

Environmental crazing in a glassy polymer: the role of solvent absorption

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According to a recent theory of Andrews and Bevan, the work of solvent craze formation, \mathcal{F}_0 is governed by the cavitation properties of a solvated zone of polymer at the craze tip. In particular, the shear yield stress of this zone and its temperature dependence dictate the variation of \mathcal{F}_0 with temperature. In order to investigate this matter further, samples of poly-methylmethacrylate were swollen to equilibrium in a variety of alcohols at different temperatures, and the equilibrium polymer fraction ϕ_2 determined as a function of temperature and solvent. The variation of yield stress with ϕ_2 , solvent and temperature was also investigated, and the glass transition temperatures determined as functions of ϕ_2 and solvent.

The temperature at which the equilibrium swelling was just sufficient to depress the polymer T_g to a co-incident value was found to correspond closely to the "characteristic temperature", identified by Andrews and Bevan, at which the temperature dependence of \mathcal{F}_0 changes abruptly. This is shown to be in complete accord with the cavitation theory referred to.

1. Introduction

Andrews and Bevan [1, 2] measured the minimum work of craze formation (per unit area of craze) for poly(methylmethacrylate) in a series of aliphatic alcohols. This quantity, \mathcal{F}_0 , exhibited the characteristic temperature dependence shown in Fig. 1, where the break in the curve occurred at a temperature T_c , characteristic of the solvent.

A theoretical equation was derived for the quantity \mathcal{F}_0 on the assumption that the work of crazing was equal to the quasi-static work of formation of the craze cavities, thus [2],

$$\mathcal{F}_0 = 2.42(h\gamma/\rho)f^{2/3} + 0.33 Y\psi hf \quad (1)$$

where h is the craze thickness, γ the interfacial energy of the voids, ρ the mean distance between void centres, f the void fraction, Y the shear yield stress and ψ a constant of value 4.4. The authors argued that the form of Fig. 1 was predicted by Equation 1 since the term in Y accounted for the temperature dependence at $T < T_c$ whilst the term in γ accounted for the constancy at $T > T_c$. This clearly involved the assumption that $Y = 0$ at $T \geq T_c$, and T_c was therefore tentatively identified with the glass transition temperature of a solvated zone at the craze tip where, of course, the cavitation takes place. Andrews and Bevan showed that the values of T_c plotted

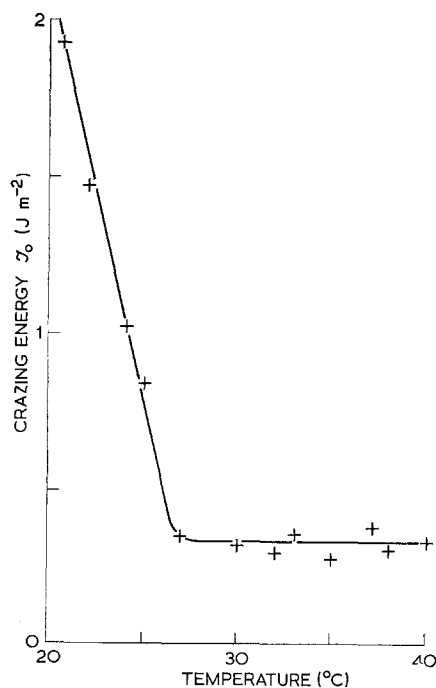


Figure 1 Work of crazing, \mathcal{F}_0 , as a function of temperature for PMMA in ethanol (after Andrews and Bevan [2]).

against solvent solubility parameter, lay on a smooth curve extrapolating to the T_g of the polymer at the solubility parameter of PMMA.

Confirmation of the theory clearly required the establishment of several points, namely:

- (i) that depressions of the polymer T_g to the temperatures T_c are possible with the solvents concerned, and that these depressions for different solvents fall in the same sequence as the T_c values;
- (ii) that the temperature dependence of Y at $T < T_c$ should be of the correct magnitude to provide the temperature dependence of \mathcal{F}_0 via Equation 1.

It was the purpose of the present work to provide this confirmation, and tests were therefore carried out on PMMA swollen in various alcohols to determine the following information for each solvent.

- (i) the dependence of equilibrium swelling on temperature;
- (ii) the dependence of yield stress on temperature and the swelling;
- (iii) the glass transition temperature as a function of the swelling.

It was found possible, using this information, to predict closely the characteristic temperature, T_c of Andrews and Bevan from equilibrium data alone. The results strongly support the theory advanced by these authors, that the work of crazing (and thus critical crazing stress or strain) is governed by the cavitation properties of a solvated zone at the craze tip. The present work goes further to show that the degree of swelling of this zone is the equilibrium swelling to be expected at the temperature of test. This implies that the only effect of the dilational stress field at the craze tip is to accelerate the kinetics of solvent absorption.

2. The swelling of PMMA by low molecular weight alcohols

2.1. Experimental details

Plane sheet specimens of 1 mm thick PMMA (ICI Ltd) were prepared with the approximate major surface dimensions 30×7 mm. The specimens were dried under vacuum for 2 h at 348 K, prior to weighing in a stoppered container on a micro-balance sensitive to 10^{-8} kg. Batches of three such specimens were placed in flasks containing methyl, ethyl, *n*-propyl, *iso*-propyl and *iso*-butyl alcohol controlled at 293 and 318 K. The specimens were periodically removed from their flasks, rapidly dried with filter and tissue

paper and weighed in the stoppered container. After weighing, the specimens were immediately returned to their respective flasks.

The volume fraction, ϕ_2 , of polymer in the PMMA/alcohol mixture was calculated as:

$$\phi_2 = (1 - \phi_1) = (W_2/\rho_2) (W_1/\rho_1 + W_2/\rho_2)^{-1} \quad (2)$$

where W_1 and W_2 are, respectively, the weight of alcohol in the swollen mixture and the original weight of PMMA, and ρ_1 and ρ_2 are, respectively, the density of the alcohol at the test temperature and the density of the PMMA.

Estimates (obtained from control experiments) of the equilibrium water sorption at 293 K for the PMMA used in this work, and the solids leached out during a typical swelling experiment, were as follows:

equilibrium water sorption	$5.3 \cdot 10^{-3}$ wt/wt
leached solids	$5.0 \cdot 10^{-3}$ wt/wt.

2.2. Experimental results and discussion; equilibrium swelling

Because of their permanent chemical interconnections, cross-linked polymers are insoluble but are swollen by a variety of liquids. Linear (uncross-linked) polymers such as PMMA, may either enter into solution, remain unaffected or swell depending on the physical characteristics of the liquid. Alcohols are relatively incompatible with PMMA and are generally found to swell rather than dissolve the polymer.

The interaction of non-polar polymers and liquids can often be rationalized by use of thermodynamic parameters, namely the polymer/solvent interaction parameter [3], χ or the solubility parameter δ [4]. It can be shown that, to a good approximation, a polymer will be completely miscible with any liquid for which χ is less than 0.5 or alternatively for which $(\delta_2 - 2.25) < \delta_1 < (\delta_2 + 2.25)$ (MJ m^{-3})^{1/2}, where the subscripts 1 and 2 refer, respectively, to the liquid and the polymer. Theoretically-determined values of χ and δ are, however, inapplicable to polymers (such as PMMA) and liquids (such as alcohols) which exhibit specific and/or polar interactions. Several attempts to rank liquids which exhibit polarity and/or hydrogen bonding have been more or less successful [5-14]. To the present time, it has been found virtually impossible to satisfactorily evaluate χ for polymers or liquids which interact through hydrogen bonding. However, Bondi and Simkin [15] and several of the authors cited above, have clearly indicated that the degree of hydrogen bonding, for the lower members of the alcohol homolo-

gous series, is nearly constant at a given temperature and decreases only slowly over the temperature range 180 to 480 K.

It is therefore quite reasonable to consider that the order of interaction of PMMA with alcohols is given by the difference in solubility parameter of the polymer and liquid. Table I (after Burrell and Immergut [16]) shows the solubility parameter at 298 K for the various alcohols considered here and also the difference, $\Delta\delta$, between the alcohol and PMMA solubility parameters. (The solubility parameter, δ_2 , of PMMA is taken as $19.03 \text{ (MJ m}^{-3})^{\frac{1}{2}}$.)

TABLE I (after Burrell and Immergut)

Alcohol	δ_1 (MJ m^{-3}) [±]	$\Delta\delta$ (MJ m^{-3}) [±]	V_1 molar volume ($\text{cm}^3 \text{ mol}^{-1}$)
Methyl	29.67	10.64	41
Ethyl	25.98	6.95	59
<i>n</i> -Propyl	24.35	5.32	74
<i>iso</i> -Propyl	23.52	4.49	76
<i>n</i> -Butyl	23.32	4.29	—
<i>iso</i> -Butyl	21.48	2.45	92

The solubility parameter is a derived thermodynamic quantity and we observe that the ability to dissolve PMMA also increases with increasing molar volume of the solvent (V_1).

Figs. 2 and 3 reproduce the sorption isotherms for the PMMA/alcohol systems, plotted as ϕ_2 as a function of (time of immersion)^½. These data show that, at equilibrium, the higher alcohols do

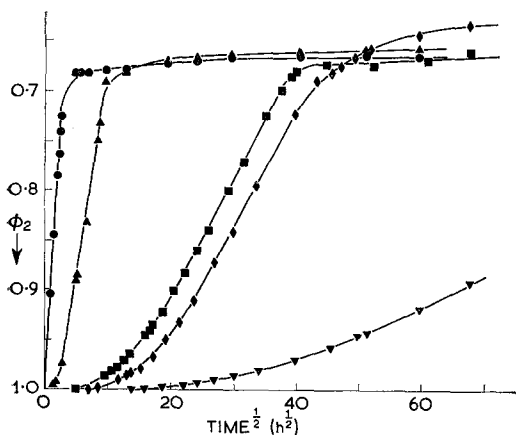


Figure 2 Sorption isotherms for alcohols in PMMA at 318 K; ϕ_2 is volume fraction of polymer (note inverted scale). (●) methanol, (▲) ethanol, (■) *n*-propanol, (◆) *iso*-propanol, (▼) *n*-butanol.

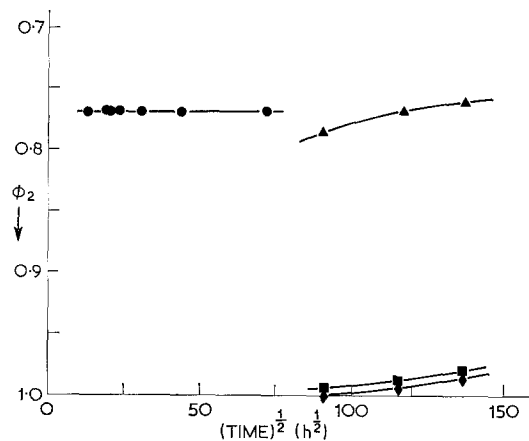


Figure 3 As Fig. 2 but at 293 K. (●) methanol, (▲) ethanol, (■) *n*-propanol, (◆) *iso*-propanol.

tend to achieve a somewhat greater degree of swelling than the lower ones, but the effect is not marked. (It may be noted that for *iso*-butyl alcohol at 318 K, a small degree of dissolution occurred in the early stages, as might be anticipated from Table I, but at a later stage diffusion into the bulk and swelling occurred as competitive modes. Quite evidently the rate of diffusion, after dissolution of the polymer surface layers, exceeded the rate of dissolution.)

The equilibrium volume fractions, ϕ_2 , for each alcohol, shown in Table II, were obtained at 318 K, and 293 K where possible, from the sorption isotherms. For the lower temperature, ϕ_2 was also obtained from desorption isotherms (after quenching from 318 to 293 K) after 740 h. The equilibrium ϕ_2 values for both methyl and ethyl alcohol were practically identical from sorption and desorption measurements.

In addition to the above, other samples of PMMA were refluxed to equilibrium swelling at a range of higher temperatures, and the equilibrium ϕ_2 values so obtained, are also shown in Table II.

Inspection of Table II reveals that the effect of temperature on the equilibrium ϕ_2 values is marked, showing the expected decrease with increasing temperature. Summarizing, it is found that the equilibrium degree of swelling of PMMA by various alcohols increases slowly as $\Delta\delta$ decreases, and that the effect of increasing temperature is to decrease ϕ_2 .

TABLE II

Alcohol	Equilibrium ϕ_2					
	Temperature (K)					
	293	298	308	318	328	338
Methyl	0.77	0.74	0.71	0.67	0.60	0.55
Ethyl	0.76	0.75	0.71	0.66	0.62	0.54
<i>n</i> -Propyl	0.74	—	—	0.65	0.62	—
<i>iso</i> -Propyl	0.72	—	—	0.63	—	—
<i>n</i> -Butyl	0.71	—	—	—	—	—
Methylated spirit	0.64	—	—	—	—	—

2.3. Experimental results and discussion; kinetic aspects

The equilibrium volume fractions cited in Section 2.2 are thermodynamically determined quantities and give no information about the kinetics or rate of attainment of the equilibrium condition. The kinetic data is represented in the sorption isotherms of Figs. 2 and 3. It is not pertinent to the crazing process to discuss in detail the physical processes giving rise to these sorption isotherms, since it is believed that stress-accelerated sorption occurs at the craze tip, but a few general conclusions can be drawn.

The sorption isotherms at 318 K, presented in Fig. 2, show that the lowest alcohols penetrate and swell PMMA far more rapidly than do the higher ones, and this can be regarded as an effect of solvent molecular volume. The system PMMA/methyl alcohol shows classical diffusion or Fickian behaviour, while the PMMA/higher alcohol systems exhibit a time lag prior to penetration, followed by an increasing rate of diffusion until the classical steady state is established.

The sorption isotherms at 293 K, (see Fig. 3), are incomplete. At this lower temperature the time for sorption is considerably increased, as evidenced by the PMMA/propyl alcohol isotherms which show only slight penetration after approximately one year of immersion.

It was not found practical to conduct experiments which more nearly reproduce craze tip conditions, i.e., to measure the alcohol uptake under externally stressed conditions. Quite obviously the sorption kinetics of specimens subject to externally applied stress will differ from those considered here, but the effects of such conditions will be discussed, in the light of the present data, at a later stage.

3. The yield of swollen PMMA and the glass transition temperature

3.1. Experimental details

Plane sheet specimens of 1 mm thick PMMA were prepared with the approximate major surface dimensions 10×6 mm.

The sheets of PMMA were suspended in flasks containing methyl, ethyl, *n*-propyl and *n*-butyl alcohol, and were refluxed to equilibrium swelling for a variety of temperatures. (The approximate time required to achieve equilibrium swelling was deduced from the previously discussed sorption isotherms.) Control samples were also immersed with the sheets and the values quoted for the equilibrium volume fraction ϕ_2 , were determined from weighings of the control samples. When equilibrium swelling had been achieved, the sheets of PMMA were rubber-like, and tensile specimens (having an approximate gauge length of 20 mm) were cut out with a specially designed edge cutting tool. The tensile specimens were subsequently replaced in their respective flasks at the reflux temperature and allowed to re-equilibrate. Just prior to tensile testing, the specimens were fitted with rubber jawed clamps, the cross sectional dimensions were measured with a micrometer and the samples re-equilibrated. Tensile testing was carried out on an Instron tensile testing machine fitted with a temperature controlled liquid immersion chamber. When required for testing the "clamped up" specimens were rapidly transferred to the tensile machine immersion chamber. A suitable period of time was allowed for temperature equilibration (of the order 5 to 15 min depending on the temperature difference between the reflux and test temperature) and tensile testing was commenced.

The tensile behaviour of polymeric materials is strain rate-dependent, but since it was not practical to test over a wide range of strain-rates, one particular rate ($4.17 \times 10^{-3} \text{ sec}^{-1}$, corresponding to a cross-head speed of 0.5 cm min^{-1}) was selected.

Tensile testing was also carried out in air on unswollen (as received) PMMA at the same strain-rate and using a temperature controlled environmental chamber.

3.2. Experimental results and discussion

The experimental technique for tensile testing equilibrium swollen specimens over a range of temperatures, necessarily required the transference of the specimen from a high to a low

temperature. It was considered possible that such a change of temperature could lead to desorption of alcohol from the specimen, with the consequent increase in ϕ_2 . In order to establish how much alcohol was lost by such a transference, a desorption isotherm was experimentally determined for the system PMMA/methyl alcohol. (Methyl alcohol is kinetically the most rapid desorber of the alcohols employed.) A PMMA specimen, swollen to equilibrium at 328 K was rapidly transferred to a bath of methyl alcohol at 243 K, these temperatures representing the extremes used in the experimental work, and the decrease in weight was determined as a function of time. It was found that after 40 min of immersion the weight loss had reached a value which remained constant for a time in excess of 4 h. This loss of methyl alcohol resulted in an average increase in ϕ_2 of only 0.03. It is considered that this loss represented desorption from the surface layers of the specimen and that the bulk of the sample remained unaffected. After 15 min of immersion (the longest time required for temperature equilibration), the average increase in ϕ_2 was 0.02, which was small with respect to the initial value, and it was concluded that even under these most stringent conditions, the initially measured values of ϕ_2 were representative of the bulk of the test specimen.

Tensile testing was conducted through the range of temperatures 253 to 323 K, and for the system PMMA/air through the range 298 to 393 K. The particular value of yield stress measured was defined as that at which the load/extension curve passed through a maximum. The yield stress was considered to be zero when little or no curvature was observed on the load/extension plot (e.g., lowest curve in Fig. 4) and the temperature at zero yield stress has been taken as the glass transition temperature for the system under the test conditions. This will not necessarily correspond to T_g measured in other ways, but will not be far removed. In any case, it is the zero-yield-stress temperature which is relevant to this study rather than a thermodynamic T_g .

The load-extension plots, see Fig. 4, were typical of a polymer below its T_g , showing a decreasing yield stress with increasing temperature, and on close approach to T_g the strain at failure rapidly increased to show rubber-like extensions in excess of 300%. The transition from a yielding solid to an elastomer occurred over a

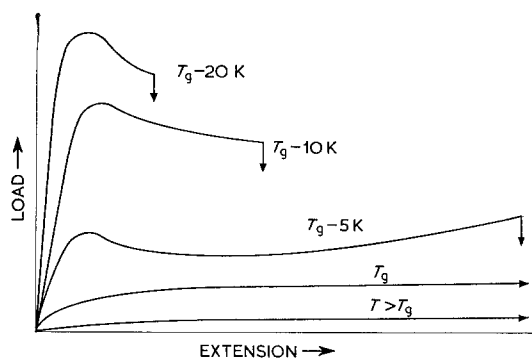


Figure 4 Typical load extension curves of swollen PMMA at different temperatures relative to T_g .

temperature range of about 4 K and, as shown in Fig. 4, the location of T_g was a relatively simple matter due to the considerable change of the load/extension plot over this small temperature range.

Crazing occurred during the tensile testing of alcohol-swollen PMMA, the crazes propagating normal to the tensile axis. It was observed that as $T \rightarrow T_g$ the craze structure became coarser and that at $T > T_g$ crazing no longer occurred.

Fig. 5 shows the yield stress as a function of

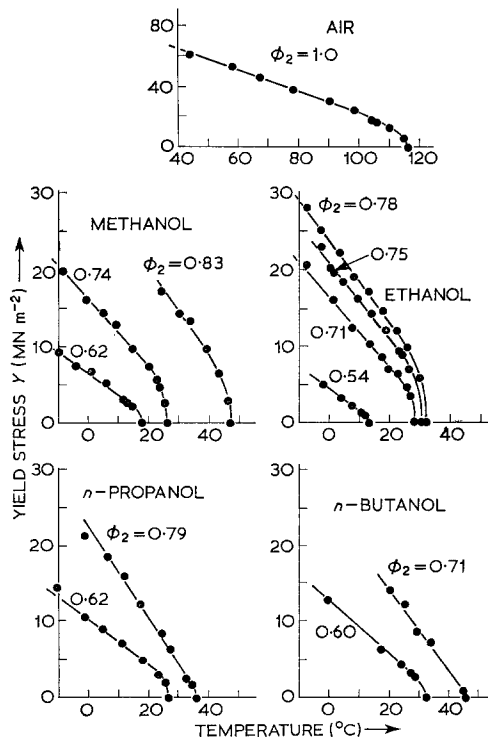


Figure 5 Yield stress of swollen PMMA as a function of solvent, ϕ_2 and temperature (strain rate $4.17 \times 10^{-3} \text{ sec}^{-1}$).

temperature for various values of ϕ_2 , and each experimental point is the average of three or more results. It was observed that, for any given alcohol, both the glass transition temperature and the slope of the yield stress/temperature plot decreased with decreasing equilibrium ϕ_2 .

A plot of the slope of the yield stress/temperature curves (dY/dT) as a function of volume fraction of swollen PMMA (see Fig. 6), shows there to be a unique linear relationship for the range of ϕ_2 investigated. For the strain rate employed, dY/dT is governed by the composition of the swollen mixture and is apparently independent of the alcohol used.

Extrapolation to $dY/dT = 0$, suggests that at approximately $\phi_2 = 0.24$, the polymer/alcohol mixture becomes liquid-like.

The absolute position of the yield stress/temperature curve on the temperature scale is, of course, fixed by the particular alcohol involved in the swollen mixture, being "anchored" on the temperature axis, by the zero yield stress condition.

In Fig. 7 the glass transition temperature (defined by the zero yield stress condition) is shown as a function of the equilibrium volume fraction of swollen PMMA, for the four alcohols investigated. The value of T_g at $\phi_2 = 1.0$ is given by the yield stress/temperature plot for the system PMMA/air.

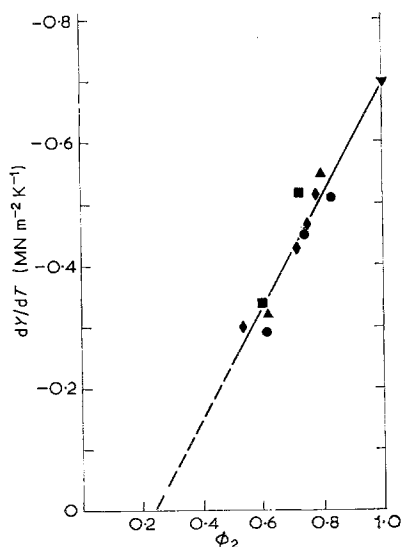


Figure 6 Slope of yield stress versus temperature plots as a function of ϕ_2 . (▼) air, (●) methanol, (▲) ethanol, (◆) *n*-propanol, (■) *n*-butanol.

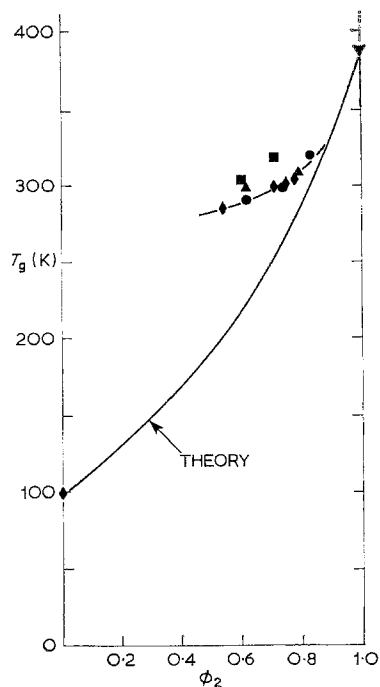


Figure 7 Glass transition temperature as a function of ϕ_2 for various solvents (line gives Kelley-Bueche theory). (▼) air, (●) methanol, (◆) ethanol, (▲) *n*-propanol, (■) *n*-butanol.

We observe that for all the alcohols, T_g is increasingly depressed with decreasing ϕ_2 . Jenckel and Heusch [17] and Kelley and Bueche [18] have also presented data which shows that the glass transition temperature of glassy polymers is depressed by plasticizing agents. Postulating that the polymer and diluent free volumes are additive and that the free volume fraction has a critical value at T_g , which is the same for both polymer and diluent, Kelley and Bueche have derived the following relation between T_g and polymer/diluent composition (expressed conveniently in terms of volume fractions):

$$T_g = \frac{\phi_2 T_{g2}(\alpha_l - \alpha_g) + \phi_1 T_{g1} \alpha_l}{\phi_2(\alpha_l - \alpha_g) + \phi_1 \alpha_l} \quad (3)$$

where the subscripts 1 and 2 denote respectively the diluent and polymer, and α_l , α_g are respectively the coefficients of thermal expansion above and below T_g . Kelley and Bueche considered that equation provided a good representation of the experimentally determined variation of T_g with composition, for the systems polystyrene/diethyl benzene and PMMA/diethyl phthalate.

In Fig. 6 the Kelley and Bueche curve is shown for the system PMMA/ethyl alcohol, using a value for T_g of 100 K, for the solvent (after Faucher and Koleske [19]). Considerable deviation of the results from the theoretical curve is found to occur for $\phi_2 < 0.9$. We note that Braun and Kovacs [20] and Boyer [21] have also observed a discontinuity in the T_g /composition plot, both for the experimental data of Jenckel and Heusch and of Kelley and Bueche.

An explanation of the deviation of the PMMA/alcohol results is not at the present time clear, although Braun and Kovacs [20] have developed a theory based on the concept of a free volume of relaxation, which accounts for a discontinuity in the T_g/ϕ_2 plot.

The deviation may result from PMMA/alcohol interaction through hydrogen bonding.

For a given value of ϕ_2 , both methyl and ethyl alcohol depress T_g by about the same amount, while for *n*-butyl alcohol the depression is somewhat less. This observation is in general agreement with the view that the small molecules of low density liquids create more free volume than the larger molecules of higher density liquids, and thus achieve a greater depression of the glass transition temperature.

Summarizing the yield stress/temperature results, it was found that a unique linear relationship existed between the slope of the yield stress/temperature plot and the equilibrium volume fraction, for all the PMMA/alcohol systems. The glass transition temperature of the PMMA/alcohol mixtures was observed to be depressed to a greater or lesser extent by the whole range of alcohols, at any given value for ϕ_2 . The free volume theory of the depression of T_g by plasticizers was not found to apply, the experimental results deviating from the theoretical curve at a relatively high value of ϕ_2 .

4. Application to environmental crazing

4.1. The characteristic temperature

As Fig. 1 shows, T_c is the point at which an abrupt change occurs in the temperature dependence of \mathcal{F}_0 . As Andrews and Bevan [2] pointed out, this change can be explained in terms of Equation 1 if T_c is the temperature at which the yield stress becomes zero, i.e., T_g as defined in this paper. It is already clear from Fig. 5 that T_g depressions of the necessary magnitude can occur with these solvents to vindicate the idea that T_c is the glass transition temperature of a swollen zone at the craze tip.

However, the present data enables us to be much more precise than this.

Let us assume that the tip zone absorbs solvent rapidly (in contrast to the bulk of the specimen) on account of the dilatational stress field acting there, but that the total amount of solvent absorbed is an equilibrium quantity not affected by stress. Then, as the temperature of crazing increases towards T_c the equilibrium polymer content of the zone, ϕ_2 , will decrease as shown by the data in Table II. In Fig. 8, this equilibrium ϕ_2 is plotted against equilibration temperature, T_e , for two of the solvents (ethanol and *n*-propyl alcohol) by way of example.

At the same time, since ϕ_2 is decreasing, the zone T_g will be falling in accordance with the data of Fig. 5. This fall of T_g with ϕ_2 is also shown in Fig. 8 for the same two solvents. A unique temperature, T^* , is defined in Fig. 8 for each solvent at which the curves of T_e and T_g against ϕ_2 intersect. At this temperature alone, swelling of the polymer to equilibrium will result in a material which is just at its T_g (or zero yield-stress temperature).

In Fig. 9 the intersection temperature T^* is plotted against the characteristic temperature T_c as given by Andrews and Bevan, each point corresponding to a given solvent. The line in Fig. 9 represents the equality $T_c = T^*$ and agrees closely with the points.

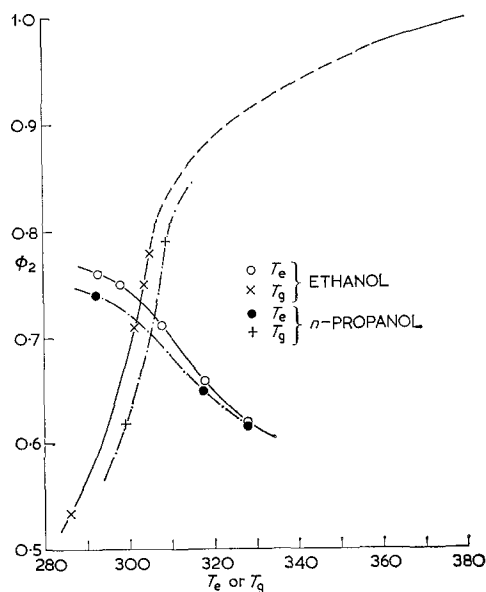


Figure 8 Equilibrium ϕ_2 versus equilibration temperature T_e and glass transition temperature T_g for ethanol and *n*-propyl alcohols.

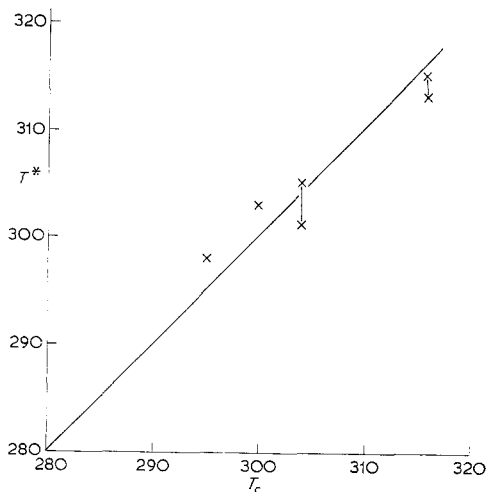


Figure 9 T^* plotted against characteristic temperature T_c . Line gives $T^* = T_c$ equality.

It thus appears that T_c is the temperature at which the local yield stress at the craze tip falls to zero, in complete harmony with the explanation given by Andrews and Bevan. The equality $T_c = T^*$ implies that an equilibrium swelling characteristic of unstressed polymer is achieved at the craze tip and that the role of stress is simply to accelerate sorption of the solvent in that region.

4.2. The temperature dependence of \mathcal{F}_0 below T_c

The slope $d\mathcal{F}_0/dT$, for $T < T_c$, was given by Andrews and Bevan as -0.2 to $-0.4 \text{ Jm}^{-2} \text{ K}^{-1}$ for all the solvents used. These authors also derived a theoretical expression.

$$d\mathcal{F}_0/dT \sim 0.33 hf\psi(dY/dT) \quad (4)$$

which, with appropriate values of h , f and ψ gave a value of $-0.48 \text{ Jm}^{-2} \text{ K}^{-1}$ using values for dY/dT obtained from Fig. 5 of this paper. This calculation however, neglected the fact that ϕ_2 is changing with temperature, so that since:

$$Y = F(T, \phi_2) \quad (5)$$

where F is a function, then

$$\frac{dY}{dT} = \frac{\partial Y}{\partial T} + \frac{\partial Y}{\partial \phi_2} \frac{\partial \phi_2}{\partial T} \quad (6)$$

In the region of interest, i.e., where $\phi_2 \sim 0.70$, the quantity $\partial Y/\partial \phi_2$ is typically of the order of 60 to 90 MN m^{-2} depending on solvent and temperature (from Fig. 5). The quantity

$\partial \phi_2/\partial T$ is of the order of $-5 \times 10^{-3} \text{ K}^{-1}$, so that the second term in Equation 6 is of the order of -0.3 to $0.5 \text{ MNm}^{-2} \text{ K}^{-1}$, almost exactly comparable to the value of $\partial Y/\partial T$ at $\phi_2 = 0.70$.

Including this term therefore, the theoretical estimate for $d\mathcal{F}_0/dT$ is approximately doubled to about $-1 \text{ Jm}^{-2} \text{ K}^{-1}$, some 3 to 5 times greater than observed.

The most likely source of this error is the uncertainties which attach to the values selected for h and f , the craze thickness and void fraction respectively. The values taken by Andrews and Bevan were actual physical values as measured or deduced from the literature. However, most of the work of cavitation is, plausibly, consumed in the early stages of the process before the cavities are large enough to interact (the cavitation theory ignores interaction).

Once interaction takes place cavity enlargement must be considerably easier, and it may thus be argued that the appropriate values of h and f to be used in Equation 4 should be significantly smaller (say 0.5 times) than those appropriate to the completed craze. Such a correction factor as suggested would almost wholly compensate for the discrepancy between the calculated and observed values of $d\mathcal{F}_0/dT$.

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