Effect of absorbed water on the thermal relaxation of biaxially stretched crosslinked poly(methyl methacrylate)

John M. Barton
Materials Department, Royal Aircraft Establishment, Farnborough, Hampshire, UK

For three samples of the title materials the thermal relaxation characteristics were determined in rising temperature experiments and found to be dependent on water content. On heating, the polymers revert to the unstretched state and the onset temperature of this relaxation decreases with increasing water content. The most highly crosslinked polymers have the highest equilibrium water content at room temperature, the lowest relaxation onset temperature when saturated, and the highest relaxation onset temperature when dry. The effect of water on thermal relaxation is consistent with the observed depression of glass transition temperature. The relaxation of one of the materials was also studied isothermally. The effect of water is a temperature shift in the curve of log (maximum relaxation rate) against temperature. For a water content of 3.4 wt % this temperature shift is 25K, the same as the observed reduction in T_g. The effect of temperature on the maximum relaxation rate is of the form of the WLF equation. The apparent activation energy for thermal relaxation is lower in the saturated polymer.

INTRODUCTION

Crosslinked poly(methyl methacrylate) is widely used to make optically transparent components for aircraft. For such applications the materials can be supplied in the form of sheets which have been biaxially stretched while hot to improve the resistance to fracture and solvent crazing. Above a characteristic temperature the molecular relaxation processes occur sufficiently rapidly for the materials to change their dimensions and revert to the unstrained state. The thermal relaxation determines the maximum temperature at which the materials can be used. This paper is concerned with the effect of absorbed water on the thermal relaxation phenomenon.

EXPERIMENTAL

Materials

The materials were received in the form of sheets of either 0.125 or 0.25 in thickness, from three different commercial sources. They are designated materials A, B and C, respectively. The materials are all crosslinked poly(methyl methacrylate) containing a biaxial strain of 66 ± 2% along the major axes of the sheets.

Samples were taken from the materials either in the unrelaxed state or after relaxation in an air oven at 160°C for 1.5 h. The samples were cut with a saw and the cut surfaces were smoothed by abrasion with fine emery paper. For the thermal relaxation measurements the approximate dimensions of the samples were 0.5 x 0.5 x 0.15 cm with major axes corresponding to the major axes of the original sheets.

Conditioning of samples

Some of the samples were weighed on a microbalance and then immersed in distilled water at room temperature. Periodically samples were withdrawn and weighed after removing surplus water from their surfaces with filter paper. Other samples were dried to constant weight in a vacuum oven at 40°C. The water absorption reached equilibrium after about 14 days, while the vacuum-dried samples attained constant weight after about 8 days.

Acetone swelling

Samples of the relaxed materials, in the form of cubes with sides of about 0.64 cm length, were weighed and then immersed in acetone at room temperature. Periodically the samples were withdrawn and the weight recorded 60 sec after removal of surplus solvent with filter paper. Equilibrium swelling was attained within 26 days.

Differential scanning calorimetry (d.s.c.)

A DuPont 990 Thermal Analyser was used with the d.s.c. cell. The instrument was operated with a nitrogen flow of about 30 cm^3/min. The glass transition temperatures of the fully relaxed materials were measured on samples weighing about 15 mg. The d.s.c. scans were at a heating rate of 10 K/min and the T_g was taken as the temperature at the inflection of the heat flow–temperature curve in the glass transition region.

Thermomechanical analysis (t.m.a.)

The instrument was the DuPont 943 t.m.a. In the thermal relaxation measurements an unloaded quartz probe with a flat end of 0.6 cm diameter was used. The sample was

0032–3861/79/081018–07$02.00

Table 1 Water content of samples

Sample condition	Wt % water Material A	 Material B	 Material C
As-received (unrelaxed)	1.37	0.48	1.38
Saturated (unrelaxed)	3.47	2.06	3.52
Saturated (relaxed)	3.53	2.20	–

positioned on the sample platform and the probe was lowered just to touch the surface of the sample. The expansion of the samples along their minor axes was recorded as a function of temperature at constant heating rate or as a function of time at constant temperature. For the isothermal measurements the furnace was equilibriated at the required temperature while remote from the sample holder. After setting up the sample in the instrument the preheated furnace was then placed in position.

For measurements of modulus of relaxed samples above their T_g a quartz probe with a hemispherical tip of 0.254 cm diameter was used. After equilibriation at the required temperature the probe was lowered to touch the surface of the sample and the lowering screw was advanced by an extra quarter turn which imposes a contact load of 50 mg. The required load was then carefully placed on the load tray and the penetration recorded as a function of time. After a fixed period the load was removed and the sample allowed to recover for the same period. This procedure was repeated several times for each value of the load.

RESULTS AND DISCUSSION

Absorption and desorption of water

The results of measurements of equilibrium weight gain during immersion in water at room temperature and of weight loss in vacuum at 40°C for the materials are summarized in *Table 1*. The water contents of the samples recorded in *Table 1* were estimated by assuming that the water content of the vacuum-dried materials was zero and that the only volatile component was water. For materials A the standard deviation on weight gain during immersion of 7 specimens was 4.8% of the mean, while the equivalent figure for weight loss in vacuum on 6 specimens was 0.7%. For materials A and B the water content of both unrelaxed and relaxed samples was measured after saturation with water at room temperature and the data are in good agreement. Also for as-received samples of materials A and B the moisture content was determined with a DuPont moisture analyser and the results were 1.18 and 0.49% for A and B, respectively, in good agreement with the gravimetric data.

Degree of crosslinking

The degree of crosslinking of the polymers was estimated from measurements of Young's modulus above the glass transition temperature and from acetone swelling data.

Young's modulus was determined on samples of the relaxed materials 2–3 mm in thickness. Penetration under load of the spherically tipped quartz probe of the t.m.a. was measured at about 161°C. Equilibrium penetration was attained for loads of 5 or 10 g after 5 min for materials A and C and after 10 min for material B. Young's modulus was derived from the penetration data using Finkin's equation[1]:

$$E = [3(1-\nu^2)FR/4H^3]\,[y^{1/2} + 0.252y + 0.1588y^{3/2} + 0.2245y^2 + 0.3069y^{5/2} + 0.2980y^3]^{-3} \qquad (1)$$

where E is Young's modulus, ν is Poisson's ratio, F is the applied load, R is the radius of the probe tip, H is the sample thickness. The parameter y is Rd/H^2, where d is the depth of penetration of the probe.

The equation applies to the penetration of elastic sheets of finite thickness by a sphere of much greater modulus than that of the sample, and assumes zero friction between the sample and its rigid support.

It is assumed that Poisson's ratio is 0.5 for the samples in their rubber-like state above T_g and then the first term of equation (1) becomes $9FR/16H^3$. Gillen[2] has claimed that the numerical constants associated with the y^2, $y^{5/2}$ and y^3 terms in equation (1) are in error and should be 0.2405, 0.3149 and 0.4486, respectively. However, the difference in calculated modulus obtained with the two sets of constants is very small (<1 in 10^6 for typical experimental data) and can be neglected.

From the kinetic theory of rubber elasticity for a high molecular weight crosslinked polymer the modulus in the rubbery state is related to the degree of crosslinking by the equation[3]:

$$G \simeq \rho RT/M_c \qquad (2)$$

where G is the equilibrium shear modulus, ρ is the density of the polymer, R is the gas constant, T is the temperature, and M_c is the average molecular weight between crosslinks. If Poisson's ratio is assumed to be 0.5, $G = E/3$, so that M_c can be estimated from E using equation (2).

The densities of the relaxed polymers were determined at room temperature from the weights and linear dimensions of rectangular prisms, 2 to 6 cm^3 in volume. From a measurement of linear expansion for material C between 20° and 160°C using the t.m.a. the ratio of length at 160°C to length at 20°C was 1.0082. Assuming isotropic expansion the densities at 160°C were calculated by assuming that $\rho(20)/\rho(160) = (1.0082)^3$.

The results are given in *Table 2* and they indicate that the molecular weight between crosslinks of materials A and C is approximately the same, and is significantly less than that of B.

The acetone swelling data are related to M_c by the Flory–Huggins equation[4]:

$$\rho/M_c = -[\ln(1-\nu_2) + \nu_2 + \mu\nu_2^2]/V_1\nu_2^{1/3} \qquad (3)$$

where ρ is the density of the unswollen polymer, ν_2 is the volume fraction of polymer in the solvent swollen network, μ is the polymer–solvent interaction parameter, and V_1 is the molar volume of solvent (73.359 cm^3/mol for acetone). The parameter ν_2 may be calculated from the relationship:

$$\nu_2 = (W/\rho)/(W/\rho + W_s/\rho_s) \qquad (4)$$

where W (W_s) is the weight of polymer (solvent) in the swollen system. The polymer–solvent interaction parameter for poly(methyl methacrylate) is reported[5] for chloroform (0.377), tetrahydrofuran (0.447), and heptanone-4 (0.509), at 25°C, but not for acetone. In the present work 0.5 has been used as an approximate value for μ. The values of ν_2, calculated from equation (4) using the observed swelling

Table 2 Degree of crosslinking

	Penetration							Swelling	
Material	T (K)	Load (g)	$10^3 d$ (cm)	$10^{-6} E$ (Pa)	ρ at 20°C (g cm^{-3})	ρ at 160°C (g cm^{-3})	M_c	V_2	M_c
A	161	5 10	3.34 5.31	3.69 3.61	1.172	1.144	3390	0.4097	1906
B	163	5 10	3.41 4.66	2.24 2.38	1.172	1.144	5390	0.2378	9734
C	163	5 10	3.24 4.50	3.28 3.78	1.179	1.150	3910	0.4178	1804

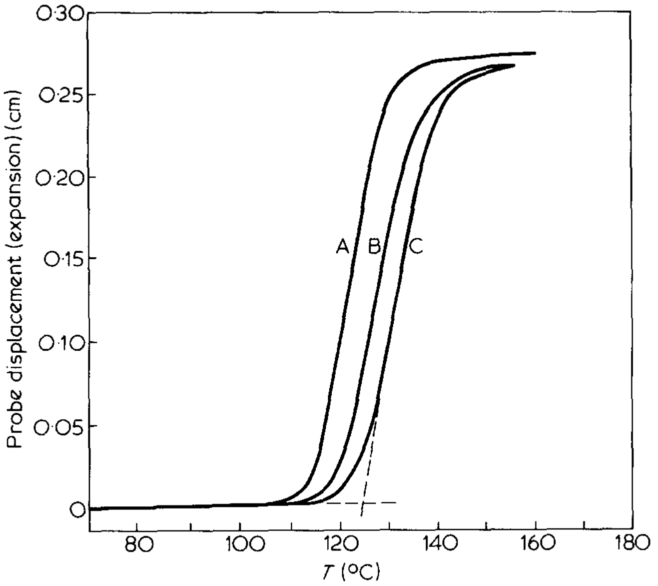

Figure 1 Relaxation of material A (as received) at different heating rates. A, 2; B, 5; C, 10 K/min

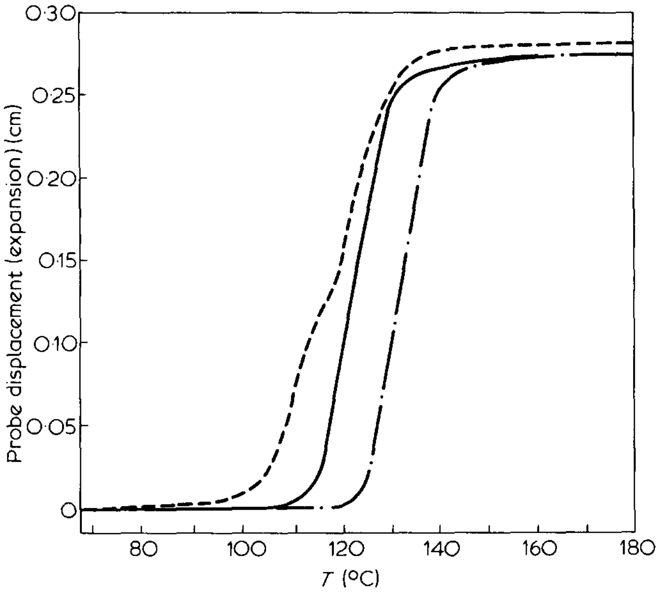

Figure 2 Relaxation at 2 K/min heating rate for material A: — — —, saturated with water; ———, as-received; — · — · —, dried in vacuum

data and taking ρ_s to be 0.792[6], and the corresponding values of M_c calculated from equation (3) are included in *Table 2*. While not showing very good agreement with M_c derived from modulus the values of M_c from swelling measurements do show the same pattern in that materials A and C have similar values of M_c, whereas material B is considerably lower in degree of crosslinking.

Equation (2) is an approximation assuming that the polymer is an ideal network. A more precise expression would involve corrections for restricted intramolecular rotation and for chain ends, which are not bound into the network[3], but the necessary information on the detailed structure of the polymers is not available. In equation (3) M_c is strongly dependent on the value of μ. For example for material B if μ is assumed to be 0.4 rather than 0.5 the calculated value for M_c is 4787, a two-fold reduction. It follows that the estimates of M_c, while not of absolute value, do show relative differences between the polymers.

Relaxation at constant heating rate

Relaxation curves for material A in the as-received state, measured at 2, 5 and 10 K/min heating rates, are shown in *Figure 1*. It is seen that the relaxation curve moves to higher temperatures with increasing heating rate. Each curve can be characterized by an onset temperature T_1, at the start of observable relaxation, and an extrapolated onset temperature T_2, defined by the intersection of the extrapolated inflexion region of the curve with the baseline. These points are indicated on *Figure 1* at 107° and 124°C for the sample heated at 10 K/min. A more sensitive indication of T_1 was obtained from the derivative output of the t.m.a. (rate of probe displacement).

The relaxation curves obtained at a heating rate of 2 K/min for the dry, as-received, and saturated samples of material A are illustrated in *Figure 2*. The presence of water significantly lowers the onset temperature for relaxation. There is a difference of 43°C between this temperature for the dry sample (113°C) and the wet sample (70°C).

The results at a heating rate of 2 K/min for the three materials are summarized in *Table 3*. The dependence of the characteristic temperatures T_1 and T_2 on water content is shown in *Figure 3*. Although there is considerable scatter in the data the values of T_1 and T_2 for all the materials show an approximately linear negative correlation with water content. The linear correlation coefficient for T_1 is −0.965 and for T_2 it is −0.919. The slopes are −9.6K and −4.0K for T_1 and T_2, respectively. The larger decreases in T_1 and T_2 for materials A and C on saturation with water correspond to the greater water content of these materials. The greater equilibrium water absorption and the consequent lower minimum relaxation onset temperatures of the more highly crosslinked materials were unexpected.

Table 3 Relaxation at 2 K/min heating rate

Material	Water content (wt %)	T_1 (°C) Average	T_1 (°C) Range	T_2 (°C) Average	T_2 (°C) Range	No. of samples tested
A	0	113		124		1
	1.37	97		115		1
	3.47	79	15	109	9	3
B	0	116		123		1
	0.48	109		122		1
	2.06	102		111		1
C	0	118	5	126	0	2
	1.38	106	2	118	6	2
	3.52	82	4	113	6	7

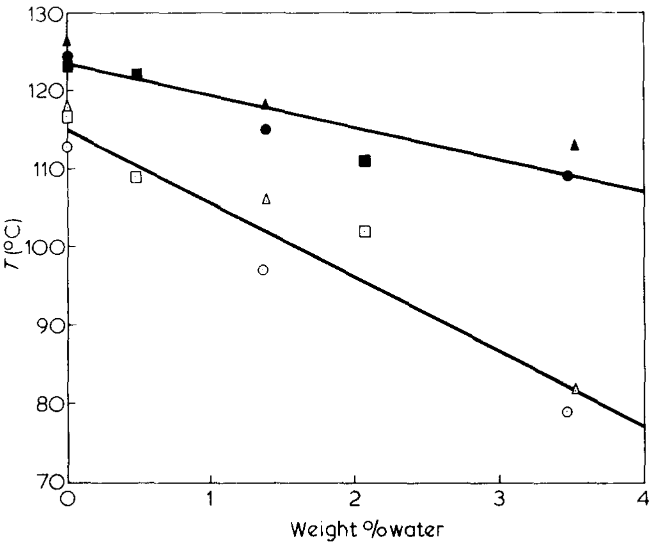

Figure 3 Dependence of temperature of relaxation onset on water content. T_1, Material A, B, C (○, □, △); T_2, Material A, B, C (●, ■, ▲)

As far as is known, the materials do not differ appreciably in their overall chemical composition. The molar concentration of crosslinking units will be relatively low. For example the infra-red spectra do not show significant differences. It is therefore unlikely that such large differences in water absorption as those observed could be explained by different chemical structures. Although the materials were manufactured by different methods the difference in water absorption also occurs in samples which have been thermally relaxed to the unstrained state, which should have eliminated any variations in physical structure due to processing. It is possible that the morphology of the materials varies with the level of crosslinking and that the water absorption is dependent on the morphology. Differences in morphology might be revealed by electron microscopy and an investigation of this possibility would be worthwhile.

Kato and Kambe[7] have examined the thermal relaxation of cold-drawn bisphenol A polycarbonate by dynamic t.m.a. This polymer also showed a maximum relaxation in the glass transition region, but in contrast to the present materials, significant relaxation also occurred in the temperature range between room temperature and T_g. The effect of moisture was not investigated. Kato and Kambe[7] applied Ozawa's theory[8] for the dynamic thermal analysis of reactions to the thermal relaxation phenomenon, to obtain an apparent activation energy for the relaxation, E, in terms of the heating rate, ϕ, the temperature at the maximum rate of relaxation, T_m, and the gas constant, R:

$$E = -(R/0.4567)\ [\mathrm{d}\ \log\phi/\mathrm{d}(1/T_m)] \tag{5}$$

The theory assumes that the relaxation process depends on a discrete relaxation time with an Arrhenius temperature dependence. For the main relaxation in polycarbonate E was 460 kJ/mol[7]. The thermal relaxation of material A was followed at heating rates of 2, 5 and 10 K/min. T_m was obtained from the inflexion in the relaxation–temperature curves. Plots of log ϕ against $1/T_m$ at the three levels of wate content are shown in *Figure 4*.

From the slopes of the lines and equation (5) E is 303, 203 and 197 kJ/mol for the dry, as-received, and saturated samples, respectively. The apparent activation energy for relaxation of material A is thus strongly depressed by water. For the dry sample, E is lower than for polycarbonate[7]; implying that the polycarbonate chains require more energy for relaxation.

Relaxation at constant temperature (material A)

Plots of expansion ($h - h_0$) against time are given in *Figure 5* for as-received samples of material A at various

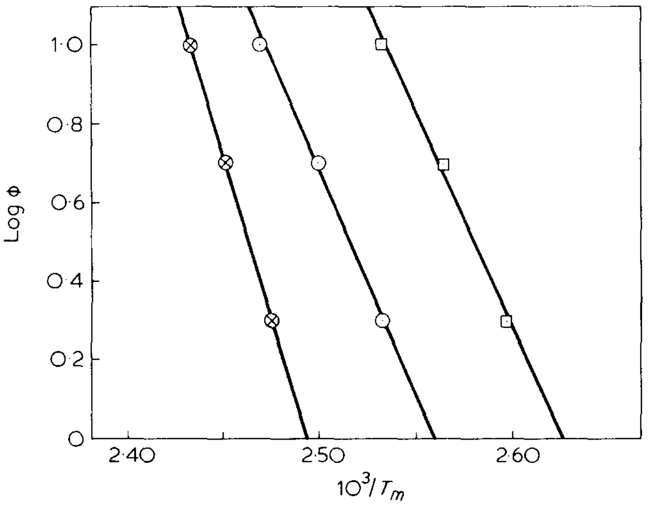

Figure 4 Log heating rate in K/min, ϕ, plotted against reciprocal temperature of maximum relaxation rate, $10^3/T_m$

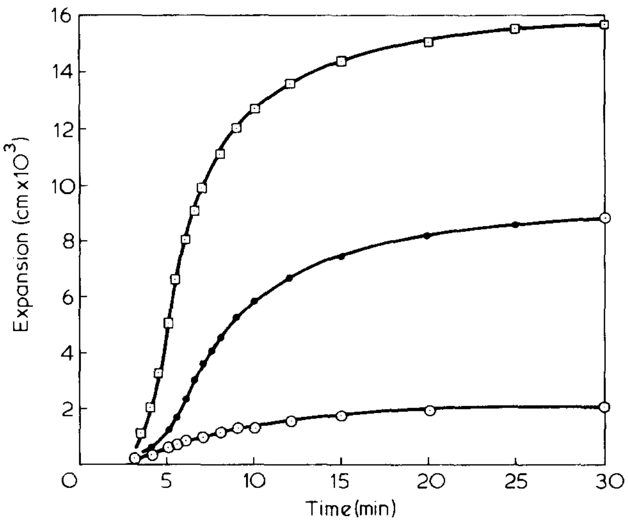

Figure 5 Isothermal relaxation of material A (as-received): ○, 108°C; ●, 113°C; □, 120°C

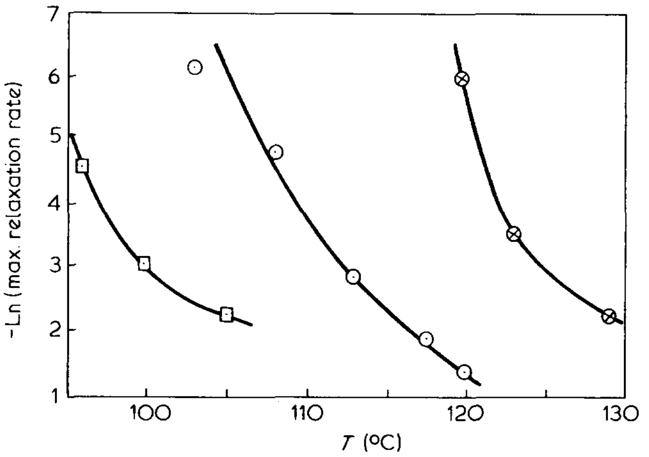

Figure 6 Dependence of ln (maximum relaxation rate) on temperature for material A: □, saturated with water; ○, as-received; ⊕, dried in vacuum

temperatures. The sigmoidal shape of the curves is a characteristic common to all of the samples tested. After elapsed times of 30 min the data correspond to 9.1, 26.8 and 67.3% of the total possible relaxation, at 108°, 113° and 120°C, respectively. This illustrates the large increases in relaxation rate which occur over a relatively small temperature interval.

A useful measure of the rate of relaxation is the maximum slope of the curves, $(dh/dt)_{max}$. The fractional relaxation or recovery can be defined as

$$r = (h - h_u)/(h_r - h_u) \qquad (6)$$

where h represents the height of the sample and the subscripts u and r refer to the completely unrelaxed and relaxed states, respectively. From equation (6), the rate of relaxation dr/dt, is related to the rate of expansion, dh/dt, by the equation:

$$dr/dt = (dh/dt)/(h_r - h_u) \qquad (7)$$

Logarithmic plots of the maximum rate of relaxation, as defined by equation (7), against temperature, are shown in *Figure 6*. The effect of increasing water content is to shift the relaxation rates to lower temperatures. *Figure 7* shows the same data plotted against $T + T_0$ where T is the experimental temperature and T_0 is a normalization temperature characteristic of the water content of the samples. The data points lie close to a common curve so that the effect of absorbed water on the relaxation behaviour can be described by a characteristic temperature decrement, T_0.

The dependence of T_0 on water content is shown in *Table 4*. Comparative data from the dynamic measurements at 2K/min heating rate are the parameters ΔT_1 and ΔT_2, where ΔT_1 (ΔT_2) is the difference between $T_1(T_2)$ for a sample containing water and the dry sample. For a given water content, T_0 lies between ΔT_1 and ΔT_2.

The curve in *Figure 7* represents the temperature dependence of the logarithmic maximum relaxation rate for dry materials. The temperature dependence of many physical properties of polymers in the glass transition region is described by the WLF equation[9]:

$$\log a_T = \log \frac{\eta_T}{\eta_{T_a}} = \frac{C_1(T - T_a)}{C_2 + T - T_a} \qquad (8)$$

where a_T is the ratio of viscosity, η, at a temperature T to that at a reference temperature T_a; C_1 and C_2 are material-dependent constants.

If the maximum relaxation rate, R_T, is assumed to be proportional to the viscosity, then equation (8) can be written in the form:

$$-\log R_T = [C_2/C_1(T - T_a)] + (1/C_1) - \log R_{T_a} \qquad (9)$$

Equation (9) predicts a linear dependence of $-\log R_T$ on $1/(T - T_a)$. The data of *Figure 7* were replotted in the form of equation (9) for a reference temperature T_a = 100°C which is well below T_g, and replacing T in equation (8) by $T + T_0$.

The resulting linear plot is shown in *Figure 8*. The linear regression gave slope, 169.6; intercept, −3.55; and correlation coefficient, 0.9778.

The ordinate of *Figure 8* is a natural logarithmic scale so that the slope/2.303 is the ratio of the WLF constants C_2/C_1 = 73.6. This is very much greater than the 'universal value' of ~3 to 5. In the free volume interpretation of the WLF equation[9] the ratio C_2/C_1 is strongly dependent on free volume. A possible explanation of the unusually large value found for C_2/C_1 is that the present materials are in a highly

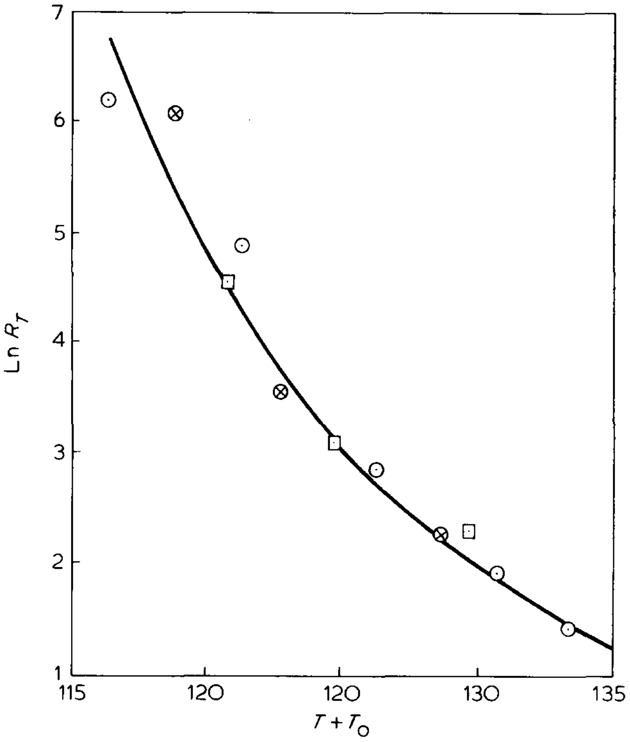

Figure 7 Logarithmic master plot of maximum relaxation rate, $-\ln R_T$, against $T + T_0$: □, saturated with water, T_0 = 25°C; ○, as-received, T_0 = 13.5° C; ⊕, dried in vacuum, T_0 = 0°C

Table 4 Effect of water on the relaxation temperature parameters of material A

Water content (wt %)	T_0 (°C)	ΔT_1 (°C)	ΔT_2 (°C)
0	0	0	0
1.37	13.5	16	9
3.4	25	34	15

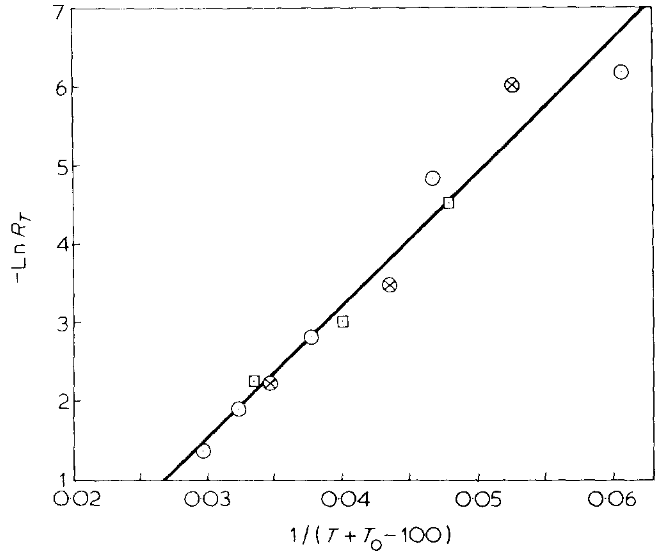

Figure 8 Logarithmic plot of maximum relaxation rate, −ln R_T, against 1/(T + T_0 − 100) for material A: □, saturated with water; ○, as-received; ⊕, vacuum dried

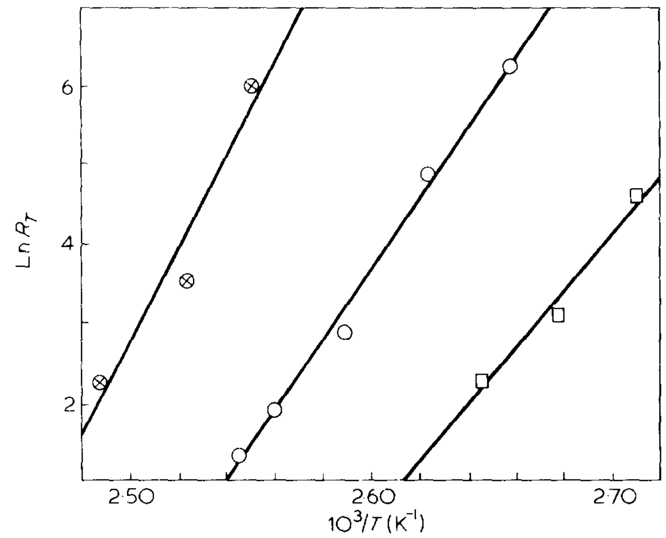

Figure 9 Logarithmic plot of maximum relaxation rate, −ln R_T, against reciprocal temperature for material A: □, saturated with water; ○, as-received; ⊕, vacuum dried

strained state and are therefore likely to have excess free volume compared to the relaxed state.

If it is assumed that the maximum rate of relaxation is inversely proportional to the relaxation time, then the isothermal analogue to equation (5) and *Figure 4* is a plot of $\ln R_T$ against $1/T$, which should be linear with slope $-E/R$.

The isothermal data are plotted in this form in *Figure 9*. The plots are only approximately linear, and the apparent activation energy values, E, from the linear regression slopes are 484, 359 and 291 kJ/mol, respectively. These are considerably larger than the corresponding data obtained from constant heating rate experiments, but they do show the same trend of decreasing with increasing water content. The lack of agreement between the rising temperature and isothermal activation energy may reflect an oversimplification in the models used, including the assumption of a discrete relaxation time. A more precise description of the data might incorporate a distribution of relaxation times and activation energies. The present treatment is, however, of some value as an empirical approximation.

Glass transition temperature T_g *measurements*

The measurements of T_g were made on samples of relaxed materials either after drying in vacuum or with the room temperature equilibrium water content. It was not possible to determine T_g by the d.s.c. method on unrelaxed samples as the change in dimensions occurring in the transition region produced anomalous and noisy heat flow readings. The dry samples were conditioned at 180°C for 15 min and then rapidly cooled to room temperature before heating at 10 K/min in the d.s.c. This conditioning was intended to ensure a standard thermal state before measurement of T_g. The saturated materials were not conditioned above T_g before the d.s.c. scan in order to avoid loss of water. The results of the T_g measurements are given in *Table 5* where T_{g_0} and T_{g_f} are the T_gs of the dry and saturated samples, respectively. The depression in T_g due to water is 25, 14.5, and 27K for materials A, B and C, respectively. For material A this is in accord with the isothermal relaxation measurements from which the temperature shift of the relaxation rate on saturation with water (T_0) is also 25K. Because of the greater equilibrium water absorption of materials A and C compared with B, T_{g_f} is lower for the former. This is consistent with the similar effects observed on relaxation onset temperatures in the dynamic experiments.

Carter and Kibler[10] have developed a quantitative theory for the depression of T_g by water, based on changes in configurational entropy due to hydrogen-bonding of water at polar sites. The model gave results in agreement with observed data within experimental error for an epoxy and a polyimide resin. The model relates the T_g of the dry polymer, T_{g_0}, to the T_g of the material containing f g water per g of dry polymer, T_{g_f}, by the equations:

$$T_{g_f} = T_{g_0}\,[1 - (Ry/M_s\Delta C_p)] \qquad (10)$$

where

$$y = r\ln(1/r) + (1-r)\ln[1/(1-r)] \qquad (11)$$

and

$$r = (M_s/M_w)f \qquad (12)$$

In these equations M_s is the effective molecular weight of a site bonding 1 molecule of water or the ratio of the molecular weight of the repeating unit to the number of sites per unit; ΔC_p is the increment in heat capacity at the T_g of dry polymer; R is the gas constant; and M_w is the molecular weight of water.

The values of ΔC_p for the materials are given in *Table 5*. These were calculated from the increments in heat flow at T_g, by the relationship $\Delta C_p = \Delta(\mathrm{d}q/\mathrm{d}t)/(\phi m)$, where ϕ is the heating rate in K/sec and m is the sample mass. The heat flow increment $\Delta(\mathrm{d}q/\mathrm{d}t)$ was found by linear extrapolation

Table 5 Effect of water on T_g

Material	T_{g0} Observed	T_{gf} (°C)	ΔC_p ($JK^{-1}g^{-1}$)	T_{gf} Calculated for M_s = 200	T_{gf} Calculated for M_s in ( )
A	135	110	0.253	90	110 (340)
B	127	112.5	0.268	92	112.5(550)
C	130	103	0.254	85	104 (320)

of the heat flow curves from above and below T_g and measurement of the distance between the extrapolated lines at T_g.

For pure poly(methyl methacrylate) if it is assumed that there is one available site for bonding a molecule of water every two repeating units, and that all available sites are filled in the saturated polymer, then $M_s = 200.2$. The values of T_{gf} calculated from these assumptions are shown in *Table 5* and are about 20K lower than those observed. Values of M_s which give T_{gf} in good agreement with experiment are also shown in *Table 5*. These values of M_s correspond to about 1 molecule of water bonded to 3 repeating units of polymer for A and C, and 1 molecule of water per 5 or 6 repeating units of material B. This is consistent with the higher equilibrium levels of water absorption for A and C.

CONCLUSIONS

The materials differ in their degree of crosslinking and the most highly crosslinked polymers (A and C) also show the largest equilibrium water absorption. It would be interesting to study the morphology of the materials to seek an explanation of this phenomenon.

The temperature of onset of relaxation decreases with increasing water content. It is possible to predict the main features of the relaxation behaviour at a given heating rate if the water content is known. These effects are consistent with the observed reductions in T_g due to absorbed water.

For material A the maximum relaxation rate at constant temperature is related to the water content, and the effect of temperature on the maximum relaxation rate is of the form of the WLF equation. The apparent activation energy for thermal relaxation, obtained from rising temperature measurements, is lower in the saturated material.

ACKNOWLEDGEMENT

I thank Dr M. J. Lofthouse and Mr P. Burroughs of DuPont Instruments for moisture analyses.

REFERENCES

1 Finkin, E. F. *Wear* 1972, **19**, 277
2 Gillen, K. T. *J. Appl. Polym. Sci.* 1978, **22**, 1291
3 Nielsen, L. E. in 'Mechanical properties of polymers and composites', Marcel Dekker, New York, 1974, **1**, p 176
4 Treloar, L. R. G. 'The physics of rubber elasticity', Oxford University Press, London, 3rd Edn, 1975, p 142
5 Wolf, B. A. in 'Polymer Handbook' (Eds J. Brandup and E. H. Immergut), Wiley, New York, 2nd Edn, 1975, p IV-133
6 'Handbook of Chemistry and Physics', Chemical Rubber, Cleveland, 44th Edn, 1963
7 Kato, T. and Kambe, H. *J. Appl. Polym. Sci.* 1978, **22**, 1767
8 Ozawa, T. *J. Thermal Anal.* 1970, **2**, 301
9 Ferry, J. D. 'Viscoelastic properties of polymers', Wiley, New York, 1961
10 Carter, H. G. and Kibler, K. G. *J. Composite Mater.* 1977, **11**, 265