JOURNAL OF MATERIALS SCIENCE 24 (1989) 1936-1940

Effect of absorbed water, temperature and strain rate on the yield strength of two methylmethacrylate-based plastics

P. J. BURCHILL
Materials Division, Materials Research Laboratory, Defence Science and Technology Organisation, Maribyrnong, Victoria, Australia

The yielding behaviour in compression has been determined for two poly(methylmethacrylate) (PMMA)-based materials when dry or saturated with water. Measurements were made over the temperature range 0 to 60° C and at test speeds varying by 1000-fold. Wet material, as expected, shows a lower yield strength but this cannot be predicted from the strength of dry material and the change in the glass transition temperature. Yield strengths of wet material may be just as accurately calculated from that of dry material by subtracting 10 MPa for each per cent of water absorbed. A data analysis method for superimposing yield strength values at various strain rates to different temperatures is given which does not rely on a mechanical shifting of curves.

1. Introduction

Two methylmethacrylate-based polymers, one being a modified polymer developed for aerospace use, the other a good quality homopolymer (PMMA) were used in this study. The effect of temperature and strain rate on the yield of PMMA has been studied by many workers [1–4]. Observations have been made of dry material and show that the relationship between yield strength and logarithm of strain rate is not linear. The most comprehensive study has been by Bauwens-Crowet [3] who showed that a theoretical expression based on the Ree–Eyring theory does not fit the data over the whole range of strain rates. The theoretical expression separated the effects of the α and β loss processes on yielding. An alternative statistical theory describes yielding as being controlled by the probability that a given polymer segment is in an excited state [5], and that a number of these segments are involved co-operatively in the reorganization of the polymer chain. The fit to experimental data in this case is much better; however, it requires a time/temperature shift of the data to the glass transition temperature, and this shift is still described in terms of the thermodynamics of the α and β processes.

Compatible mixtures of a polymer and a diluent will have a glass transition temperature, T_g (α-relaxation), between those of the components [6]. The apparent reduction in T_g of the polymer by the diluent is due to a reduction in the enthalpy change associated with the α-relaxation process [7, 8] arising from a greater interchain mobility. This is also observed in polymers with absorbed water [9–11]. Below T_g these diluents, if acting as plasticizers, also lower the yield strength. Thus it might appear that knowing the drop in T_g, the yield strength could be calculated from known time/temperature dependence data of dry material. For PMMA, a β-relaxation can be detected at ambient temperatures [12]. It is found that the temperature at which the loss is a maximum due to this relaxation is not affected by plasticization [13, 14] unlike the α-relaxation (T_g). Therefore, if there is any affect on the β-relaxation here by water then it is only the energy barrier, and not on the enthalpy change.

This report describes an approach for obtaining a master curve from experimental data of yield against strain rate at various temperatures. The assumptions regarding the effect of absorbed water are tested. In addition, master curves are given for water-saturated and dry Plexiglas-55 and Plexiglas-201.

2. Theory

The temperature dependence of the yield strength of PMMA has been analysed by Bauwens-Crowet [3] in terms of the Ree–Eyring theory [15]. A relation for the yield strength in terms of the strain rate and the rates of the α- and β-relaxation processes is given by the expression

$$\frac{\sigma_y}{T} = A_\alpha\left(\ln 2C_\alpha\dot{e} + \frac{Q_\alpha}{RT}\right) + A_\beta \sinh^{-1}\left[C_\beta\dot{e}\exp\left(\frac{Q_\beta}{RT}\right)\right] \qquad (1)$$

A_α and A_β are constants, C_α and C_β contain the rate constants for the α and β processes, which have activation energies Q_α and Q_β. $\dot{e}$ is the strain rate, R the gas constant, T the absolute temperature, and σ_y is the yield strength [3, 16].

The parameters for this equation were determined by a graphical method which consisted of mechanically superimposing data measured at different temperatures to give a master curve of σ_y/T against $\log(\dot{e})$ for

0022-2461/89 $03.00 + .12

TABLE I Comparison of parameter values given by Bauwens-Crowet with those derived by the method used in this report

Parameters	Bauwens-Crowet	This report
Q_α (kJ mol^{-1})	412	340
Q_β (kJ mol^{-1})	107	115
A_α (10^3 N mm^{-2} K^{-1})	6.97	8.22
A_β (10^3 N mm^{-2} K^{-1})	36.7	35.8
C_α (sec^{-1})	5×10^{-52}	2×10^{-42}
C_β (sec^{-1})	4.67×10^{-17}	1.50×10^{-18}

373 K. Data from high temperature, low strain rate and low temperature, high strain rate measurements, and the slope of the line along which the data are shifted to give a master curve define these parameter values. Equation 1 only fits the data at the extremes of log $\dot{e}$ values where the data lie on the asymptotes.

The line along which data values are shifted to the master curve at a reference temperature, T_R, is defined by the horizontal and vertical shift functions, sx and sy [3], given by

$$sx = \frac{Q_\beta}{2.303R}\left(\frac{1}{T_R} - \frac{1}{T}\right) \tag{2}$$

$$sy = A_\alpha\left(\frac{Q_\alpha}{Q_\beta} - 1\right) sx \tag{3}$$

A numerical method of shifting the data to give a master curve is given in the next section.

The master curve given by Bauwens-Crowet is best fitted by the equation given by Fotheringham and Cherry [5]

$$\dot{e} = K\left\{\exp\left[-\frac{Q}{RT}\sinh\left(\frac{\sigma v}{RT}\right)\right]\right\}^n \tag{4}$$

in which σ is the yield stress, v the activation volume, Q the activation energy, K a constant containing the frequency factor, and n is the number of polymer segments that have to move co-operatively.

TABLE II Strain rate and temperature dependence of yield strength for dry Plexiglas-201

Log (strain rate) (sec^{-1})	Yield strength (MPa)				
	274 K	296 K	313 K	333 K	349 K
−4.425	126.6	88.4	75.5	60.0	43.8
−3.821		105.7			
−3.425	142.8	107.0	86.1	70.5	52.9
−2.821		122.5			
−2.425	162.6	125.5	101.5	83.8	63.3
−2.121		135.4			
−1.821		133.6			
−1.425	190.9	151.5	118.8	101.3	78.2
−0.821		166.2			

TABLE III Strain rate and temperature dependence of yield strength for water-saturated Plexiglas-201

Log (strain rate) (sec^{-1})	Yield strength (MPa)			
	274.2 K	296 K	313 K	332.5 K
−4.424	106.0	74.2	54.1	36.6
−3.821		76.3		
−3.425	118.9	80.6	63.7	43.1
−2.821		95.5		
−2.425	140.7	105.5	77.3	52.7
−2.121		110.7		
−1.821		118.1		
−1.425	169.6	128.1	93.3	65.6
−0.821		143.0		

TABLE IV Strain rate and temperature dependence of yield strength for dry Plexiglas-55

Log (strain rate) (sec^{-1})	Yield strength (MPa)			
	274.2 K	296 K	313 K	332.5 K
−4.428	132.0	100.5	80.0	56.5
−3.826		107.9		
−3.428	152.0	113.5	92.4	67.7
−2.826		124.7		
−2.428	175.2	134.3	107.4	80.8
−2.127		138.9		
−1.826		147.9		
−1.428	205.7	157.3	128.1	96.4
−0.826		178.3		

3. Data analysis method

Construction of a master curve for the function $f(\sigma_y/T, \log \dot{e})$ was obtained by a translation of the origin. This translation is determined by the temperature difference between that for the test data and the master curve temperature which in this analysis has been set at 296 K. The shift along the log $\dot{e}$ axis is given by

$$\Delta \log \dot{e} = K(1/296 - 1/T) \tag{5}$$

The shift along the σ/T axis is given by

$$\Delta \frac{\sigma}{T} = L\Delta \log \dot{e} \tag{6}$$

The constants K and L were determined by an iterative procedure so that the data points fall on a smooth curve defined by a polynomial such that the residual error between calculated and shifted experimental values of σ/T is a minimum.

The master curve given by Bauwens-Crowet has been found to be well fitted by a quadratic. Hence, as a check on this analysis procedure, her data values of σ/T at different strain rates and temperatures were treated. The shifted experimental points at the extremes of the master curve were fitted to straight lines to define the asymptotes and so the parameters in Equation 1 could be calculated. The values given by this approach are compared with those reported [3] in Table I. The goodness of the fit is also shown by the size of the residual error which was equivalent to ± 2.4 MPa in the yield strengths. The residual error after fitting Cherry and Fotheringham's equation using data shifted according to parameters given by Bauwens-Crowet was about 5% less than that

TABLE V Strain rate and temperature dependence of yield strength for water-saturated Plexiglas-55

Log (strain rate) (sec^{-1})	Yield strength (MPa)			
	274.2 K	296 K	313 K	332.5 K
−4.428	96.4	64.1	42.6	24.3
−3.826		70.9		
−3.428	113.1	78.7	52.1	30.4
−2.826		86.2		
−2.428	133.3	96.3	65.2	39.6
−2.132		100.9		
−1.832		107.0		
−1.428	163.3	118.4	84.6	53.5
−0.826		139.1		

TABLE VI Values of parameters defining the shift line and the coefficients of the polynomial $\sigma/T = a + b(\log \dot{e}) + c(\log \dot{e})^2$

Material		K	L	a	b	c
Plexiglas-201	dry	4707	−0.058 203	0.637 65	0.103 280	0.006 919
	wet	4416	−0.064 815	0.569 37	0.113 639	0.009 199
Plexiglas-55	dry	4905	−0.055 917	0.682 58	0.113 217	0.007 827
	wet	3896	−0.084 474	0.557 11	0.123 861	0.010 639
Bauwens-Crowet data		5996	−0.037 200	0.580 36	0.087 996	0.005 912

from fitting a quadratic. Activation energy for the α-relaxation is known [12] to be dependent on the temperature at which it is studied, and the pre-exponential factor will be similarly affected. Hence the differences in Table I for these quantities between the two methods are not considered important. The values for the β-relaxation are in reasonable agreement.

4. Experimental details

4.1. Materials

Plexiglas-55 (Rohm and Haas) and Plexiglas-201 (Roehm GmbH) were purchased as sheets nominally 6.3 mm thick. Test specimens as right circular cylinders approximately 22 mm long and 6 mm diameter were machined from the sheets. These specimens were conditioned at 393 K for 24 h and cooled slowly to room temperature. Half the specimens were stored over phosphorus pentoxide while the remainder were kept in distilled water at room temperature for 18 months before testing. Glass transition temperatures were measured by differential scanning calorimetry using hermetically sealed pans and a heating rate of 10 K min^{-1}.

4.2. Test procedure

The yield load was measured using an Instron 1122, and the yield strain (e) was calculated from the cross-head displacement to yield. Yield strength was calculated from

$$\sigma_y = F(1 - e)/A_0 \qquad (7)$$

in which F is the applied load and A_0 is the original cross-sectional area. The test temperature was controlled by immersing the specimens in a constant temperature water bath. Water absorption during the test of dry material is insignificant and does not change the yield strength.

5. Results

The measured yield strength (σ_y) for dry and water-saturated materials at cross-head displacement rates from 0.05 to 200 mm min^{-1} and temperatures from 274 to 333 K are given in Tables II to V. For each set of data, the measurements have been shifted as described to give a master curve for 296 K. Values of the shift parameters K and L, and the coefficients of the quadratic for the master curve are given in Table VI. These curves for dry and wet Plexiglas-201 and Plexiglas-55 are shown in Figs 1 and 2, respectively. The residual error in σ/T for each case was equivalent to a standard deviation in yield strengths of ±2.3 MPa.

The water content of saturated Plexiglas-201 and 55 was measured on these specimens and found to be 2.3 and 4.0 wt % respectively. Glass transition temperatures of the dry materials were determined by differential scanning calorimetry to be 387 and 390 K, respectively, while for the water saturated materials they were 370 and 366 K.

6. Discussion

6.1. Effect of water content, strain rate and temperature

The effect of water saturation on the yield strength of Plexiglas-201 and 55 appears to be fairly uniform over the range of temperature and strain rate used in this study. For Plexiglas-201, water saturation reduces the yield strength by 23 MPa with a standard deviation of 4 MPa, while for Plexiglas-55 the reduction is 39 MPa with an error of 3 MPa in these results. An analysis of the difference in yield strength of wet and dry material shows that as strain rate increases the difference in yield strength increases. Temperature of measurement appears to have no significant effect on the difference in yield strength between wet and dry material. Hence, ignoring temperature, increasing the strain rate by

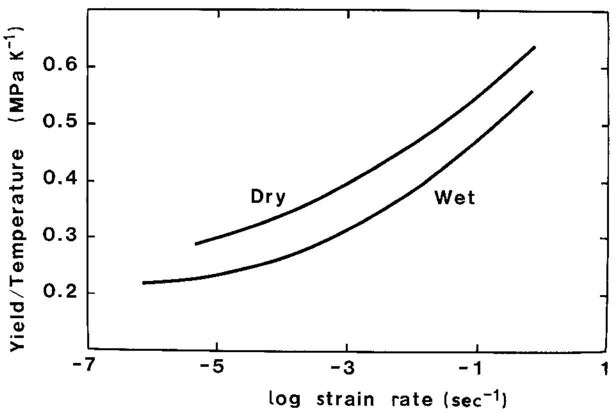

Figure 1 Master curves for the variation in yield strength with strain rate for dry and wet Plexiglas-201 at 296 K.

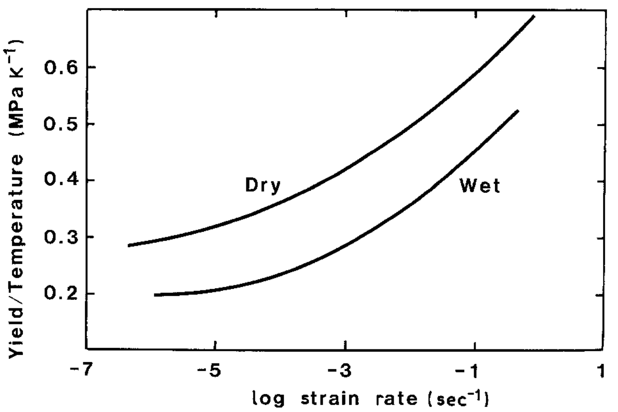

Figure 2 Master curves for the variation in yield strength with strain rate for dry and wet Plexiglas-55 at 296 K.

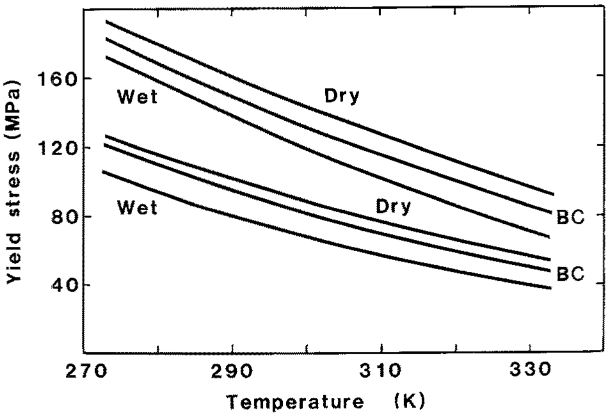

Figure 3 Variation in yield strength with temperature for Plexiglas-201, dry and wet, at two strain rates. For the upper set of curves $\log e = -1.4$ and for the lower $\log e = -4.4$. The curve labelled BC has been generated from data of Bauwens-Crowet [3].

1000-fold increases the difference between wet and dry material by 4.7 and 6.5 MPa for Plexiglas-201 and Plexiglas-55, respectively.

Ignoring any affect due to strain rate the yield strength differences quoted above are found to be proportional to the water content of the material. It appears that a reduction of 10 MPa in yield strength has occurred for each 1% water absorbed. This is very similar to a previous finding on the effect of water on craze resistance [17]. There each 1% water absorbed reduced the craze resistance by 8 MPa. Crazing is a very localized form of yielding induced by flaws and the presence of any absorbable liquid. Thus it can be said that water produces similar reductions in yield strength for both compressive and tensile loadings. The effect of intermediate water contents on yield strength can be safely estimated by linear interpolation between wet and dry material.

6.2. Calculation of yield strength from master curves

The master curve data for each material given in Table VI will allow an estimation of the yield strength of each material with a standard deviation of less than 3 MPa. For a temperature other than 296 K, the yield strength may be calculated from the master curve via an origin shift. In this way a curve for yield strength against temperature for a given strain rate has been constructed. The data for each material wet and dry are given in Figs 3 and 4, and compared with a curve derived from Bauwens-Crowet's data. Her data are consistently lower than those reported here for dry material. This may be due to different specimen size, or material.

6.3. Effective temperature shift

If the effect of water in lowering both the yield strength and the T_g of these materials might be considered similar, then a yield strength of wet material could be estimated given the data for dry material and the drop in T_g. In this study the decrease in T_g due to saturation with water was found to be 17 and 24 K for Plexiglas-201 and Plexiglas-55, respectively. Fig. 5 displays the curves for dry Plexiglas-55 at 320 K and the wet material at 296 K. It shows that the yield strength of wet material will be incorrectly estimated at high and low strain rates by applying a shift of 24 K to the data of dry material. Similar results are found for Plexiglas-201.

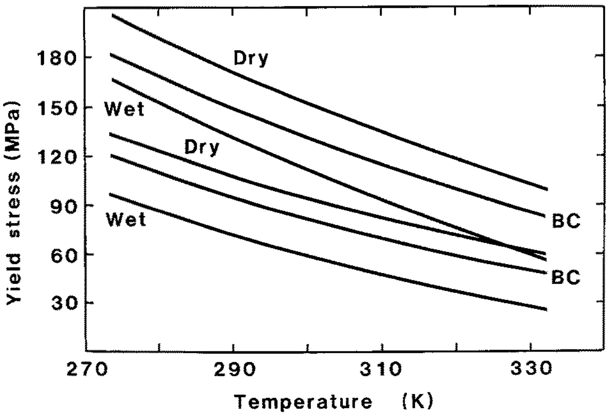

Figure 4 As Fig. 3 but for Plexiglas-55.

The empirical equation parameters (Table VI) show that these curves cannot be superimposed by shifting along a straight line. The effect of plasticization by water is not linear with log (strain rate).

6.4. α and β relaxations

Plasticizers are known to lower the temperature at which the α relaxation is observed while the β relaxation is unaffected. Thus in a two site model for relaxation, the free energy difference between the sites is lowered for the α transition [8] but not for the β transition, which is what might be expected for interchain and intrachain mobilities [14]. The α relaxation activation energies (Q_α) for the dry and wet plastics (Table VII) show an increase with water content. This increase probably reflects the fact that the highest temperature at which yield strength was measured was closer to T_g in the wet material. It has been observed before that Q_α increases to a maximum at T_g [12].

The values of Q_β are reduced slightly, showing that water lowers the energy barrier to the β-relaxation by about 1 kJ mol^{-1} for each per cent of water absorbed. However, it is known that plasticization does not affect the temperature at which the energy loss due to this relaxation is a maximum. Thus the enthalpy change is probably not affected by plasticization.

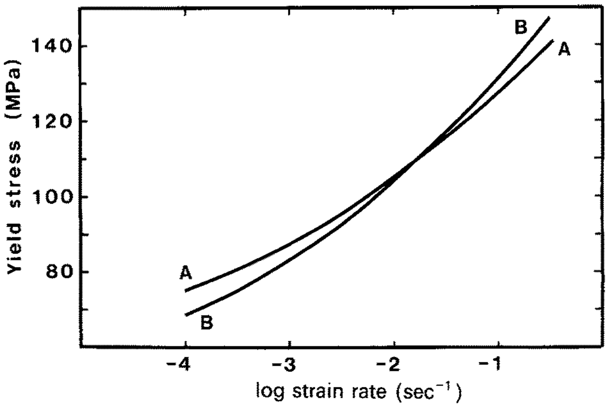

Figure 5 Yield strengths of Plexiglas-55 plotted against log strain rate, dry at 320 K, water saturated at 296 K.

TABLE VII Parameter values for Equation 1 for dry and wet Plexiglas-201 and Plexiglas-55

Parameter	Plexiglas-201		Plexiglas-55	
	Dry	Wet	Dry	Wet
Q_α (kJ mol^{-1})	282	329	234	432
Q_β (kJ mol^{-1})	93	84	94	74
A_α (10^3 N mm^{-2} K^{-1})	11.38	9.74	16.28	7.66
A_β (10^3 N mm^{-2} K^{-1})	28.0	29.6	27.1	37.7
log (C_α) (sec^{-1})	−33.60	−42.86	−28.07	−59.73
log (C_β) (sec^{-1})	−13.58	−12.07	−14.08	−10.51

7. Conclusion

The results have shown that the change in yield strength due to saturation with water of methylmethacrylate-based polymers is not linear. This is seen when the change is viewed as equivalent to an increase in test temperature of dry material. Water appears to reduce the yield strength by about 10 MPa for each percentage of water absorbed. However this difference in strength between wet and dry material increases by about 20% when the strain rate is increased a 1000 fold. Saturation with water is accompanied by an increase in volume of 1.35% and 2.28% [18] for Plexiglas-201 and Plexiglas-55, respectively. The change in position of the α-relaxation reflects this swelling which produces a decrease in the energy difference between conformers. For the β-relaxation, the ease with which conformational change occurs increases, but the relative populations are not altered.

References

1. R. E. ROBERTSON, *J. Chem. Phys.* **44** (1966) 3950.
2. R. A. DUCKETT, S. RANINOWITZ and I. M. WARD, *J. Mater. Sci.* **5** (1970) 909.
3. C. BAUWENS-CROWET, *ibid.* **8** (1973) 968.
4. J. J. LOHR and J. A. PARKER, *AIAA J.* **3** (1965) 666.
5. D. FOTHERINGHAM and B. W. CHERRY, *J. Mater. Sci.* **11** (1976) 1368.
6. G. TEN BRINKE, F. E. KARASZ and T. S. ELLIS, *Macromol.* **16** (1983) 244.
7. I. M. WARD, "Mechanical Properties of Solid Polymers" (Wiley, London, 1983).
8. J. D. HOFFMAN, G. WILLIAMS and E. PASSAGLIA, *J. Polym. Sci. C* **14** (1966) 173.
9. T. S. ELLIS and F. E. KARASZ, *Polymer* **25** (1984) 664.
10. S. P. ROWLAND (ed.), "Water in Polymers", American Chemists Society Symposium Series, 1979 (American Chemical Society, Washington, 1980).
11. P. PEYSER and W. D. BASCOM, *J. Mater. Sci.* **16** (1981) 75.
12. N. G. McCRUM, B. E. READ and G. WILLIAMS, "Anelastic and Dielectric Effects in Polymeric Solids" (Wiley, London, 1967).
13. J. HEIJBOER, *Int. J. Polym. Mater.* **6** (1977) 11.
14. K. SHIBAYAMA, T. TANAKA and M. KODAMA, Proceedings of the 5th International Congress on Rheology, Vol. 3 (University of Tokyo Press, Tokyo, Japan, 1970) p. 451.
15. T. REE and H. EYRING, in "Rheology", Vol. II, edited by F. R. Eirich (Academic, New York, 1958) pp. 83–143.
16. C. BAUWENS-CROWET, J. C. BAUWENS and G. HOMES, *J. Polym. Sci. A2* **7** (1969) 735.
17. P. J. BURCHILL, G. MATHYS and R. H. STACEWICZ, *J. Mater. Sci.* **22** (1987) 483.
18. P. J. BURCHILL, unpublished data, 1985–8.

Received 16 June
and accepted 27 September 1988