JOURNAL OF MATERIALS SCIENCE 9 (1974) 289–292

Pressure dependence of the shear modulus of various polymers

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A torsion pendulum has been used to measure the shear modulus of a range of polymers as a function of applied hydrostatic pressure at 20° C. The pressure medium was usually nitrogen gas and the maximum pressure 20000 psi. The results show that the shear modulus of each polymer is increased by the application of pressure, and the magnitude of the increase is greatest for experiments carried out at temperatures just above an atmospheric relaxation temperature. The increase in shear modulus takes a finite time, of the order of minutes, to be achieved, the equilibrium value being reached in a shorter time at higher temperature.

1. Introduction

The elastic properties of polymers are very different from those of most other solids – their tensile and shear moduli are significantly lower than, for example, metals or inorganic solids. Polymers consist of long chain molecules which in amorphous polymers are randomly arranged. Semi-crystalline polymers are made up partly of ordered regions and partly of amorphous regions. The elastic moduli of polymers cannot arise primarily from the bending or stretching of the main chain or indeed of crystallites; if it were, the modulus would be far larger than that observed. The elastic properties are mainly due to the uncoiling or sliding of chains over one another in response to an applied stress. The molecular mobility of the chains is strongly influenced by the available free volume. If the polymer is compressed, the free volume will be reduced; the intermolecular forces between segments will increase and the elastic modulus would be expected to increase.

Hydrostatic pressure has been shown to have a significant effect on the mechanical properties of polymers. Ainbinder *et al* [1] showed that the Young's modulus of a number of polymers increased when pressure was applied. Mears *et al* [2] found similar behaviour in polyethylene and polypropylene. Measurements of shear modulus as a function of pressure were carried out by Rabinowitz *et al* [3] on polymethylmethacrylate, polyethylene terephthalate and polyethylene. The shear moduli of these polymers increased with pressure. More recently Pugh *et al* [4] measured the pressure dependence of the Young's modulus of polystyrene, polymethylmethacrylate, high density polyethylene and nylon 66 up to an applied pressure of 7 kbar. The modulus of polystyrene and polymethylmethacrylate increased slightly with pressure but the increase was far greater for the polyethylene and nylon samples.

Most investigators have observed the pressure dependence of modulus by measuring the gradients of stress/strain curves obtained at different pressures, a different sample being used at each pressure. The results described in this paper, by contrast, were obtained by using one polymer sample at various applied pressures.

The shear modulus was determined by means of a torsion pendulum which was constructed within a high pressure chamber as previously described [5]. Specimens were subjected to strains of less than 1% at 1 Hz and the pressure was varied from atmospheric to 20 000 psi (1.4 kbar). In general the pressure medium employed was nitrogen gas. However, because nitrogen plasticizes PTFE, the experiments on this polymer were carried out in helium gas. In the experiments where the shear modulus was measured as a function of pressure the polymer was left for at least an hour at any one particular pressure before any measurements were made.

The low density polyethylene was WNC 71 (ICI) of density 0.9028 while the high density polyethylene was Marlex 6001 of density 0.9600.

The polypropylene was extrusion moulded, of medium crystallinity and density 0.8738. The natural rubber sample was cured for 20 min at 142°C and was formed from 100 parts by weight of smoked sheet, 4 parts by weight of zinc oxide, 4 parts by weight of tetramethyliuram disulphide, and 1 part by weight of phenyl beta naphthylamine. The rigid polyvinyl chloride consists of 150 parts by weight of Breon PVC, 0.75 parts by weight of calcium stearate and 1.5 parts by weight of an organo tin stabilizer. The plasticized PVC is similar but 50 parts by weight of Breon is replaced by the same weight of dialkyl phthalate. The polyvinyl fluoride was a sample prepared by Du Pont while the PVDF was Kynar 200 (Pennsalt). The PCTFE was quenched from the melt and had a density of 2.082, while the PTFE was a commercial medium crystallinity sheet. The nylon 6 was injection moulded and of density 1.112 at 20°C while the PMMA was ICI "Perspex" and the Bakelite type E10P. The PET was amorphous ICI "Melinex" of density 1.337 g cm^{-3} at 23°C while the PC was amorphous Makrolon.

2. Results

Figs. 1 to 3 show the room temperature pressure dependence of the polymers which have been studied in this investigation. The shear moduli are increased by the application of hydrostatic pressure, but by differing amounts. The largest increase over the total pressure range of *c.* 20 000 psi is a fourfold increase for the plasticized PVC while the shear modulus of polypropylene is also increased by a large amount. These two polymers have glass transition temperatures of 18 and 2°C at 1Hz and the effect of pressure is to shift the temperature of the transition upwards towards that of the test (21°C): the effective onset of the glassy state causes the large increase in the shear modulus. For all the other polymers the modulus varies almost linearly with pressure.

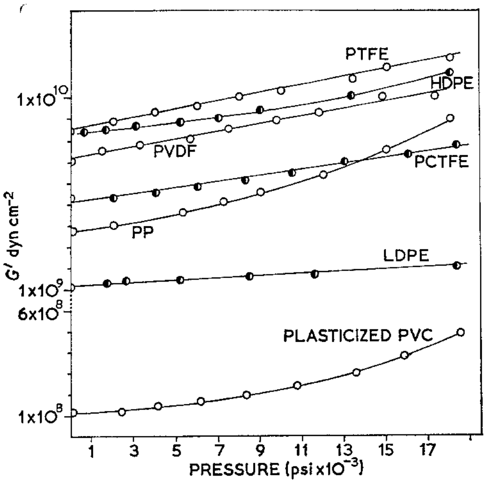

Figure 1 Pressure dependence of the shear moduli of various polymers at 20°C.

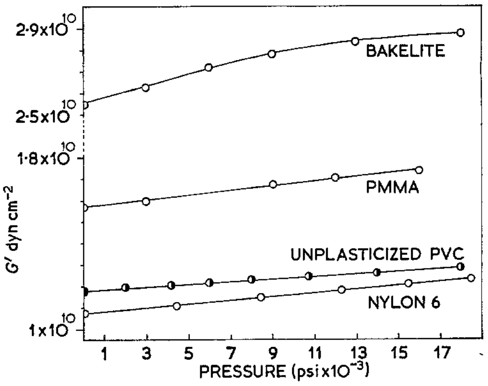

Figure 2 Pressure dependence of the shear moduli of various polymers at 20°C.

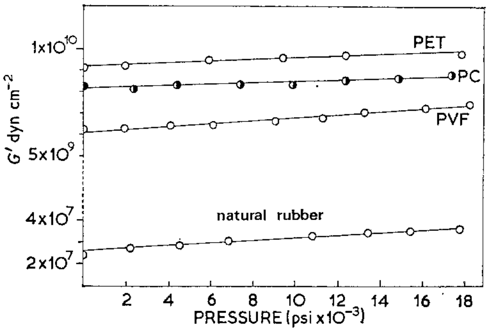

Figure 3 Pressure dependence of the shear moduli of various polymers at 20°C.

Fig. 4 shows the time-dependence of the shear modulus at 10 000 psi for plasticized PVC, low density PE, and PCTFE at 20°C and PCTFE at 45°C. The modulus reaches its maximum value after a finite time which is of the order of 5 min. This time-dependence is presumably due to shear stresses which are produced when a hydrostatic pressure is applied to a non-homogeneous medium. Thus the applied pressure does not simply press the molecules closer together – it slides them into new positions against a "viscous" resistance. When the temperature of the test is increased as for PCTFE the equilibrium

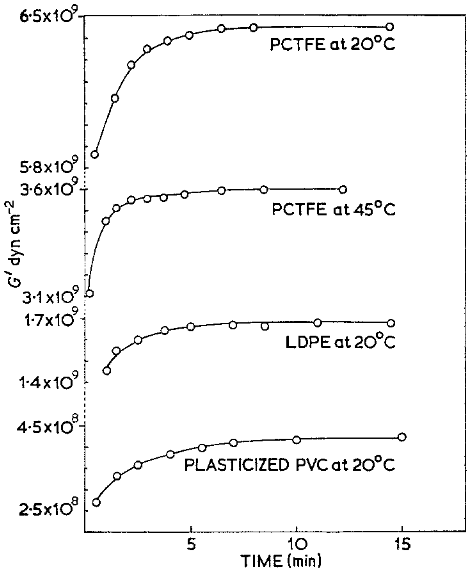

Figure 4 Time dependence of the shear modulus G′ at 10 000 psi.

maximum value of G' is reached in a shorter time. Associated with this polymer at 20°C is a relaxation time of the order of 1.5 min while at 45°C the relaxation time falls to 0.5 min. This time-dependent process has an "activation energy" of about 5 kcals.

3. Discussion

Mears *et al* [2] have studied the theoretical increases in modulus with pressure for cases where the tensile modulus is comparable in magnitude with the applied hydrostatic pressure. By using finite strain elasticity theory they derive the linear relationship

$$G' = G_0' + \frac{(5 - 4\nu)(1 - \nu)}{(1 + \nu)} p$$

where G' is the shear modulus at pressure p, G_0' the atmospheric pressure value of the shear modulus, and ν is Poisson's ratio which is assumed constant. The gradients of the curves of G' against p (Figs. 1 to 3) can be used to compute values of ν if this equation is assumed correct. For the non-linear curves the gradient has been approximated to that of a straight line joining the G' values at atmospheric and peak pressure. The results are shown in Table I.

In our experiments the maximum applied pressure is about 1.24×10^9 dyn cm^{-2} so that Mears' theory should be particularly applicable to LDPE, rubber, plasticized PVC and PP. None of these polymers give reasonable theoretical values of ν, nor indeed do many of the polymers in Table I. Our results do not therefore support this theory.

Fig. 3 includes a plot of G' against p for the natural rubber sample. The theory of rubber elasticity gives the following result for the shear modulus of an elastic network

$$G' = NkT \frac{\mathbf{r}_i^2}{\mathbf{r}_f^2}$$

where N is the number of network chains per cubic centimetre, k is Boltzman's constant, T is the temperature, $\mathbf{r}_i^2$ is the square of the vector

TABLE I

Polymer	G_0' dyn cm^{-2}	$1/G_0' \frac{dG'}{dp}$ dyn^{-1} cm^{-2}	Calculated ν
PET	9.11×10^9	6.06×10^{-11}	0.63
PC	9.29×10^9	5.10×10^{-11}	0.69
PVC rigid	1.18×10^{10}	7.05×10^{-11}	0.55
LDPE	1.10×10^9	6.59×10^{-10}	0.58
PVDF	7.00×10^9	4.49×10^{-10}	0.16
PTFE	8.50×10^9	3.07×10^{-10}	0.22
PCTFE	5.33×10^9	3.59×10^{-10}	0.32
HDPE	8.30×10^9	2.82×10^{-10}	0.26
Rubber	2.47×10^7	3.83×10^{-10}	0.98
PVF	6.21×10^9	1.52×10^{-10}	0.52
Nylon 6	1.08×10^{10}	1.34×10^{-10}	0.40
Bakelite	2.54×10^{10}	1.05×10^{-10}	0.22
Plasticized PVC	1.24×10^8	2.35×10^{-9}	0.75
PP	3.79×10^9	1.09×10^{-9}	0.07
PMMA	1.57×10^{10}	1.00×10^{-10}	0.38

$\mathbf{r}_i$ associated with the ith network chain and $\mathbf{r}_f^2$ is the mean square end to end length that the chain would assume in free space if the network junctions were severed. Tobolsky and Shen [6] maintain that $\mathbf{r}_f^2$ is a function of volume and therefore of pressure and modify the equation of state for the force F in a rubber network to

$$F = \mathrm{A}\left(\frac{V_0}{V}\right)^{\gamma}\left[\frac{L}{L_0} - \frac{L_0^2}{L^2}\frac{V}{V_0}\right]$$

where L_0 is the length and V_0 the volume of a rectangular strip of rubber at zero force and zero pressure, L is the length and V the volume at temperature T and pressure p, $\gamma = \mathrm{d}\ln \mathbf{r}_f^2/\mathrm{d}\ln V$, and A is a constant.

$$\gamma = \frac{-\,\mathrm{d}\ln G'}{\mathrm{d}\ln V} = \frac{-\,\mathrm{d}\ln G'}{\mathrm{d}p}\,\frac{\mathrm{d}p}{\mathrm{d}\ln V}\,\frac{\mathrm{d}\ln G'}{\mathrm{d}p}\;.\,x^{-1}$$

where x is the compressibility. Using our data and a value for x given by Weir [7] $\gamma = 0.003$. Therefore while Tobolsky and Shen may be correct in their assumption that $\mathbf{r}_f^2$ is a function of volume, this particular value of γ shows that the effect must be very small indeed.

4. Conclusion

The shear moduli of all the polymers studied have been found to increase by the application of hydrostatic pressure. In most cases the modulus varies almost linearly with pressure. Plasticized PVC and PP are exceptions because of the presence of the atmospheric glass transition just below the temperature of the test. The application of pressure shifts these polymers into the glassy state and hence increases the modulus by a greater amount. Secondary relaxations in PTFE and PMMA are known to be shifted upwards in temperature by the application of pressure and to occur at temperatures close to that of the test (at 1 Hz) [8]. However, in our experiments, the moduli of these polymers does not increase markedly with pressure. For PMMA this is presumably because the β relaxation is accompanied by only a small fall in modulus. In the case of PTFE the test temperature is just below the atmospheric β relaxation temperature, so that the upward shift of this relaxation with pressure has a far smaller effect on the modulus than it would if the test temperature had been above the atmospheric relaxation temperature. The presence of secondary relaxations complicates the pressure dependence of shear modulus and can only be completely removed by carrying out experiments at temperatures below that at which relaxations occur at atmospheric pressure.

The pressure dependence of the shear modulus has been observed to be time-dependent and for three polymers studied the modulus reaches equilibrium within 15 min. This arises partly because the application of pressure to a non-homogeneous medium produces a shear stress. This causes chains to slide over each other against a "viscous-like" resistance: the effect is time dependent and at higher temperatures the time to reach equilibrium is shorter. The time-dependence also arises because of the finite time required for molecules in the amorphous regions to reach equilibrium after the application of pressure. This suggests that thermodynamic treatments are unjustified in considering hydrostatic pressure as a simple variable.

Acknowledgements

We wish to express our thanks to the Thomas and Elizabeth Williams Scholarship Fund for an award to one of us (E.J.P.) and to Dr P. B. Bowden for helpful discussions.

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Received 21 May and accepted 6 July 1973.