polymers containing dispersed void inhomogeneities are discussed. Relationships based upon the infinitesimal theory of the deformations of an externally pressurized hollow sphere are compared with more complex equations of state which consider finite deformations at the center of a hollow sphere. It is concluded that the experimental data for the compressibility of voided solids containing less than 0.5% of initial void volume are best represented by the simpler equations of state derived from infinitesimal theory.

Introduction

The development of compressibility techniques has historically followed the path of least resistance. Equations of state for gases and their pressure–volume relations were investigated in the latter part of the 17th century. One hundred years later, John Canton reported "Experiments to Prove that Water is not Incompressible" in 1762.[1] By the early 1900's, the compressibility of many common liquids had been determined in the pressure range of a few hundred to a few thousand atmospheres. Indirect methods for measuring the bulk modulus of metals by measuring the change in length of internally pressurized tubes were described by Mallock[2] in 1904. Subsequently, more or less direct methods have been developed which measure the compressibility of a wide variety of solids.

Attempts to make direct measurements of the compressibility of solids by early investigators were hampered by the crude means available for determining the minute deformations involved. As an alternative, initial

emphasis was given to the development of high pressure apparatus whereby the hydrostatic compliance was increased to a measureable level. In this regard, the work of Bridgman in the field of high pressure physics is well known. Bridgman's reports,[3] generally issued before 1950, still represent the only available compressibility data for a great many solids, including various rubbers and polymers. These data are principally for the pressure range above 2,000 atm. and are only of general interest in assessing the PV behavior of materials near atmospheric pressure. Similar data for various natural and synthetic rubbers were reported by Weir[4] between 1950 and 1955. These data were principally for the region above 1000 atm. Such attempts as were made by Weir to measure compressibility near atmospheric pressure were reported as semiqualitative because of the large errors involved with the operation of the high pressure equipment at low pressure levels.

Solid rocket propellants represent a class of composite materials whose compressibility behavior at low pressures must be known to relate to their overall mechanical performance in solid rocket motors. These materials are exposed to hydrostatic stresses (rocket chamber pressures) of 100 atm. or less in most cases. Composite solid propellants are generally prepared by mixing large volume fractions of crystalline oxidizer into a liquid polymer under vacuum. The mixture then solidifies, generally in a mold, as the liquid ingredient polymerizes. Complete wetting of the crystalline ingredients by the polymer or binder is not always achieved in processing. The resulting spaces at the unwetted surfaces are referred to as vacuoles or microvoids. Suitable methods for characterizing the compressibility of these materials near atmospheric pressure will be described in this paper.

Low pressure compressibility techniques are necessary to study the effect of various inhomogeneities in solid materials where complete consolidation is more the exception than the rule. This report will be concerned with the small amounts of gaseous inclusions or vacuoles which are common to rubberlike substances and composites rather than with the vacancy or lattice defects of crystals. In high pressure tests, the gaseous inclusions or voids may contribute what amounts to a negligible portion of a material's total compliance, whereas at lower pressures, particularly at the onset of pressurization, such inclusions are a controlling factor in the PV behavior.

Composite solid propellants are a very special class of materials, but the low pressure methods which were developed to study their compressibility are believed to have wide application. Perhaps the most interesting feature of the compressibility techniques to be described is the facility for measuring both the adiabatic and isothermal PV behavior of materials in the same apparatus. Contributions of recent investigators such as Foster et al.,[5] Hellwege et al.,[6] Heydemann et al.,[7] and Wood and Martin[8] to the field of polymer compressibility are recognized. No attempt has been made to draw a complete comparison between the methods discussed in the literature and those described here.

Uniaxial Component of Compressibility

This system was developed by the author to study the stress-induced anisotropy of polyurethane rubber under hydrostatic compresssion. The results of this work were presented orally at the annual meeting of the Society for Experimental Stress Analysis in May 1960 and subsequently published[9] in the journal of the society. A more complete description of the method[10] was outlined in a report describing its application to the measurement of the bulk modulus of various plastics. Van der Wal et al.[11] utilize the identical system in studying the thermal expansion and compressibility of filled polymers. The method discussed here differs from that of Heydemann et al.[7] principally in the use of the linear variable differential transformer (LVDT) external to the pressure vessel, which is believed to be an experimental advantage.

The essential details of the apparatus for measuring a single component of the hydrostatic compliance are shown schematically in Figure 1. Rubbery or relatively flexible composite specimens are usually prepared that have a length to diameter ratio such as that illustrated (length/diameter ratio ≤ 4). This relatively short specimen is designed to slip-fit the bore of the pressure vessel and thereby minimize bending or buckling effects.
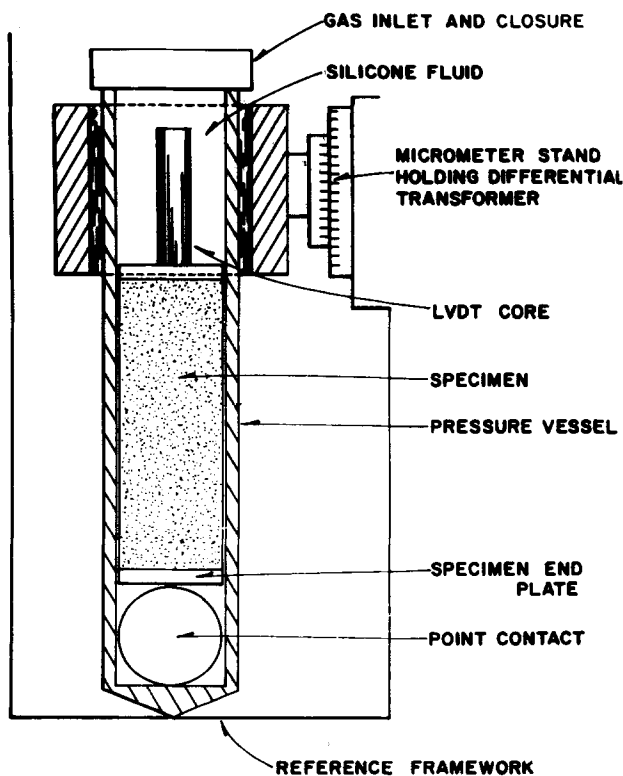

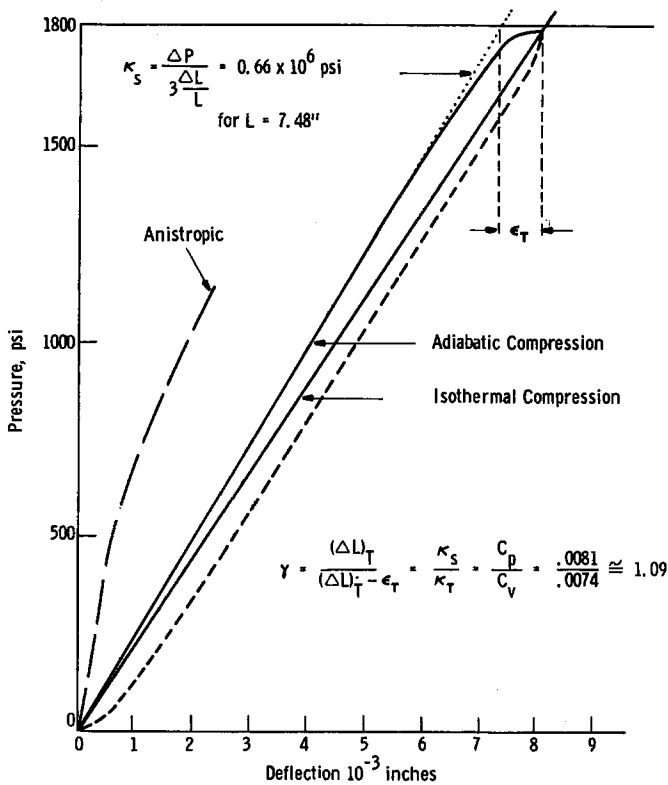Fig. 1. Schematic diagram of uniaxial bulk modulus tester.

Fig. 2. Uniaxial compliance data for Plexiglas.

When surrounded by the confining fluid that is ordinarily employed to minimize heating of the specimen from contact with the pressurizing gas, the specimen deflects freely along its length during the application of hydrostatic pressure. Metal end tabs or caps are cemented to the specimen ends as indicated. These ensure intimate and stable contact of the bottom of the specimen with the metal point in the base of the pressure vessel to which motion of the upper end of the specimen is referenced. The upper tab allows mechanical attachment of the LVDT core whose motion, relative to the external transformer, measures the deflection during a pressurization cycle. For the approximate specimen geometry shown in Figure 1, the end tabs or plates and LVDT core compressions contribute only a minor portion of the observed axial deformation. In this sense, the method is essentially a direct one, since it does not rely upon extensive corrections to the observed deformations in calculating the compliance. Better precision is obtained in measuring rigid plastics by using longer specimens, since buckling and bending is not a problem with long specimens of stiff materials. The metal end tabs may be eliminated and the transformer core attached directly to the specimen for either plastics or nonmagnetic metals.

Pressure–deflection records, such as that shown for poly(methyl methacrylate) (PMMA) rods in Figure 2, are obtained by continuous autographic plotting of the pressure and deflection transducer outputs in $X–Y$ fashion. The internal energy, and as a consequence the temperature, of a specimen increases with the application of hydrostatic pressure. However, the rate of pressurization can easily be adjusted to achieve a significant portion of the adiabatic PV response curve for materials of low thermal conductivity, as shown in Figure 2, before significant heat loss from the specimen to its surrounding can transpire. Pressurization rates of 500 psi/sec. are found to be quite satisfactory for polymeric specimens approximately 0.75 in. in diameter. This corresponds to a pressurization cycle of about 3 sec. duration. It is clear from Figure 2 that some effect of the heat lost from the adiabatically compressed specimen is evident in the latter portion of the cycle. This non-adiabatic region may be ignored and the adiabatic bulk modulus of the material calculated from the slope of the essentially linear initial portion of the response curve.

Isothermal data are obtained with this system by pressurization at very low rates where the internal energy released by the compression is continuously dissipated to the surroundings to the extent that no sensible temperature changes occur in the specimen. Alternatively, stepwise pressurization may be employed with sufficient delay after each step to allow thermal equilibrium to be restored in the system. The end points, at thermal equilibrium, of a succession of pressurization steps such as this will form the locus of the isothermal PV curve. This is not illustrated, and only a single pressurization cycle is recorded in Figure 2.

The calculation of the adiabatic bulk modulus for PMMA from the uniaxial deformation under hydrostatic pressure for the specimen length noted is made at the top of Figure 2. This calculation assumes that the material is isotropic and that all components of the compliance are equal and one-third the value of the bulk compliance in accord with infinitesimal theory. The strains involved in this calculation are of the order of 10^{-3}, and second-order terms which relate the uniaxial components of compliance to the bulk compliance are clearly negligible. The calculation of the adiabatic bulk modulus as shown on Figure 2 is then quite an accurate approximation from this point of view. Slight nonlinearities which are normal for the PV behavior of liquids, rubbers, and plastics like PMMA are not considered here, but will be discussed in a later section.

Similar considerations apply to the calculation of the isothermal bulk modulus from the data of Figure 2. The ratio of the adiabatic and isothermal moduli for PMMA are calculated as an example at the bottom of Figure 2. Since this ratio is also that of the specific heats at constant pressure and volume, the important thermodynamic parameter Gamma is measured for PMMA.

A dashed curve is also shown on Figure 2 and labeled "nonlinear." This curve is quite typical of the nature of the uniaxial component-of-compliance data that is often obtained for certain types of highly filled polymeric
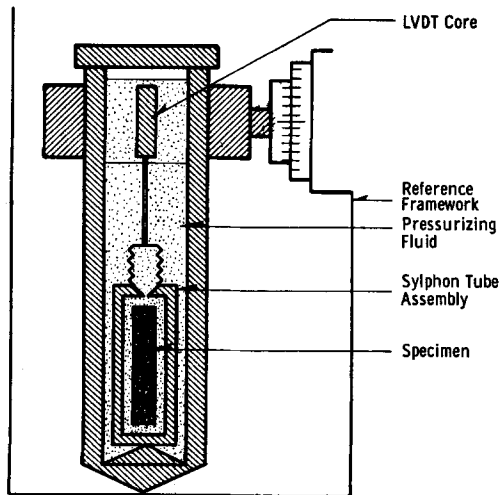
Fig. 3. Sylphon tube volumetric compressibility tester.

materials like solid propellants. The nature of the nonlinearity is found to depend upon the rate of pressurization for such materials. This indicates that the uniaxial responses of materials of this type are indeed inelastic in hydrostatic compression. The author has not explored the nature of this time-dependent effect except to determine that it does exist in the range of pressurization rates that are ordinarily employed with this system. It is interesting to note, however, that these same materials invariably evince a linear PV behavior when tested by volumetric methods, to be described, using the same range of pressurization rates as in the uniaxial case. The application of the multiaxial measurement system[9] that was applied to polyurethane rubber would undoubtedly provide data which would clarify the nature of the deformation of composite materials of this type under hydrostatic stress.

Some small effort has been made to apply the uniaxial compressibility technique to the characterization of materials which have an obvious basic material anisotropy. The author has studied the uniaxial component of compliance of composite materials which contain multitudinous needlelike metal inclusions. When these needles or staples are oriented predominately in a given plane of the bulk composite, the value of the uniaxial component of compliance of rodlike specimens, taken from a bulk sample, varies considerably under slowly applied hydrostatic stresses and depends upon the orientation of the staple ingredient. Combinations of the component compliances obtained for specimens in which the stable orientation is alternately parallel and perpendicular to the length of the specimen, result in calculated values of the bulk modulus which are only in fair agreement with that determined for the material from volumetric compressibility measurements. Supporting data for these remarks are not presented here but they are offered for whatever *ad hoc* value they may have in a general

discussion of the uniaxial component-of-compliance method for determining compressibility.

Volumetric Compressibility Methods

Compressibility, as an unqualified word in the literature of high pressure physics, implies hydrostatic stresses and concatenate measurements of the resulting volumetric deformation of a test material. Bridgman[12] describes a variety of volumetric compressibility techniques, all intended for use at high pressure.

Two modified classical compressibility methods are described for characterizing the compressibility of nonmetallic materials or materials that have bulk moduli less than a few million psi. The modifications consist basically of applying modern electronic techniques to the problem of measuring the minute fractional volume changes that occur in solids at relatively low pressures. Both methods utilize the LVDT system for deformation measurement discussed previously. Maximum pressures of 3,000 psi are employed with one system, while higher pressures, up to 15,000 psi, are used with the other in testing less compressible solids with comparable degrees of precision.

Continuous autographic records of pressure–volume behavior are obtained with both compressibility methods over their entire pressure ranges. These measurements originate at atmospheric pressure and are complete well below the point of the initial measurement in most high pressure data. Thus, the important region of compressibility near atmospheric pressure is explored. This is an especially important region to consider when solids are not completely consolidated and contain highly compressible inhomogeneities or voids.

Sylphon Tube System

The compressibility of materials that have bulk moduli as great as 1×10^6 psi may be satisfactorily characterized with a sylphon system like that shown schematically in Figure 3. This includes most fluids, polymers, and highly filled polymers such as contemporary composite solid rocket propellants.

A sylphon is a metal bellows affixed to a rigid tube or vessel. Volume changes of a fluid filling the sylphon are measured by deflections of the free end of the bellows as pressure is applied to the sealed tube. Since the deflection of the bellows presumes to measure the volume change within the tube, it is important that the reference end of the sylphon be immobile during pressure changes. This may be accomplished, as indicated in Figure 3, by resting the polished end of the sylphon upon a sharp metal point in the base of the close fitting pressure tube.

Volume changes of a solid specimen sealed in the sylphon under vacuum are obtained by subtracting the calculated volume change of the confining fluid from the total. This requires that the fluid be suitably characterized beforehand by an analytic PV relation or equation of state. Volume

changes for the solid may be obtained graphically by subtracting the response curves of the fluid–specimen recording from that of the fluid alone. Negative volume change corrections (less than 0.5%) to account for the compression of the tube are also applied. The pressure state within the sylphon is considered to be that measured for the surrounding transmitting fluid in the pressure vessel, minus a correction for the pressure gradient due to the spring-piston characteristics of the bellows. For the very flexible metal bellows that were used, this is negligibly small and gradients of internal and external pressure less than 10^{-3} are expected.

The sylphon tube of this system clearly replaces the rodlike specimen of the uniaxial method described in reference to Figure 1. The body of the differential transformer is again external to the pressurized cavity of the system and only the relatively incompressible metal core of the LVDT is exposed to the pressure. The uniaxial compliance of the core may be measured independently and applied as a correction to the total bellows deflection. This is ordinarily a negligible amount of the total bellows motion, however. The pressurizing tube or vessel must be fabricated from stainless steel or other nommagnetic materials to utilize this method for measuring deflection, whereby the main portion of the motion transducer is not exposed to the test pressure.

As in the uniaxial compliance system, pressurization rates may be controlled by throttling compressed gas into the pressure vessel inlet at various rates, or by hydraulic means. Continuous records of pressure versus bellows deflection are then drawn in X–Y fashion using an appropriate electronic recorder to monitor the pressure and deflection transducer electrical output signals. Such records are identical in character to those shown in Figure 2, but the deflection axis may be calibrated in terms of volume by referring to the volume–deflection relation established for the bellows.

A typical sylphon tube for determining the compressibility of solid propellants has an internal or cavity volume of about 1 in.³. This cavity size accommodates specimens 0.6 in. in diameter and 3.6 in. in length. Bellows units which have an unstrained length of 1.0 in. and nominal cross-sectional area of 0.320 in.² were also employed. This small bellows size allows sufficient precision in the pressure-deflection records to characterize the compressibility of materials having bulk moduli as large as 10^6 psi and containing initial void contents of 1 vol.-% or less.

Measurements of much better precision than those reported in this paper might be expected if a sylphon system of considerably larger volume than that described were utilized. The lower limit of practical sylphon size noted was selected in designing an apparatus for testing propellants because of the hazardous nature of the test. Such limitations would not apply to inert materials, and much more precise values of important thermodynamic parameters, such as the ratio of the bulk moduli or the ratio of specific heats, should be easily obtained with a similar system of larger volume. Most experimental errors of the method would be expected to diminish

with increasing specimen size to some limit based upon economic considerations.

Annular Pump System

The effective internal volume of a pressure vessel may be changed by forcing a piston through a sealing gland into the vessel cavity. The volume displaced depends upon the cross-sectional area of the piston, its displacement, and the rigidity of the vessel. The pressure which develops with intrusion of the piston depends upon the compressibility of the contained fluid, and of any solids in the cavity. This delineates the basic features of the annular pump compressibility measurement.

A system of this type for measuring the compliance of less compressible solids than those accommodated by the sylphon method described previously is shown schematically in Figure 4. A particular design used for testing solid propellants with pressures to 15,000 psi is shown in Figure 5. The pressurizing piston indicated schematically in Figure 4 is shown at the right of the photograph in Figure 5. The pressure transducer protrudes from the pressure vessel at the bottom of the unit. Low compliance pressure transducers and a massive pressure vessel are used to minimize gross volume change of the system with internal pressurization. Various commercially available pressure transducers of the attached strain-gage-bridge type are suitable for the autographic recording of pressure changes.

Gross volume changes in the system are determined continuously by monitoring the piston travel with an LVDT deflection transducer. When a solid specimen is sealed in the cavity with a confining fluid and pressurized at a controlled rate, its volume change at any pressure level is calculated by correcting the observed gross volume change record for the expansion of the cavity, compression of the pressurizing fluid, and compression of the
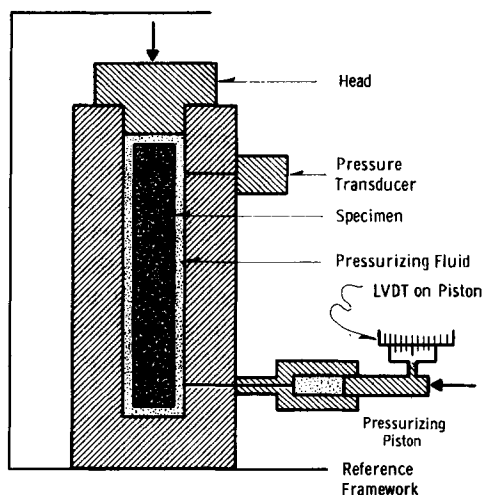

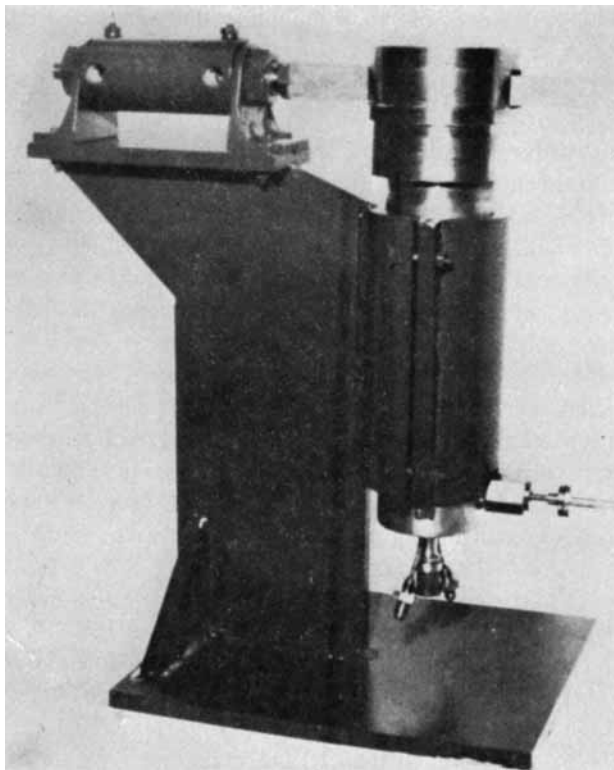Fig. 4. Annular pump volumetric compressibility tester.

Fig. 5. High-pressure volumetric compressibility.

piston seals and those used in the cavity closure plug.   These corrections
are generally substantially larger fractions of the total volume changes than
those which are needed for the sylphon system.   However, this method has
the advantage that larger fractional changes of volume can be measured
with a given precision than with the sylphon tube, which has a limited useful
range of bellows deflection or volume change capacity.   Thus, relatively
compressible specimens can be characterized even when they contain rela-
tively large amounts of initial void.   The sensitivity and precision of this
system depends basically upon the size and dimensional uniformity of the
piston.   The capacity for volume change increases with the effective intru-
sive length of the pressurizing piston as long as the volume fraction of the
confining fluid remains relatively small.   This method, aside from the
LVDT system and continuous recording of transducer output, is quite
similar to that described by Weir[13] in connection with the measurement of
rubber compressibility.

The system compliance may be determined experimentally from pres-
sure–deflection measurements of various combinations of confining fluid-
filler materials of known compressibility.   The difference between the
observed volume changes and those calculated for the standards, at various

pressure levels, represent the corrections to be applied subsequently. These corrections, which include the effects of the various compressible components, are found to be an essentially linear function of the pressure.

The pressure–volume change records obtained with the annular pump system are similar in appearance to those shown for the uniaxial data of Figure 2. Again, this method lends itself to the determination of both adiabatic and isothermal compressibility data, depending upon the rate of pressurization.

Theory of Compressibility and Application to Experimental Results

The bulk modulus is defined in theory of elasticity as

$$\kappa \equiv -V(\partial P/\partial V) \tag{1}$$

where P and V are the instantaneous hydrostatic stress and volume, respectively. The initial volume of the specimen at atmospheric pressure V_0 is customarily used as a reference in reporting bulk modulus values from experimental data rather than the instantaneous volume. The bulk modulus is then defined as

$$\kappa = -V_0(\partial P/\partial V) \tag{2}$$

The significant difference between the adiabatic and isothermal compressibility of poly(methyl methacrylate) that was discussed in connection with the data of Figure 2 is typical of that to be expected for most polymers. This difference is easily measured for fluids and polymerics by the methods described here, and is important to a complete and useful characterization of their compressibilities. It is customary to distinguish between the adiabatic bulk modulus, κ_S, for an isentropic process, and the isothermal bulk modulus, κ_T, by subscripting both the symbols for these moduli, and their related thermodynamic differentials $(\partial P/\partial V)_S$ and $(\partial P/\partial V)_T$. Much of the compressibility data in the literature have been obtained by stepwise pressurization techniques. Pressure–volume data, taken after thermal equilibrium was attained following each pressurization step, were then used to calculate the isothermal bulk modulus. Estimates of the adiabatic modulus have commonly been obtained by recourse to the familiar thermodynamic relations

$$\gamma = C_P/C_V = \kappa_S/\kappa_T \left[1 + (Tv\beta^2\kappa_S/C_P] = [1 + (\partial T/\partial P)_S\beta\kappa_S] \tag{3}$$

This approach requires a knowledge of the specific heat at constant pressure C_P, the specific volume v, and the bulk coefficient of thermal expansion β, at temperature T. With the methods described in this report, the parameter γ is obtained experimentally from the adiabatic and isothermal compressibility data. The other more easily determined properties of eq. (3) may then be used to calculate the specific heat, C_P, without recourse to calorimetric measurements in the usual sense. Experimental methods developed by the author to measure the thermodynamic differen-

tial $(\partial T/\partial P)_S$ of eq. (3) have been described[14] and will be published in more detail.

Ultrasonic or wave-propagation techniques are commonly used to obtain adiabatic compressibility data for liquids and polymers. Wood[8] discussed the somewhat qualitative manner in which such results must be compared with those from quasi-static compressibility measurements of the type described here. The adiabatic compressibility data reported for PMMA on Figure 2 and the isothermal data for glycerol and methyl alcohol given in Table I are in reasonable agreement with dynamic (1 Mc./sec.) bulk modulus values for these materials given in the literature, but are generally somewhat lower in value than the high-frequency moduli obtained from wave-propagation techniques. The isothermal bulk moduli of the liquids reported in Table I are converted to adiabatic values by the application of their well-known properties to eq. (3) for this comparison. The latter are in better agreement with values for the adiabatic bulk modulus of glycerine obtained by the method of co-worker Kostyrko,[15] who utilizes wave-propagation techniques of uncommonly low (50–500 kc./sec.) frequency.

The remaining discussion of this section will relate to the nonlinear nature of the compressibility of liquids in their role as confining fluids for volumetric methods. This will illustrate to some degree the meaning of Bridgman's remark, "Compressibility is a dirty business," and will include some further remarks regarding the factors which must be considered in applying the volumetric compressibility techniques which were described somewhat briefly before.

TABLE I

Curve-Fitting Parameters for Murnaghan's Equation
of State for Compressibility of Various Materials

	Initial bulk modulus, $\kappa_i \times 10^6$, psi	Coefficient of compressibility k	Nonlinearity factor $(k/\kappa_i) \times 10^{-6}$, psi^{-1}
Silicone fluid[a]	0.120	5.1	43
Glycerol[a]	0.608	8.3	14
Methyl alcohol[a]	0.206	7.1	34
Solid composite propellants[a]	0.5–0.9	2–3	3.0–4.0
Mercury[b]	3.5	11–12	3.1–3.4
Ammonium per-chlorate[c]	2.6	—	—
Sodium chloride[b]	3.3	2–6	1–2
Aluminum	10.6	—	—

[a] Determined from compressibility data below 2,000 psi, sylphon method.

[b] Bridgman's data above 25,000 psi.

[c] The origin of this value is rather obscure, although it is found to be in accord with experimental data for solid propellants in which it is a major ingredient, where total compliance is assessed from a volume fraction combination of the individual compliances of the ingredients.

The experimental problems of implementing compressibility methods for solids begin with the selection of a suitable confining fluid. Ideally, this would be an incompressible, chemically inert, thermally inexpansive fluid–which sounds like the prologue to many of the restrictive discourses on the problems of continuum mechanics. Unfortunately, such fluids do not exist, and nonreactivity of the confining fluid with the test specimen is often the controlling factor in its choice. This is particularly true for measurements of chemically reactive materials like solid propellants. Dow Corning DC-200 fluid, 10 cs. viscosity, for example, has been found to be one of the few liquids that are relatively inert in contact with the active propellant ingredients. On this basis, silicone oils have been used extensively as confining fluids for compressibility tests of solid rocket propellants. On the basis of its other properties, it is a poor choice, being highly compressible, thermally expansive, and having widely different isothermal and adiabatic compliances.

Other less compressible liquids, such as mercury and glycerol, have also been utilized as confining fluids in testing solid propellants. These present some inherent experimental difficulties, aside from chemical reactivity, in that complete removal of entrapped gases and the required intimate contact of these fluids with the nonwetted, rough-textured surface of the specimen cannot be easily achieved. This is especially troublesome when the PV records are to be used to determine the initial void content in a solid specimen in the manner to be described presently.

As mentioned previously, either graphical or analytical corrections of the compressibility records for solids confined by a fluid may be employed to separate the behavior of the solid from the total results. An analytical pressure–volume relation, or equation of state for the confining fluid, is needed if other than graphical reduction of the data is to be employed. Many equations of state have been proposed to deal with pressure coefficient of compressibility for both liquids and solids. One proposed by Murnaghan[16] for solids, in its simplest form, has been found to be quite adequate for characterizing the PV behavior of confining fluids as well. It relates the pressure, and ratio of volume with respect to initial volume, in an expression with two constants, k and κ_i.

$$P = (\kappa_i/k) \ [(V/V_0)^{-k} - 1] \tag{5}$$

κ_i has the value of the bulk modulus of the substance at zero pressure, while k falls into a relatively narrow range of values (4–15) for a great many materials. The more pressure-dependent materials have characteristically large values for k.

Expression (5) may be written more simply in terms of the instantaneous bulk modulus, κ, of eq. (1) as

$$\kappa = kP + \kappa_i \tag{6}$$

where κ is then clearly a linear function of P. Murnaghan[16] points out that Bridgman's compressibility data for indium to 100,000 kg./cm.^{2} are
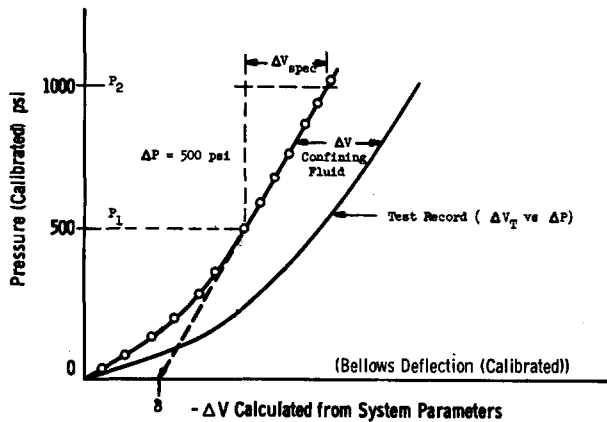
Fig. 6. Graphical analysis of hydrostatic compressibility data (void-free).

well characterized by eq. (6). Blatz[17,18] discusses eq. (6) in connection with the application of finite elastic theory to the characterization of the compressibility of polymeric materials and shows that Bridgman's data for rubbers at high pressure (i.e., above 2000 kg./cm.²) are quite well typified by a linear dependence of the bulk modulus on pressure in accord with eq. (6).

When the bulk modulus of eq. (6) is normalized to the compressibility of the material at zero pressure, i.e.,

$$(\kappa/\kappa_i) - 1 = (k/\kappa_i)P \tag{7}$$

the coefficient of P in the right-hand term of eq. (7) may be regarded as a comparative measure of the nonlinearity of the material's compressibility for a unit pressure change. Approximate values of k/κ_i are noted in Table I for various materials that are discussed in this report. These values reflect the author's judgment regarding the best fit of the experimental data on a log–log plot of (V/V_0) and $[1 + (k/\kappa_i)P]$. They are useful as a means for characterizing the nonlinear PV behavior of materials and allow the use of analytical corrections for the effect of the confining fluid to be applied to volumetric compressibility measurements. This is an important factor in the reduction of data from compressibility measurements.

The nonlinear form of the illustrative PV records for solids in a confining fluid of Figure 6 are exaggerated for the sake of clarity, from those typically recorded for solid specimen tests. Ordinarily, test records for composite solid propellants, confined in a minimum amount of fluid, are only slightly, but detectably nonlinear in the narrow range of pressures used and this is primarily due to the confining fluid behavior. In this regard, Table I tabulates values of the pressure coefficient of compressibility k for various fluids and solids. The parameter k should be regarded as only an approximate index or comparative measure of the nonlinear compressibility of a material, in view of the subjective nature by which it is determined.

The compressibility of many solid propellant formulations has been measured by all of the methods described, principally in the pressure region from atmospheric pressure to 2000 psi. The nonlinearity of these highly filled composites is estimated to be a 1% effect in this pressure range by considering the nonlinearity of the polymeric constituent which is ordinarily present in volume fractions of 0.2 or less. The accuracy of the PV data obtained in testing small specimens is ordinarily insufficient to detect significant nonlinearities in the reduced data. In such cases, the data are generally characterized by the slope of a straight line giving the best fit to the data to obtain bulk modulus values. More precise characterization of these or similar frangible composites would be possible if the ultimate techniques for maximum precision were painfully exploited. This would require the use of precision specimens shaped to fill as much space in the system cavities as possible. Extremely precise determinations of the volumes of the specimen and confining fluid would also be required. These requirements are generally compromised somewhat for the sake of economy and safety in the application of the methods to solid rocket propellants.

Volumetric Compressibility with Voided Solids

The basic compressibility behavior of well-consolidated solids is complicated by the inclusion of highly nonlinear constituents, or inhomogeneities such as voids. Void fractions of less than 0.05% in a polymeric solid may have no easily measurable effect on the majority of its thermal or mechanical properties. However, such included void fractions in polymers affect their compressibility near atmospheric pressure to a surprising degree. Compressibility measurements have been found to be a most sensitive quantitative means for determining the initial void content in solids, quite beyond other methods, such as density determinations.

Solid rocket propellants commonly contain crystalline oxidizer fillers of irregular shape in volume fractions of 0.60–0.80. It is somewhat surprising that these materials, prepared in very large quantities in the manner of cake batter, consistently have little if any included gases or voids. However, even such small amounts of included void as may occur are important to the structural integrity of these materials from the compressibility viewpoint, since they always function in rocket motors under hydrostatic stresses. The compressibility methods described are particularly suitable to the measurement of relatively small amounts of included void content in polymers or composite materials and hence to the study of the effect of included voids on the mechanical and ballistic properties of solid propellants.

Numerous tests of solid propellants have shown that the compressibility of the void component supported by the composite matrix is generally well represented by an exponential function of the pressure. With increasing pressure, the initially high overall compressibility is eventually reduced to that of the void-free material. This is indicated graphically by the illus-

tration of typical voided solid propellant PV behavior on Figure 7. The data points that represent the compressibility of the solid are calculated by correcting the gross record for the volume-change contribution of the confining fluid and system.

Useful estimates of the initial void content may be made by extrapolating the essentially linear portion of the PV curve at higher pressures which is characteristic of the void-free solid behavior to the volume-change axis. This intercept is labeled δ in Figure 7. Similar estimates of initial void content may be made by extrapolating the gross PV record to zero pressure, if the curvature in the records due to the confining fluid is followed. More satisfactory data reduction techniques require that analytic expressions which describe the PV behavior of the constituents discussed earlier be used. The decided advantages of digital computer methods for the reduction of data of this type may then be obtained.

Equations of state for solids, such as that ascribed to Murnaghan,[16] must be suitably extended to include the effects of the void content as a parameter when materials containing even minute amounts of void are to be characterized by low pressure techniques. The simplest model for studying the compressibility of a solid containing dispersed microvoid is likely that of a thick-walled spherical shell in which the enclosed space corresponds to the volume fraction void. The behavior of such a model, externally pressurized, has been compared with experimental data for the compressibility of a variety of composite solid propellant formulations containing various amounts of highly dispersed included initial void. An infinitesimal analysis of the deformation of an externally pressurized sphere has been discussed in a report[19] concerned with the compressibility of solid propellants containing microvoids. The expression that was derived relating pressure and volume change to the elastic properties of the void-free solid and its initial void content, δ, is:

$$\frac{V}{V_0} = \frac{e^{-P/\kappa}}{[(1 - \delta e^{-3P/4\mu})/(1 - \delta)]^{\,4\mu/3\kappa + 1}} \tag{8}$$

Predictions of compressibility behavior for voided solids based on eq. (8) and reasonable values for the basic material properties are found to be in basic agreement with the observed compressibility of solids containing small amounts of widely dispersed microvoids. Expression (8) may be reduced to a simpler form by considering that $\kappa \gg \mu$ and that $e^{-P/\kappa}$ may be approximated by V/V_0 to give

$$\Delta V^*/V_0 = (\Delta V/V_0) + \delta\,(1 - e^{-3P/4\mu}) \tag{9}$$

Equation (9) has been applied to characterize the compressibility of materials in which the bulk modulus is very much greater than the shear modulus, and the pressure range of testing does not approach the bulk modulus value of the void-free material. $\Delta V^*/V_0$ and $\Delta V/V_0$ are defined as fractional volume changes based on the initial volume, with and without void content, respectively.
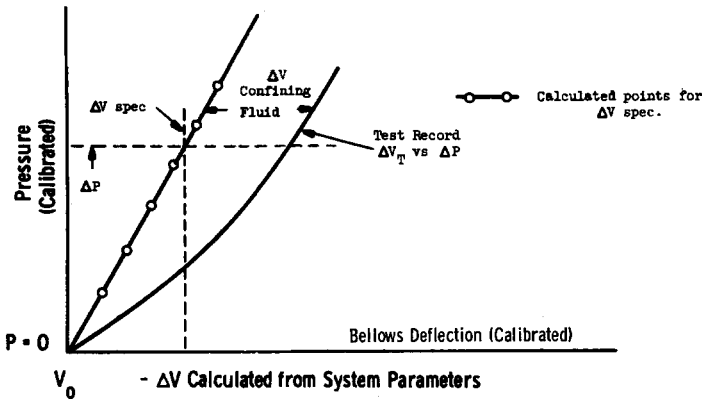
Fig. 7. Graphical analysis of hydrostatic compressibility data (with initial void).

The total volume change of the shell then appears to consist of two parts, as suggested by the form of eq. (9). The first is that of the shell material of the model, and the second part gives the void volume contribution of the initial void content δ, modified by an exponential multiplier containing terms due to pressure, shear modulus of the shell material, and a constant shape factor, as a negative exponent.

An expression may be derived for a model in which the coaxial void is cylindrical in shape, by the considerations similar to those used to obtain eq. (9). This is

$$\Delta V^*/V_0 = (\Delta V/V_0) + \delta(1 - e^{-P/\mu}) \tag{10}$$

The compressibility of solids with spherical or cylindrical void spaces predicted by eqs. (9) and (10), derived from infinitesimal elastic theory, differ from one another only in the shape factor constant of the exponential term. A great deal of experimental data for voided solids shows the void-compression contribution to be an exponential function of the pressure. Beyond this important area of agreement with experiment, these analyses would not be expected to agree completely with physical reality, in view of their simple premises.

That void spaces should be primarily spherical, cylindrical or even an unchanging combination of regular shapes during their complete compression to zero volume, seems unlikely, especially for composites. The compressibility data for a series of voided composite propellant specimens, shown on Figure 8, illustrates one instance of a form of departure from ideal compression that is sometimes observed and would be expected if buckling should ensue at some critical pressure level, as it likely does. Specimen 14 of Figure 8 is observed to follow the PV behavior predicted by eq. (9) up to 400 psi. At higher pressures, the volume change is larger than that which would be expected from the simple theory until virtually complete compression of the void is achieved. This type of behavior was very evident in the nature of the experimental data obtained for the compressibility of closed
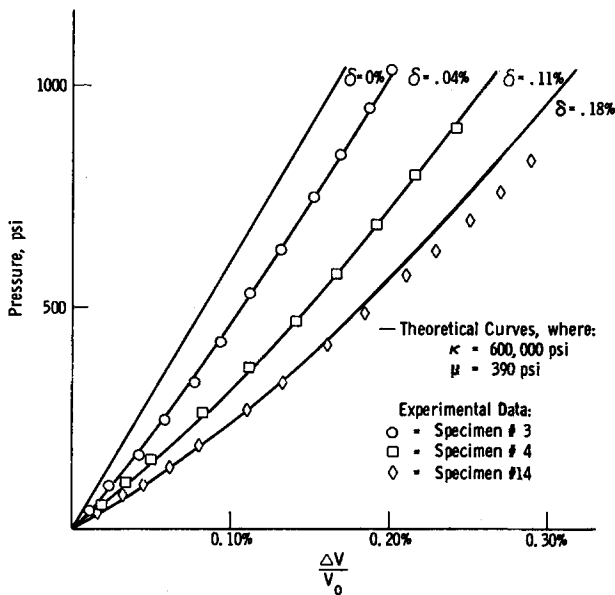
Fig. 8. Comparison of experimental and theoretical pressure–volume behavior for a composite.

cell foams having a much higher void content than those common to solid propellants. In the majority of instances, slightly voided composites do not exhibit the clearly defined behavior, attributed to buckling of the cell structure, as noted for specimen 14 and can therefore be quite well described by eqs. (9) or (10).

The use of these expressions for characterizing compressibility implies that some constant value of the shear modulus for the shell material will suffice. The effect that the value of the shear modulus parameter has on the shape of the theoretical PV curves predicted from eq. (9) is illustrated by the data of Figure 9. This shows a typical experimental PV curve and other appropriate material properties for a highly voided solid propellant. In this case, which is more the rule than the exception, the experimental data do not clearly show the presumed buckling influence of the previous instance. The dashed theoretical curve that best fits the experimental data points, shown as filled circles on the figure, was calculated for a shear modulus value of 40 psi. This is to be contrasted with the predicted behavior for a shear modulus value of 70 psi, as shown by the solid curve. The latter value of the shear modulus is that calculated from low-rate uniaxial tensile data for the material, on the assumption that the shear modulus is approximately one-third the relaxed or rubbery Young's modulus of this viscoelastic material. This could mean that buckling of the void structure is normally present and may be accounted for in applying eq. (9) to experimental data by empirical modification of the shear modulus values. It is also possible that the shear modulus value of 40 psi, for which the data
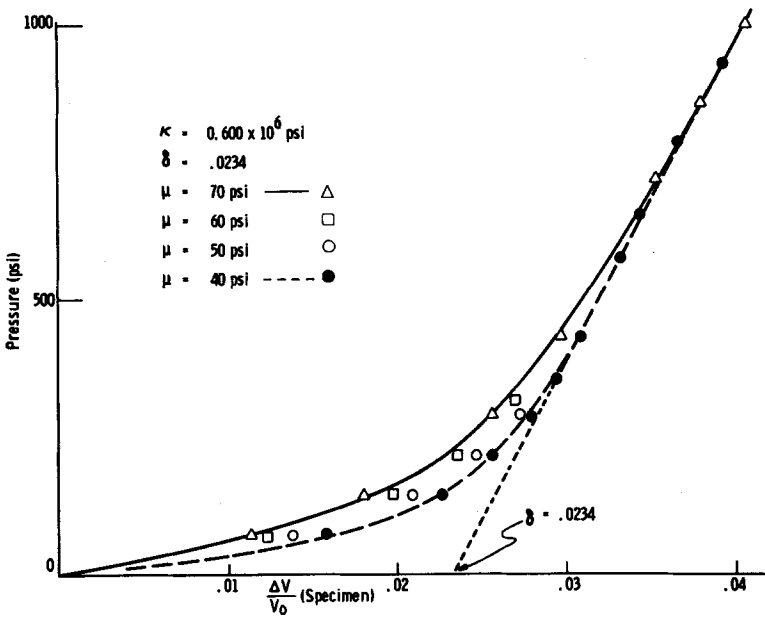
Fig. 9. Effect of shear modulus in fitting PV data for a voided composite material.
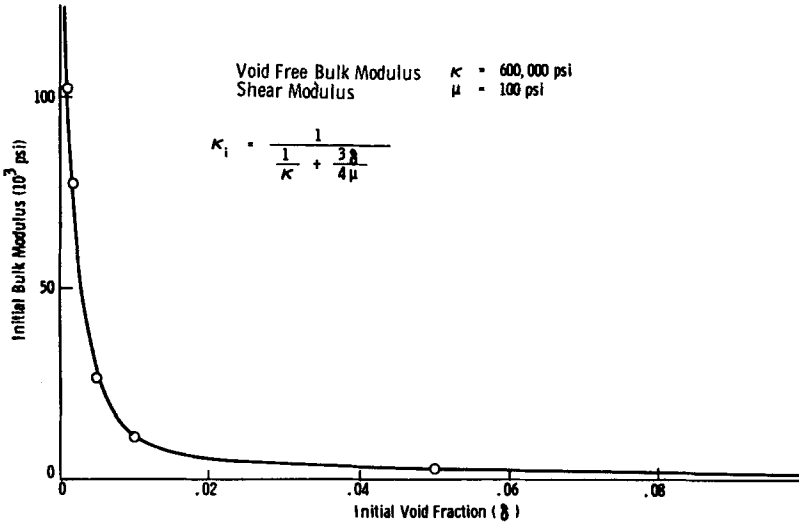

Fig. 10. Effect of initial void content on initial bulk modulus of voided solid.

gives the best fit, may be a better estimate for the value of this parameter in the small deformation field of hydrostatic compression, than those which are appropriate to the comparatively large deformation tensile behavior.

The solution given for the infinitesimal-shell model in eq. (9) may be differentiated with respect to fractional volume change, and evaluated at
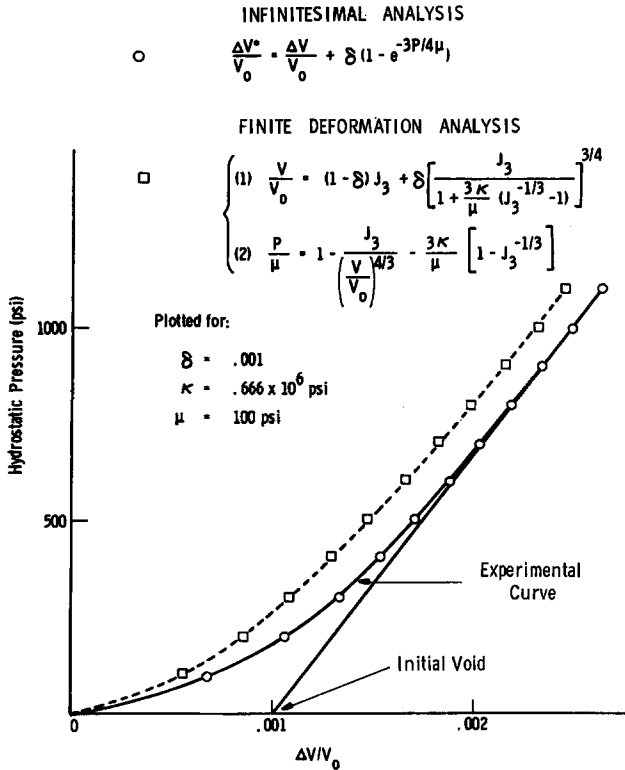
Fig. 11. Comparison of state equations for compressibility of voided solids.

zero pressure. This expression for the initial bulk modulus of a voided solid is shown on Figure 10, and the curve for a typical composite shows the extreme dependence of initial bulk modulus on the void content. While even the initial hydrostatic compressibility of cellular polyurethane foams was found to be in reasonable agreement with predicted behavior, the expression has been extensively compared only with experimental data for slightly voided composites. With voided composite materials, the expression is useful for grouping specimens into sets having similar void content for more precise subsequent measurements by examining only the initial portion of their PV behavior.

While some important applications of the equation of state have been demonstrated, it is clear that other questions that are raised regarding the applicability of single valued shear moduli, constant shape factors, and the influence of buckling, as these relate to the infinitesimal theory for voided solids, have not been resolved. A more realistic analysis should undoubtedly consider a model in which a functional interaction of the parameters obtains. This does not obviate the semiempirical practicality of expressions like eqs. (9) and (10) which are useful for describing the PV behavior of voided composites analytically.

Sophisticated analyses for the compressibility of voided solids have been reported which are concerned primarily with the effects of finite deformation around voids in the base material during hydrostatic compression. Herrmann[20] considered finite deformation only in the vicinity of the hole. This problem has also been discussed by Blatz.[21] Neither of these investigators treat the problems of shape factor, buckling, or the matter of how shear modulus values may be measured that are appropriate to the case of the minute deformations of a filled solid, however. Both finite deformation analyses are found to predict complete void compression at much higher pressures than does the infinitesimal deformation analysis, or the observed experimental behavior.

The relative applicability of the finite deformation analysis of Blatz[17,18] and the infinitesimal analysis, to experimental results, is shown on Figure 11. The experimental PV curve of Figure 11 is that obtained for a composite solid with 0.1% initial void and a void-free bulk modulus of 0.666 × 10^6 psi. The infinitesimal analysis predicts the behavior shown by the open-circle points on the figure, while the open squares show the corresponding calculations for the finite deformation equations. A shear modulus value of 100 psi, which agrees with that calculated for the material from tensile data, was used for both cases. The equations for the PV behavior of a voided solid from the finite deformation analysis are given on Figure 11. J_3 is a fitting parameter in these parametric equations.

Expression (9) predicts that the initial void volume for this example would be reduced to 0.05% of the original amount at a pressure of 1,000 psi, in excellent agreement with the observed behavior. In contrast, the finite deformation solution, for the same values of the parameters, predicts 18–20% of the initial void space remaining at a pressure of 1,000 psi. The analytic form of this analysis precludes obtaining a better fit to the data by choosing somewhat arbitrary single values of the shear modulus as a fitting parameter, as was shown to be possible for the infinitesimal equation. A functional dependence of the shear modulus on pressure or remaining void content could be used to force the finite deformation analysis into agreement with observed behavior. However, the shear modulus dependence required would have an inverse proportionality with pressure and a direct relationship to the void remaining during compression. Both of these requirements, either separately or in combination, are contrary to the effects that pressure and void content would intuitively be expected to have on the mechanical properties of solids in general. Thus, it appears that finite deformation considerations alone contribute little to an improved equation of state for voided solids, at least for composite materials like the slightly voided solid propellants with which they were tested.

Conclusions

Relatively simple experimental techniques can be used to characterize the compressibility of fluids, polymers, and filled polymers, in a range of low pressures appropriate to their ordinary application. This includes

enunciating the profound effects of included initial voids, and the considerable differences between adiabatic and isothermal behavior.

Methods have been suggested whereby compressibility data may be used in conjunction with easily measured thermal properties to calculate more difficult-to-measure thermodynamic properties, such as the specific heat at constant pressure or the ratio of specific heats.

Some composite solid propellant formulations have been shown to have a peculiar uniaxial compliance under hydrostatic pressure which is ascribed to inelastic behavior under hydrostatic stress which does not appear to be a problem with unfilled polymers.

Semiempirical equations of state have been described which allow the complex compressibility behavior of voided solids to be characterized analytically. These have been only partially successful in accounting for the behavior in terms of basic material properties without full consideration of viscoelastic effects.

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Résumé

Des techniques modifiées de la compressibilité classique sont décrites en vue de mesurer les modules en bloc adiabatiques et isothermes. Ceux-ci diffèrent des méthodes

familières principalement dans l'utilisation de transformateurs électroniques différentiels très sensibles, en vue de suivre les variations de volume et par une mesure autographique de la pression et des variations de volume au cours d'un cycle de pressurisation essentiellement quasi-statique. Les méthodes uniaxiales et volumétriques à la fois caractérisent le comportement à la compressibilité des polymères dans une région de relativement basse pression (de 0 à 100 atm.) Les données de compressibilité pour de nombreux liquides bien connus et des solides sont rapportées. La nature non-linéaire du comportement de PV des liquides est montrée être caractérisée adéquatement. par une équation d'état simple qui est aussi bien applicable aux polymères caoutchouteux. Les équations d'état pour les polymères et pour les polymères chargés contenant des lacunes dispersées de façon inhomogènes sont discutées. Les relations basées sur une théorie infinitésimale de déformation d'une sphère creuse préssurisée de façon externe sont comparées avec des équations d'état plus complexes qui considérent des déformations finies au centre d'une sphère creuse. On en conclu que les résultats expérimentaux pour la compressibilité de solides contenant des lacunes à moins de 0.5% de leur volume initial sont le mieux représentés par les équations d'état plus simples dérivées de la théorie infinitésimale.

Zusammenfassung

Modifizierte klassische Kompressibilitätsverfahren werden beschrieben, nach welchen der adiabatische und der isotherme Kompressionsmodul von Polymeren gemessen wird. Sie unterscheiden sich von den üblichen Methoden hauptsächlich durch die Verwendung empfindlicher elektronischer Deformationsfühler (Differentialtransformatoren) zur Aufnahme der Volumsänderungen und einer autographischen Aufzeichnung von Druck- und Volumsänderungen während eines im wesentlichen quasi-statischen Druckbelastungscyclus. Uniaxiale und volumetrische Methoden charakterisieren beide das Kompressibilitätsverhalten von Polymeren im Bereich verhältnismässig niedriger Drukke (0–100 Atmosphären). Kompressibilitätsdaten für einige wohlgekannte Flüssigkeiten und Feststoffe werden mitgeteilt. Die nicht-lineare Natur des PV-Verhaltens von Flüssigkeiten kann durch eine einfache, auch auf kautschukartige Polymere anwendbare Zustandsgleichung befriedigend charakterisiert werden. Zustandsgleichung befriedigend charakterisiert werden. Zustandsgleichungen für Polymere und füllstoffhältige Polymere mit einem Gehalt an dispergierten hohlraumartigen Inhomogenitäten werden diskutiert. Beziehungen aufd er Grundlage der Infinitesimaltheorie der Deformation einer Hohlkungel unter äusserer Druckbelastung werden mit stärker komplexen Zustandsgleichungen verglichen, die endliche Deformationen im Mittelpunkt einer Hohlkugel ins Auge fassen. Man kommt zu dem Schluss, dass sich die Versuchsergebnisse für die Kompressibilität hohlraumhältiger Festkörper mit weniger als 0,5% an anfänglishem Hohlraumvolumen am besten durch die einfacheren, aus der Infinitesimaltheorie abgeleiteten Zustandsgleichungen darstellen lassen.