JOURNAL OF MATERIALS SCIENCE 8 (1973) 1510–1516

Review

Effect of hydrostatic pressure on the mechanical properties of polymers: a brief review of published data

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This paper brings together most of the published data on the properties of polymers in a hydrostatic pressure environment. In particular, information is collated on the effect of hydrostatic pressure on the relaxation temperatures of a wide range of polymers.

1. Introduction

Relaxation processes in polymers are usually associated with the displacement or rotation of a chain segment or a side group. This movement demands a certain amount of available space within the bulk of the polymer. Consequently, application of a hydrostatic pressure would be expected to hinder these movements; this in turn implies that the relaxation can only occur at an increased temperature.

The following brief account brings together most of the published data on the effect of pressure on the elastic modulus, yield properties and viscoelastic characteristics of a wide range of polymers. In principle this should provide a better picture of the mechanisms involved in any particular relaxation process. Unfortunately, the information obtained is often discordant and probably depends in an ill-defined way on specimen purity and crystallinity. In addition many of the parameters required by existing theories are not known at all or are only known with a poor degree of accuracy. However, the data brought together at the end of this review provide the raw material for any further theoretical studies in this field.

2. Previous modulus measurements under hydrostatic pressure

The influence of pressure on the mechanical behaviour of organic polymers was first studied by Bridgman [1] in an examination of the tensile properties of melamine-formaldehyde resin which is brittle at atmospheric pressure. The modulus increased three-fold at 24.6 kb and the material showed a well defined yield point. Holliday *et al* [2] subsequently studied the tensile behaviour of glassy polystyrene at atmospheric pressure and 7.6 kb. The brittle behaviour at atmospheric pressure changed at the high pressure to exhibit a yield stress and increased ductility. A broader study over a more limited pressure range was carried out by Ainbinder *et al* [3] who examined the behaviour in tension and compression of polymethylmethacrylate, polystyrene, polyethylene, and polytetrafluoroethylene. Over this lower range of pressure the results show substantial increases in Young's modulus, yield stress and the strain to fracture for the polymers studied.

The moduli of elastomers at room temperature as a function of hydrostatic pressure received considerable attention from Paterson [4]. By means of a piston arrangement he measured Young's modulus as a function of pressure for natural rubber, silicone rubber, fluorosilicone, low nitrile rubber and polyurethane. Typically, for natural rubber there was a two-fold increase in modulus up to 4000 atm and a thousand-fold increase between 4000 and 6000 atm. This sudden change is associated with the effect of pressure on the glass transition temperature and for all the elastomers studied the shift was about 16°C per 1000 atm.

In 1968 Sardar *et al* [5] investigated the time stress-strain behaviour of polyoxymethylene under varying hydrostatic pressures of up to 8 kb. The Young's modulus, yield stress, and fracture stress were found to increase strongly with pressure by a factor of three at the highest pressure. The authors also carried out stress relaxation experiments and found that the modulus increase was associated with a displacement of the γ relaxation from -75 to 20° C at a pressure of 5 kb. The marked increase in yield stress with pressure is qualitatively in agreement with the general observation that the yielding of polymers is accompanied by an increase in volume. It is also consistent with the fact that at atmospheric pressure the yield stress in compression is greater than that in tension. Whitney and Andrews [6] showed that polymers dilated in tension but there was a volume contraction in compression so that the higher compressive yield stress is related to a loss in free volume. In a more recent work Christiansen *et al* [7] studied the tensile deformation of amorphous polyethylene terephthalate and polycarbonate, and a semi-crystalline polychlorotrifluoroethylene and polytetrafluoroethylene up to 8 kb. The former three polymers showed increases of yield stress, yield strain, and Young's modulus as did polytetrafluoroethylene up to 4 kb. The difference in behaviour above this pressure correlated with a change of phase in the polytetrafluoroethylene as has been shown by Flack [8]. The authors [7] also suggested that the ductile-brittle transition of a normally ductile amorphous polymer could be closely related to a specific dynamic mechanical relaxation, the temperature of observation of which increases with pressure.

Similar experiments have been carried out on polyethylene and polypropylene by Mears *et al* [9]. Using tensile experiments they find that both Young's modulus and yield stress increase significantly with applied pressure but the nature of yielding and fracture is different for the two polymers. Polyethylene deforms by shear whereas polypropylene reduces to a fine point before separation. The authors qualitatively attribute this to the squeezing together of chains in the amorphous region. The free volume decreases and the secondary forces between neighbouring segments increase so that a higher applied stress is necessary to initiate the molecular mobility associated with plastic yielding. Mears and Pae [10] studied polycarbonate and found that both Young's modulus and peak yield strength increased linearly with pressure. A further study on polycarbonate and also polytetrafluoroethylene has been made by Sauer *et al* [11]. Again the Young's modulus and yield stress increased with pressure. Polytetrafluoroethylene showed more brittle fracture with increasing pressure while the ductility of polycarbonate increased with increasing pressure. The large increase of modulus at pressures in excess of 7 kb is attributed to the shifting of secondary relaxations with increasing pressure. At atmospheric pressure the γ relaxation of polytetrafluoroethylene occurs at -110° C and the β relaxation in the polycarbonate at -80°C; 8 kb pressure causes these transitions to occur near 20° C.

Measurements of shear modulus as a function of pressure have been carried out by Rabinowitz *et al* [12] on polymethylmethacrylate, polyethylene terephthalate and polyethylene. The shear modulus and maximum shear stress increased with pressure. Similarly Vroom and Westover [13] obtained increases in Young's modulus with pressure for polystyrene, polychlorotrifluoroethylene and polymethylmethacrylate. Pugh *et al* [14] made tensile tests on polystyrene, polymethylmethacrylate, high density polyethylene and nylon 66 up to a pressure of 7 kb. Young's modulus and the yield strength of polystyrene and polymethylmethacrylate increased slightly with pressure but the increases were far greater for the polyethylene and nylon samples. Recently Jones Parry and Tabor [15] have studied the pressure dependence of the shear modulus for a wide range of polymers up to pressures of 1.4 kb. In all cases the modulus increased with the application of pressure.

3. Dielectric loss measurements carried out under hydrostatic pressure

Igonin and his co-workers [16] have made dielectric studies on polyvinyl chloride, polymethyl acrylate and polymethylmethacrylate in the glass transition region at three frequencies and pressures up to 2500 atm. The temperature of maximum loss was found to increase linearly with pressure up to 2000 atm, above which non-linearity is observed. Koppelman and Gielessen [17] investigated the dielectric loss of polyvinyl chloride in the temperature range 20 to 120° C at pressures up to 1000 atm over four decades of frequency. This is a particularly interesting investigation since it includes both the glass transition region and a further secondary β loss at a lower temperature. Increasing pressure decreases the frequency of maximum loss for both peaks. The glass transition loss moves to lower frequency faster than the secondary loss.

TABLE I

Polymer	Relaxation	Temperature of relaxation at atmospheric pressure at 1 Hz (°C)	Shift °C per 1000 atm	Method	Author
PVC	α	75	13	Dielectric	Igonin *et al* [16]
,,	α	75	19	,,	Heydemann [19]
,,	β	60	17.2	,,	,,
,,	α	75	14	Volume	Heydemann and Guicking [28]
PVC + 10% dioctyl phthalate	α	60	14	,,	,,
PVC + 20% ,, ,,	α	40	13	,,	,,
PVC + 30% ,, ,,	α	25	15	,,	,,
PVC	α	75	13.5	,,	Hellwege *et al* [27]
,,	α	75	15	,,	Bianchi [31]
,,	α	75	16	Dielectric	Igonin *et al* [16]
,,	α	75	16.5	Mechanical (1 Hz)	Zosel [39]
PVC + 20% dioctyl phthalate	α	40	16.5	,,	,,
PVC	α	80	16	,,	Billinghurst and Tabor [42]
PVC	α	85	11	,,	Jones Parry and Tabor [44]
PVC + 33% dialkyl phthalate	α	20	11.5	,,	,,
PVC + plasticiser	α	19	11	,,	,,
PVC	α	69	25	,,	,,
Irradiated	α	79	16	,,	,,
PVDC	α	81	16	,,	,,
PVDC	β	13	16	,,	,,
PVF	α	53	12	,,	,,
PVDF	α	70	28	,,	,,
PCTFE	β	97	10	,,	,,
,,	γ	− 13	10	,,	,,
PTFE	β	20	20	Volume	Yasuda and Araki [26]
PTFE	β	20	18	Mechanical (1 Hz)	Billinghurst and Tabor [42]
PTFE-FEP copolymer	α	82	13	,,	Jones Parry and Tabor [44]
LDPE	if γ	− 125	22	Volume	Heydemann and Hauck [23]
,,	if β	− 20	7	,,	,,
,,	β	− 20	0	Mechanical (1 Hz)	Jones Parry and Tabor [44]
,,	α	66	21	,,	,,
,,	α_a	61	17	,,	,,
,,	α_c	91	10	,,	,,
HDPE	α	50	16	,,	,,
,,	β	13	5	,,	,,
Polypropylene	β	2	9	,,	,,

TABLE I—*continued*

Polymer	Relaxation	Temperature of relaxation at atmospheric pressure at 1 Hz (°C)	Shift °C per 1000 atm	Method	Author
Polypropylene	α	90	5	Mechanical (1 Hz)	Jones Parry and Tabor [44]
,,	α_a	70	10	,,	,,
,,	α_c	95	7	,,	,,
,,	β	2	20	Volume	Passaglia and Martin [29]
PIB	α	− 70	24	Dynamic compressibility	McKinney and Blecher [38]
,,	α	− 70	24	nmr	Singh and Nolle [35]
,,	α	− 70	23	,,	Nolle and Billings [36]
,,	α	− 70	35	,,	Anderson *et al* [41]
,,	α	− 70	13	Ultrasonic	Nolle [45]
Natural rubber	α	− 50	24	Dynamic compressibility	McKinney *et al* [37]
,,	α	− 50	29	nmr	Anderson *et al* [41]
,,	α	− 50	16	Modulus measurements	Paterson [4]
Silicone rubber	α	− 50	16	,,	,,
Fluorosilicone rubber	α	− 50	16	,,	,,
Polystyrene	α	115	32	Mechanical (1 Hz)	Billinghurst and Tabor [42]
,,	α	115	30	Volume	Hellwege *et al* [27]
Nylon 6	α	64	16	Mechanical (1 Hz)	Jones Parry and Tabor [43]
Nylon 610	α	65	13	,,	,,
Nylon 66	α	68	10	,,	,,
PMMA	α	115	29	,,	Billinghurst and Tabor [42]
,,	α	115	24	,,	Zosel [39]
,,	α	115	23	Volume	Hellwege *et al* [27]
,,	α	115	18	,,	Heydemann and Guicking [28]
,,	α	115	20	Dielectric	Heydemann [19]
,,	β	20	7.5	,,	,,
,,	β	20	2	Mechanical (1 Hz)	Zosel [39]
,,	β	20	4	,,	Jones Parry and Tabor [44]
PVAC	α	35	15	Volume	Bianchi [32]
,,	α	35	20	,,	McKinney and Belcher [38]
,,	α	35	18	Mechanical (1 Hz)	Jones Parry and Tabor [44]
PET amorphous	α	80	16	,,	,,
PET 30% crystalline	α	96	18	,,	,,
Polycarbonate	α	150	44	Volume	O'Reilly [18]

O'Reilly [18] made dielectric studies through the glass transition for polyvinyl acetate over a pressure range of up to 3300 atm. The temperature of the loss maximum is displaced by 22°C per 1000 atm at constant frequency.

Polymethylmethacrylate and polyvinyl chloride have been studied dielectrically by Heydemann [19]. Two transitions are observed for both polymers and their behaviour is monitored as a function of pressure. Extensive dielectric studies have been carried out by Williams [20-22] and by Williams and Watts [23]. These investigations observed relaxations as a function of frequency, temperature and applied hydrostatic pressure, and the polymers studied include polymethyl acrylate, polymethylmethacrylate, polypropylene oxide and polynonyl methacrylate.

4. Volume measurements as a function of pressure

Weir [24] has made an extensive study of the compressibilities of various rubbers. Matsuoka and Maxwell [25] measured the compressibility of polystyrene and polyethylene over a temperature range 0 to 100°C and applied hydrostatic pressure of up to 2000 atm. The glass transition temperature, as measured from kinks in isobaric compressibility versus temperature curves was found to be shifted to higher temperatures by the application of the pressure. Yasuda and Araki [26] studied the β relaxation of polytetrafluoroethylene by dilatometric means. They found that the relaxation was displaced linearly with pressure at a rate of 20°C per 1000 atm. Hellwege and his co-workers [27] used a piezometer to study the compressibility of polystyrene, polymethylmethacrylate, and polyvinyl chloride throughout the transition region at pressures up to 2000 atm. They measured the shift in T_g for each polymer and found it to be in good agreement with the theoretically derived quantity $\Delta\beta/\Delta\alpha$, where $\Delta\beta$ is the difference between the bulk compressibility in the rubber and glass states, and $\Delta\alpha$ the difference between the volume expansion coefficient in the rubber and glass states. Heydemann and Guicking [28] studied polymethylmethacrylate and polyvinyl chloride plasticized by various known amounts of dioctyl phthalate. Measurements of specific volume were made as a function of temperature and applied hydrostatic pressure. The glass transition temperatures were shifted upwards with applied pressure and the shifts for the different vinyl chloride samples were identical over the pressure range studied.

Passaglia and Martin [29] carried out dilatometric studies on polypropylene over a temperature range of − 30 to + 50°C and applied hydrostatic pressure of up to 7000 atm. The glass transition was shifted non-linearly upwards, the greatest shift being at low pressures. By measuring the thermal expansion coefficient the authors were able to relate this shift successfully to the quantity $\Delta\beta/\Delta\alpha$. Hennig [30] used a sliding contact technique to determine the isothermal compressibility of polycarbonate, polyvinyl chloride, polymethylmethacrylate and polystyrene. His measurements were made at 22°C and at pressures up to 3000 atm. Bianchi [31] performed dilatometric studies on polyvinyl acetate under varying pressures and found the glass transition to be shifted by 23°C per 1000 atm. In a later study Bianchi [32] made an interesting investigation on the effect of pressure on the glass transition temperatures of polyvinyl chloride and polyvinyl acetate. The pressure was applied in three distinct ways; by applying the pressure when the polymer was in the liquid state and then cooling it isobarically through T_g, by applying the pressure in the glassy state and heating isobarically through the transition, and lastly by heating the polymer at constant volume by increasing the pressure. Three different shifts were obtained for each polymer, and the largest was three times the lowest. A very interesting study on polyethylene has recently been made by Heydemann and Hauck [33]. Compressibility measurements were made over the range − 30 to + 50°C and up to 30000 atm. A transition was observed at 23°C and 6000 atm. This is believed to be a manifestation of either the β or γ relaxation which has been displaced by pressure. The authors were unable to discriminate between these relaxations, but the work is noteworthy as the first study which has been made on the effect of pressure on secondary relaxation in polyethylene. Previously Matsuoka [34] had investigated the effect of pressure on the melting point of polyethylene.

5. Dynamic measurements under hydrostatic pressure

Singh and Nolle [35] studied the absorption of ultrasonic waves in polyisobutylene at temperatures above T_g. The temperature of maximum attenuation of longitudinal waves increases with increasing pressure at a rate of 25°C per 1000 atm. The absorption of longitudinal waves includes contributions from the shear and bulk modulus which complicates the interpretation. However, the authors succeed in finding the shift in T_g with pressure. A similar study was made on polyisobutylene by Nolle and Billings [36] using nuclear magnetic resonance. Both the line width and spin lattice relaxation times increased with increasing pressure. A change in pressure of 1000 atm was equivalent to a change in temperature of 24° C for both processes. McKinney *et al* [37, 38] have studied the dynamic compressibility of polyvinyl acetate and natural rubber vulcanizate. Measurements were made at pressures of up to 1000 atm in the temperature range − 30 to + 70° C at frequencies between 50 and 1000 Hz. The rubber showed $\partial T/\partial P$ at constant free volume to be 24° C per 1000 atm, and the glass transition temperature of the polyvinyl acetate was shifted by 20° C per 1000 atm.

A torsion pendulum was used by Zosel [39] to study the mechanical properties of polymethylmethacrylate, polyvinyl chloride, and plasticized polyvinyl chloride under varying temperature and pressure. The glass transition temperature of the polyvinyl chloride samples was shifted upwards by an identical amount for a given applied pressure. The glass transition of the polymethylmethacrylate was displaced upwards in temperature by a greater amount but the β relaxation was only slightly affected. Asay and his co-workers [40] studied the complex bulk modulus of polymethylmethacrylate by measuring attenuation and velocities at frequencies of 6.3 MHz over a temperature range of 20 to 80° C and pressures of up to 10 000 atm. By measuring the proton spin-lattice relaxation time at frequencies of 30 MHz, Anderson *et al* [41] obtained shifts in the glass transition temperature of natural rubber, polyisobutylene, polycis butadiene and ethylene-propylene co-polymer. The temperature range was − 125 to +125° C and the pressure could be applied up to 680 atm.

Billinghurst and Tabor [42] used a torsion pendulum to study the effect of pressure on the glass transition temperatures of polymethylmethacrylate, polystyrene, polyvinyl chloride and plasticized polyvinyl chloride. Modulus measurements were also made as a function of temperature and pressure for polytetrafluoroethylene and polyethylene. The glass transitions are shifted upwards in temperature by the application of hydrostatic pressure. This work was extended by Jones Parry and Tabor [43, 44] and the polymers studied included the polyethylenes, polypropylene, halogen polymers, polyvinyl acetate, polyethylene terephthalate and polyamides. In some cases the pressure dependence of secondary relaxations has been observed. In all cases pressure shifted the relaxations to higher temperatures.

Table I summarizes the main results in the literature. It should be noted that the actual value of the relaxation temperature in column 3 depends on the frequency of the test so that for example a relaxation which occurs at 50° C in a dilatometric experiment will occur at a slightly higher temperature in a torsion pendulum experiment (frequency ~ 1 Hz) and at perhaps 60 or 70° in a dielectric experiment at a frequency of, say, 1000 Hz.

References

1. P. W. BRIDGMAN, *J. Appl. Phys.* **24** (1953) 560.
2. L. HOLLIDAY, J. MANN, G. A. POGANY, H. PUGH, and D. A. GUNN, *Nature* **202** (1964) 381.
3. S. B. AINBINDER, M. G. LAKA, and YU. I. MAIRORS, *Mekkanika Polemerov.* **1** (1965) 65.
4. M. S. PATERSON, *J. Appl. Phys.* **35** (1964) 176.
5. D. SARDAR, S. V. RADCLIFFE, and E. BAER, *Polymer Sci. Eng.* **8** (1968) 290.
6. W. WHITNEY and R. D. ANDREWS, *J. Polymer Sci.* **C16** (1967) 2981.
7. A. W. CHRISTIANSEN, E. BAER, and S. C. RADCLIFFE, *Phil. Mag.* **24** (1971) 451.
8. H. D. FLACK, *J. Polymer Sci.* **A-2 10** (1972) 1799.
9. D. R. MEARS, K. D. PAE, and J. A. SAUER, *J. Appl. Phys.* **40** (1969) 4229.
10. D. R. MEARS and K. D. PAE, *Polymer Letters* **7** (1969) 349.
11. J. A. SAUER, D. R. MEARS, and K. D. PAE, *Europ. Polymer J.* **6** (1970) 1015.
12. S. RABINOWITZ, I. M. WARD, and J. S. C. PARRY, *J. Mater. Sci.* **5** (1970) 29.
13. W. I. VROOM and R. F. WESTOVER, *SPE J.* **25** (1969) 58.
14. H. PUGH, E. F. CHANDLER, L. HOLLIDAY, and J. MANN, *Polymer Eng. Sci.* **11** (1971) 463.
15. E. JONES PARRY and D. TABOR, to be published.
16. L. A. IGONIN, Y. OVCHINNIKOV, and V. A. KARGIN, *Doklady Akad. Nauk. SSSR* **128** (1959) 127.
17. J. KOPPELMAN and J. GIELESSEN, *Z. Electrochem.* **65** (1961) 689.
18. J. M. O'REILLY, *J. Polymer Sci.* **57** (1962) 429.
19. P. L. M. HEYDEMANN, *Kolloid Z.* **195** (1964) 122.
20. G. WILLIAMS, *Trans. Faraday Soc.* **60** (1964) 1556.
21. *Idem, ibid* **61** (1965) 1564.
22. *Idem, ibid* **62** (1956) 2091.
23. G. WILLIAMS and D. C. WATTS, *ibid* **67** (1971) 2793.
24. G. E. WEIR, *J. Res. Nat. Bur. Stand.* **50** (1953) 321.

25. S. MATSUOKA and B. MAXWELL, *J. Polymer Sci.* **32** (1958) 131.
26. T. YASUDA and Y. ARAKI, *J. Appl. Polymer Sci.* **5** (1961) 331.
27. K. H. HELLWEGE, W. KNAPPE, and P. LEHMAN, *Kolloid Z.* **183** (1963) 110.
28. P. L. M. HEYDEMANN and H. D. GUICKING, *Kolloid Z.* **193** (1963) 16.
29. E. PASSAGLIA and G. M. MARTIN, *J. Res. Nat. Bur. Stand.* **68** (1964) 273, 519.
30. J. HENNIG, *Kolloid Z.* **202** (1965) 127.
31. U. BIANCHI, *J. Phys. Chem.* **69** (1965) 1497.
32. *Idem, Rheol. Acta.* **10** (1971) 213.
33. P. L. M. HEYDEMANN and J. C. HAUCK, *J. Polymer Sci.* **A-2 10** (1972) 1631.
34. S. MATSUOKA, *ibid* **57** (1962) 569.
35. H. SINGH and A. W. NOLLE, *J. Appl. Phys.* **30** (1959) 337.
36. A. W. NOLLE and J. J. BILLINGS, *J. Chem. Phys.* **30** (1959) 84.
37. J. MCKINNEY, H. BELCHER, and R. S. MARVIN, *Trans. Rheo. Soc.* **4** (1969) 347.
38. J. MCKINNEY and H. BELCHER, *J. Res. Nat. Bur. Stand.* **67A** (1963) 43.
39. A. ZOSEL, *Kolloid Z.* **199** (1964) 113.
40. J. R. ASAY, D. L. LAMBERSON, and A. H. GUENTHER, *J. Appl. Phys.* **40** (1969) 1768.
41. J. E. ANDERSON, D. D. DAVIS, and W. P. SCHLICHTER, *Macromol.* **2** (1969) 266.
42. P. R. BILLINGHURST and D. TABOR, *Polymer* **12** (1971) 101.
43. E. JONES PARRY and D. TABOR, *J. Physics* (to be published).
44. *Idem, Polymer* (to be published).
45. A. W. NOLLE, *J. Appl. Phys.* **31** (1960) 1694.

Received 28 March and accepted 9 April 1973.