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Compressibility of Bulk Polymers

Knowledge of the effect of high pressure on the structure and properties of bulk polymers is a fundamental approach toward gaining an understanding of the polymeric solid state. Some years ago Bridgeman (1) studied the compressibility of a few polymers and, while later workers have been active in this area (2), only a very limited amount of data has been obtained. Recent investigations (3) have shown the importance of the polymeric solid state and the necessity of obtaining fundamental data. Lack of such data and methods for treating the data have restricted progress in the study of pressure dependent phenomena (4).

Presented in this article are the first results of an investigation of the bulk compressibility of a series of polymers together with a limited analysis of the data.

Experimental

Bulk compressibilities of polymers were determined using an apparatus similar to that employed by Mat-suoka and Maxwell (2) as shown in Figure 1. The inner bushing of this apparatus is made of hardened steel and the inner surface of the cavity was lapped and polished to 0.250", +0.001", -0.000" (0.635 cm) in diameter. This inner bushing is tightly fitted into the outside steel casing and two case-hardened steel plungers 1.625" (4.128 cm) long and 0.250", +0.000", -0.001" (0.635 cm) (Detroit Mold Engineering Co.) in diameter are inserted into the cavity above and below the polymer specimen.

The polymer specimen is a machined rod, 3" (7.62 cm) long and 0.250" (0.635 cm) is diameter. This rod is placed in the cylindrical cavity, between the upper and lower steel plungers, where it fits tightly but is still able to move smoothly.

Temperature of the specimen is maintained isothermally within $\pm 1^\circ\text{C}$ by manual control of a Variac in series with two electric heating bands placed around the tester. Measurement of the temperature is accomplished by two thermocouples inserted into wells immediately adjacent to the specimen. This apparatus has been used up to 250°C without difficulty.

The tester containing the polymer specimen is placed on the fixed platen of a Baldwin-Southwark, 60,000 lb. capacity, Universal Testing Machine and heated to the desired temperature. The loading head of the test machine is brought down so as to just touch the upper plunger of the tester. An automatic stress-strain recorder is started and load applied at the rate of 0.025" per

minute. Isothermal plots of stress versus strain are obtained for each polymer at 25°C increments which are identical with the pressure versus $\Delta V/V_{25^\circ\text{C}}$ plots shown in this paper.

Maximum load applied is usually about 8,000 pounds after which the load is removed from the specimen. During each run the tester is enclosed in a thick-walled iron casing. A load of 8,000 pounds is equivalent to a pressure of 11,000 atmospheres. With the present apparatus and case hardened plungers this is the maximum load.

Materials

Polymers were chosen so as to represent each of the principal types. The linear polymers were crystalline polyethylene (Marlex 50, Phillips Chemical Corp.) crystalline, high melting polyhexamethylenediamine adipate (Nylon 66, duPont Co.) and amorphous polystyrene (Styron 666, Dow Chemical Corp.). The crosslinked polymers were based on an epoxide (Epon 828, Shell Chemical Corp.) which is a diglycidyl ether of bisphenol A with an epoxide equivalent within the range 185 to 205 (5). This epoxide was polymerized with 1) 59.5% of dodecenyl succinic anhydride (DDSA) and 2) 13% of tris(dimethylaminomethyl)phenol tri(2-ethyl hexoate) (D). In each case the cured polymer specimen rods were given 16 hours postcure at a temperature of about 50°C above the glass transition temperature of the completely cured polymer.

RESULTS

The results of this study are shown in Figures 2 through 9. Figures 2, 3, 4, 6 and 8 are plots obtained under isothermal conditions of the applied pressure in atmospheres versus the percent change in volume while Figures 5, 7, and 9 are pressure vs. temperature plots prepared from the data of Figures 4, 6 and 8. In all cases the isotherms are nonlinear.

In many of the isotherms, changes in the slopes of the usual smooth curves occurred over narrow ranges, leading to an isotherm containing two smooth curves. For example, in Figure 4, the 178°C isotherm exhibits a change in slope (or inflection point) at coordinates, 1800 atmospheres and $\Delta V/V_{25^\circ\text{C}} = 9\%$. For the sake of clarity some of the pressure versus $\Delta V/V_{25^\circ\text{C}}$ plots have been omitted from the figures.

All of the polymers studied exhibited compressibilities of the order of 10 to 15%. The usual case is for the

compressibility to increase with increasing temperature (2) and this was, in general, found to be true for the polymers considered in this study.

After the pressure measurement was complete the specimen was allowed to cool down to 25°C and its length was measured. In every case it was found that the specimen had returned to its original length.

Compressibility of Linear Polymers

The first polymer considered in this study was low pressure polyethylene. This is a long chain molecule of repeating $\text{—CH}_2\text{—}$ (methylene) groups. It is about 90% crystalline at 25°C and melts at 136°C at atmospheric pressure. However, the application of pressure results in an increase in the melting point of the polymer. Matsuo (6) has recently determined the pressure dependence of the melting temperature. He found that at atmospheric pressure the polymer melts at 136°C while at 500 atmospheres its melting point is about 153°C. Thus, at 139°C we start with liquid polyethylene but at a very low pressure it reverts to amorphous solid polymer. Examination of our data does not reveal any volume discontinuity at low pressures.

One can generalize on the results shown in Figure 2 as follows. There is no significant change in the compressibility of polyethylene between 27°C and 94°C. This is to be expected over this temperature range since the crystallinity remains constant at about 90% (7). Even when the amorphous content is increased to almost 100%, as is the case in the 133°C isotherm, the magnitude of the compressibility only increases about 2% at 11,000 atmospheres. However, upon decrystallization and melting the compressibility increases and remains higher over the pressure range even though the pressure causes the molten polymer to revert to the amorphous solid state.

The higher compressibility of amorphous liquid and pressure induced solid polymer at 139°C can probably be explained as due to an increase in the free volume of the system upon decrystallization.

The next system considered was polyhexamethylene diamine adipate or nylon 66. It will be noted in Figure 3 that increasing the temperature from 22°C to 202°C increases the compressibility at 8,500 atmospheres by

about 4%. This relatively small increase can be explained by the highly crystalline nature of this polymer and the fact that very little decrystallization occurs when it is heated from 22°C to 202°C. Note also that the magnitude and temperature dependence of the compressibility of two highly crystalline polymers, low pressure polyethylene and polychlorotrifluoroethylene (8), are almost identical with the values shown for the nylon in Figure 3. It thus appears that highly crystalline systems respond to pressure in much the same manner and independently of the morphology of the crystals.

The compressibility of polystyrene is shown in Figure 4. This polymer exhibits several interesting points which have not been previously observed. At 25°C the pressure versus $\Delta V/V_{25^\circ\text{C}}$ plots exhibits a typical nonlinear relationship. However, isotherms starting at 112°C exhibit definite bending. For example, the 178°C isotherm exhibits a pronounced change of slope at 1800 atmospheres and $\Delta V/V_{25^\circ\text{C}} = 9\%$.

From theoretical considerations, Eisenberg (9) recently pointed out that the glass transition in amorphous polymers is not only temperature dependent but is also dependent upon the pressure and the molecular weight of the polymer. Eisenberg considers the glass transition from the standpoint of its pressure dependence and defines it as the pressure at which a transition occurs, or glass transition pressure, P_g . He assumes that the free volume concept of the glass transition (10) holds and that the effect of pressure is to "squeeze out" the free volume and as a result compress the polymer. At temperatures above the glass transition temperature, T_g , the effect of pressure is to cause the polymer to vitrify (that is, become glassy or revert to the glassy state) when a certain critical free volume is attained during the application of increasing pressure.

In our studies each compressibility run was made at constant temperature and since the same sample was employed for a series of runs the molecular weight was held constant. Thus, during a run only the pressure was changed. At temperatures above T_g with increasing pressure, the free volume is continuously reduced until a critical free volume is reached. When this point is attained we observe a change of slope in the pressure versus $\Delta V/V_{25^\circ\text{C}}$ plot (10). Once the applied pressure is greater than that required to compress the polymer to

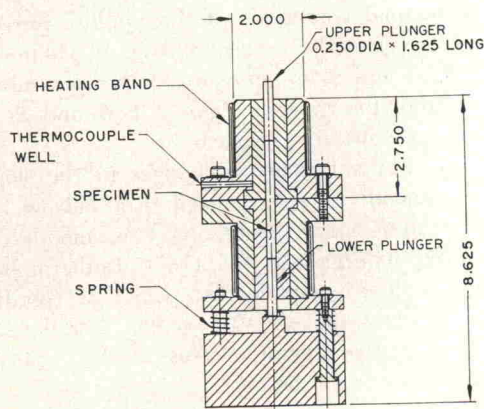


Figure 1. Compressibility Tester.

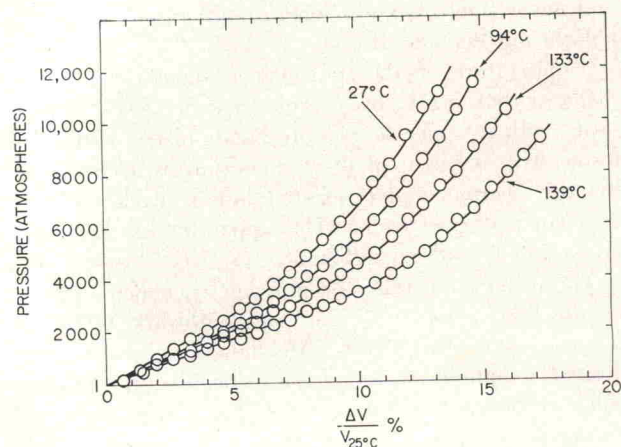


Figure 2. Compressibility of low pressure polyethylene.

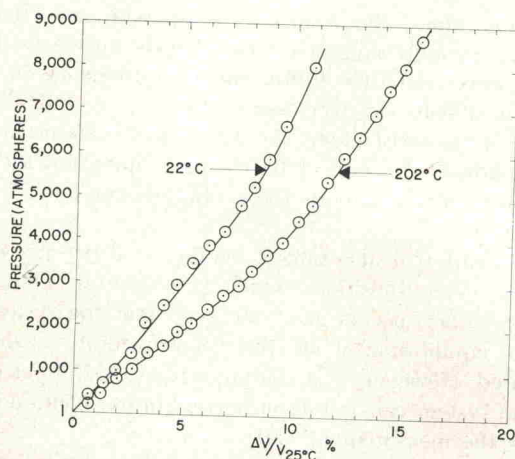


Figure 3. Compressibility of nylon 66.

its critical free volume the observed compressibility becomes that of the glassy solid and exhibits a different pressure dependence than the rubbery solid. No change of slope will occur unless the temperature is above T_g regardless of the pressure.

It follows that if we plot the pressure at which the change of slope occurs versus the temperature at which the compressibility was determined, we should obtain a plot which shows the variation of T_g with pressure and also P_g with temperature. This has been done with all the points representing changes in slope as obtained from the compressibility of polystyrene. The resultant pressure versus temperature plot is shown in Figure 5. In a few instances the change of slope was determined by drawing tangents on the original stress-strain plots from the Universal Test Machine. The point of intersection of the two tangents (above and below P_g) was taken as P_g . It should be noted that we have not plotted all the available compressibility isotherms on Figure 4 since in many cases that data points are almost superimposable.

Inspection of Figure 5 shows that the pressure versus temperature relationship is linear. If the plot is extended down to atmospheric pressure the line intersects the temperature axis at the glass transition temperature for polystyrene. For example, on Figure 5, T_g (at one atmosphere) occurs at 78°C. Literature values for T_g are

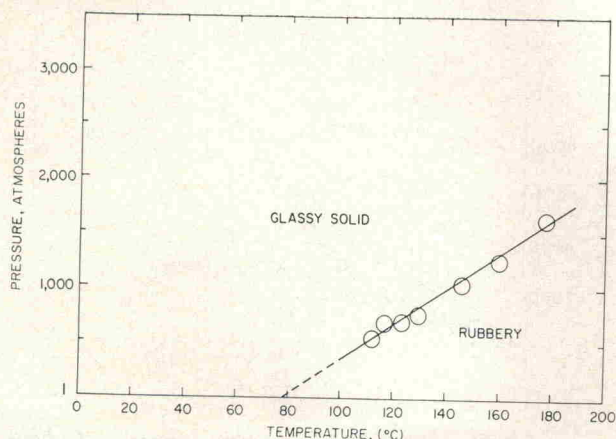


Figure 5. Phase diagram for polystyrene.

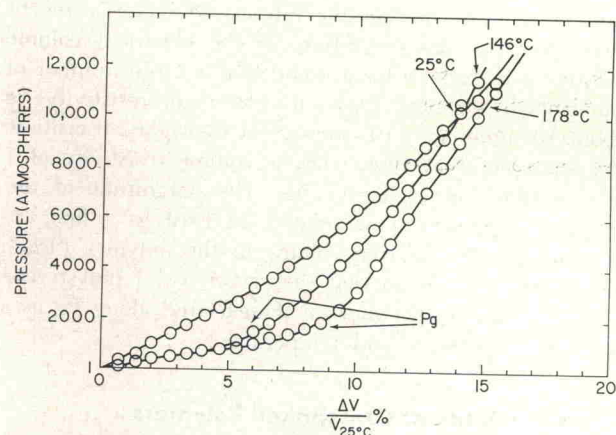


Figure 4. Compressibility of polystyrene.

81°C as determined by specific heat (11) and electrical resistivity (12a., b.) measurements. This is excellent agreement.

Plots of pressure versus temperature for amorphous polymers are glass-rubber phase diagrams for the polymer. Similar phase diagrams have been made for many inorganic compounds by Pistorius (13) and for metals by Klement and co-workers (14). Weir (15) prepared a phase diagram for polytetrafluoroethylene from a study of the pressure-volume-temperature relationships associated with changes in the crystalline structure. Pistorius (16) has recently extended the work of Weir and determined the pressure dependence of the melting point for polytetrafluoroethylene. The phase diagram for this polymer is now complete over the pressure range zero to about 8,000 atmospheres and over the temperature range 0°C to 400°C.

The straight line connecting the data points on Figure 5 is P_g for polystyrene: the region above the line represents the glassy state while the region below the line is the rubbery state. O'Reilly (17) has recently defined P_g as that pressure at which molecular rearrangements can no longer follow the applied pressure and the polymer thus exhibits (or re-exhibits) the compressibility of the glassy state. This definition is in accord with the results shown in Figure 5.

Since P_g appears to represent a state of constant free

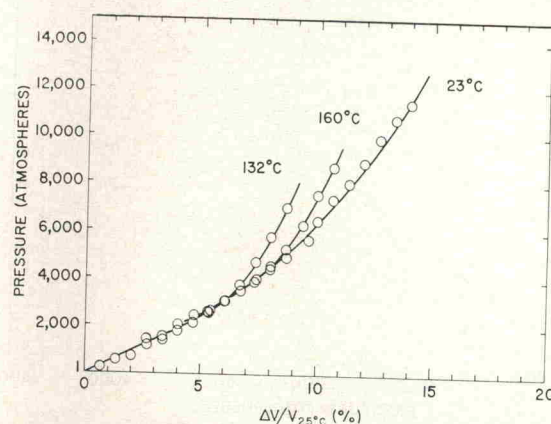


Figure 6. Compressibility of an epoxide polymer hardened with DDSA.

volume it is of considerable interest to relate a recent observation on the magnitude of the electrical volume resistivity at T_g . We have noted that a large number of amorphous polymers have an electrical resistivity of about 10^{13} ohm-cm $\pm 10^1$ ohm-cm at their glass transition. For example, polystyrene has a volume resistivity of 7×10^{12} ohm cm at T_g (12b). The magnitude of the resistivity appears to be related, at least to a first approximation, to the free volume of the polymer (12a). Thus, one can predict that the resistivity of polystyrene should be about 10^{13} ohm-cm if measured along P_g as a function of pressure and temperature.

Compressibility of Crosslinked Polymers

With the exception of a paper by Bridgeman (1, 18) and some recent Russian work on phenolic polymers (19), the literature apparently does not contain any significant data on the effects of pressure on cross-linked polymers.

The first system considered was a copolymer consisting of 40.5% of an epoxide polymer, Epon 828, and 59.5% of an acid anhydride, dodecenyl succinic anhydride. Details of the chemistry and preparation of this copolymer have been previously given (12a). As shown in Figure 6, the 23°C isotherm exhibits the usual non-linear behavior with a decrease in the coefficient of compressibility (1) at higher pressures. The 132°C isotherm shows a definite change of slope as do other isotherms at 88°, 104°, 117°, 132°, 148° and 160°C. These changes in slope are, as previously noted, due to pressure induced glass transitions.

We analyzed the data in the same manner as with the polystyrene data and the results are shown in Figure 7. It will be noted that the data points fall on a straight line. If this line is extended to one atmosphere it should intersect the temperature axis at the glass transition temperature for the polymer. Inspection of Figure 7 shows that the indicated glass transition is about 60°C while we have previously found the transition to be about 70°C. This is considered to be satisfactory agreement.

In our previous experiments (8) on linear polymers compressibility measurements were conducted at a rate of loading of 0.10" per minute. While this rate was satisfactory for linear polymers, which have relatively short

relaxation times, the results obtained with cross-linked polymers strongly suggested that a slower rate of loading is necessary (8). Therefore, the measurements on the crosslinked polymers were done at a rate of 0.025" per minute with satisfactory results. A few measurements were made at the rate of 0.01" per minute and the results were identical with those obtained at 0.025" per minute.

It appears that at a rate of loading of 0.10" per minute the glass transition, which is a typical relaxation process (12a), occurs at a rate such that the system is not in equilibrium while the compressibility is being measured. However, at a loading rate of 0.025" per minute the system can re-establish equilibrium continuously during the measurement (20).

Finally, we studied the compressibility of the system Epon 828 polymerized with 13% of tris(dimethylaminomethyl)phenol tri(2-ethyl hexoate) (Hardener D). The 22° and 35°C isotherms are normal non-linear plots, the magnitude of the compressibility at 9,000 atmospheres increasing from 12% at 22°C to 14% at 85°C. At 85°C the isotherms start to exhibit a change of slope which is indicative of a pressure induced glass transition. Additional changes in slope are noted on the 114°, 118°, 121°, 139° and 185°C isotherms. The isotherms at 22°C, 139°C and 185°C are shown on Figure 8.

We have prepared a phase diagram for this system and this is shown in Figure 9. From this plot a glass transition at zero pressure of 69°C is indicated which compares very favorably with the literature values of 66°C (12a).

General Considerations

From the data shown in Figures 2 to 9 a number of generalizations can be made. First, all the isotherms exhibit a nonlinear pressure dependence of the compressibility decreasing as the pressure is increased. The decrease in the coefficient of the compressibility with increasing pressure is a general property of solids (2) as is the nonlinear pressure dependence. The shape of the compressibility isotherms at pressures up to 10,000 atmospheres also suggests that for every polymer there exists a limiting value of the compressibility, which is probably temperature independent, and is approached

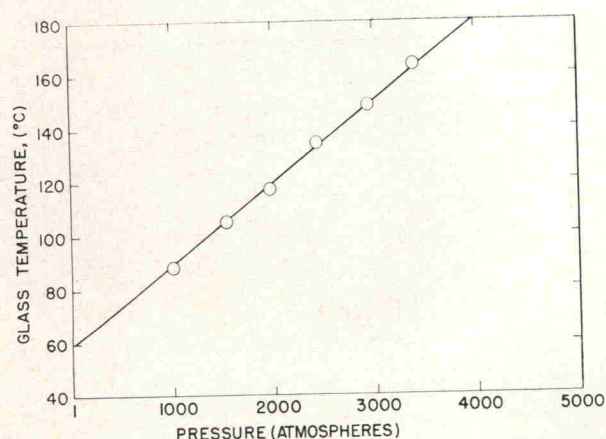


Figure 7. Phase diagram for an epoxide polymer hardened with DDSA.

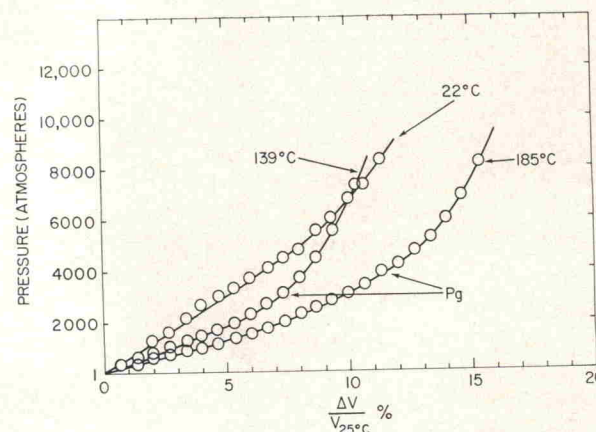


Figure 8. Compressibility of an epoxide polymer with hardener D.

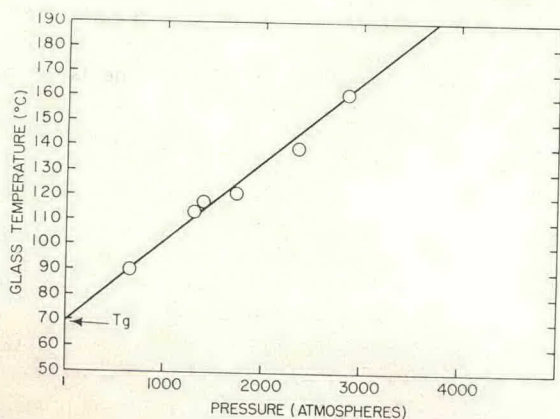


Figure 9. Phase Diagram for an epoxide polymer with hardener D.

asymptotically. At extremely high pressures it is assumed that primary chemical bonds will be broken.

It has been suggested by a number of investigators (2, 6, 21) that the observed compressibilities consist of two distinct parts. One part, which is the greatest at low pressures ($< 10,000$ atmospheres) results from the "squeezing out" of the available free volume and/or holes in the polymer. This component of the compressibility is of course temperature dependent. The second and smaller part, which occurs mostly at high pressures ($> 10,000$ atmospheres), results from the shortening of the equilibrium positions of the molecules. This component exhibits little temperature dependence.

Assuming that most of the compressibility is due to the "squeezing out" of the free volume, the results of this study imply that the available free volume of many polymers is of the order of 10 to 15%. This is also the order of magnitude which has been recently calculated for various polymers from electrical resistivity (22) and diffusion (23) studies and is higher than the WLF "universal" value of 2.5% (9). O'Reilly (17) has recently pointed out that the observed behavior of the volume of a polymer at high pressures will require modification of our present free volume model and that the pressure dependence of the fractional free volume is more complex than the temperature dependence.

The phase diagrams presented here should be very useful in polymerization studies and in molding and laminating applications. It is well established that as polymerization proceeds the glass transition temperature of the system increases (24) progressively, finally leveling off to a characteristic value for the solid completely polymerized polymer. Furthermore, to obtain the maximum extent of polymerization it is necessary to complete the polymerization at a temperature higher than the transition temperature for the completely polymerized polymer. It is therefore of considerable importance to have accurate data for the temperature at which the glass transition occurs.

For example, assume that Epon 828 with Hardener D is being polymerized at a pressure of 1000 atmospheres. Since it is well established that the final stage in the polymerization cycle must be above T_g (or P_g when pressure is a factor) we need only to consult the phase diagram to select the correct temperature. As shown in

Figure 9 at 1000 atmospheres P_g is about 100°C and adding 25°C to this value to be on the safe side we find the optimum temperature for the final stage of polymerization to be 125°C .

This illustrates one of the practical applications of the glass-rubber phase diagrams. Another application is in determining T_g for new polymers.

Finally, the errors involved in these measurements must be considered. High pressure measurements are usually subject to error due principally to the fact that no method has yet been devised to measure directly the compressibility of a solid. Unfortunately the volume of a container (such as our compressibility tester) will change slightly when subjected to pressure. Some preliminary calculations indicated that under the experimental conditions employed in this study, changes in the volume of the tester were negligible. Swenson (25), who used an apparatus similar to ours, determined the compressibility of sodium to about 20,000 atmospheres with a probable error of 2%. O'Reilly (17), who employed a compressibility tester very similar to ours noted that changes in the volume of the tester due to temperature and pressure were negligible.

Conclusions

It has been the purpose of this article to present the results obtained by high pressure measurements on a number of representative polymers and to qualitatively discuss the results. Compressibility is a thermodynamic parameter and the data and results presented here are presently being analyzed for additional thermodynamic parameters. These data are expected to contribute to explaining the observed compressibilities.

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