Free volume changes in epoxy adhesives during physical ageing: fluorescence spectroscopy and mechanical stress relaxation*

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Fluorescence probes dispersed randomly in fully-cured adhesives were used to follow changes in the matrix free volume during physical ageing in the glassy state. Upon isothermal annealing, following a quench from the equilibrium melt, the emission intensity shows a time-dependent increase, interpreted as due to the relaxation of matrix free volume. The change in fluorescence intensity with ageing time is compared with the increase in the ageing shift factor for momentary stress relaxation. These properties are found to be qualitatively self-consistent using theoretical arguments based on free volume concepts.

(Keywords: ageing; free volume; fluorescence spectroscopy; stress relaxation; epoxy adhesives)

INTRODUCTION

Physical ageing of an amorphous polymer refers to time-dependent changes in the material properties of the glassy state, generally interpreted in terms of a decrease in the free volume fraction contained in the polymer[1,2]. Of particular interest in this respect is a statistical mechanical theory of the bulk polymeric state developed by Simha and Somcynsky[3] in which the free energy contains a free volume function, h. In the melt, the pressure- and temperature-dependence $h(P, T)$ is determined by minimization of the free energy. In the glass, and in the absence of physical ageing, this function is evaluated by a combination of the free energy expression at finite chemical activity with experimental PVT data for a specified formation history. In the ageing glass, a corresponding function $h(P, T, t_a)$ at ageing time t_a is obtained by a corresponding procedure, which employs volume recovery data. Recently, Curro and co-workers[4,5] and Robertson *et al.*[6] have concluded that it is possible to establish quantitative connections between volume recovery data in polymer glasses and the change in viscoelastic shift parameter for stress relaxation during physical ageing via the Simha–Somcynsky theory.

Several spectroscopic techniques appear to be sensitive to changes in free volume of polymers. The rotational mobility of probe molecules dispersed in the polymer matrix and monitored by ESR linewidth[7–11], or fluorescence anisotropy measurements[11,12] show a temperature dependence which can be correlated with variations of the matrix free volume as described, for example, by the Williams–Landel–Ferry (WLF) parameters. Also, the emission intensity of certain fluorophores, dispersed in viscous media, decreases as the matrix viscosity decreases[13,14]. This effect is traced to an increase in non-radiative decay of excited singlets due to the enhanced mobility of the probe and the matrix as the temperature rises[13–16]. Finally, the lifetime of positrons, trapped in polymer matrices in the form of ortho-positronium, shows a change in temperature coefficient in the glass transition region[17–19]. A quantitative correlation has been found between the positron lifetime spectrum and the Simha–Somcynsky free volume or disorder function for polyvinyl acetate[20]. It is important to note that the mobility of chemical probes is a strong function of the size of the probe[21].

Comparatively few spectroscopic studies of changes in free volume during physical ageing of polymers have been reported. Sung and co-workers have utilized photo-isomerizable probes[22,23] to investigate changes in polymeric matrices. The percent *cis*→*trans* conversion is found to be sensitive to the free volume level and shows a significant decrease during isothermal physical ageing in the glass, following a quench from the equilibrium melt. By covalently attaching isomerizable labels to chain ends and chain centres, it was further demonstrated that the free volume at chain ends is greater than at the centres, and thus it is evident that a distribution of free volume elements must be considered, as utilized in the Robertson–Curro–Simha theory[6]. Similarly, Victor and Torkelson[21] employed photo-isomerizable probes of varying molecular sizes to attempt conclusions regarding changes in the size distribution of free volume during annealing in polystyrenes of different molar masses.

Changes in positron lifetime spectral parameters in polymers during long-term physical ageing have been reported[24,25]. A recent study[20,24] suggests that it is possible to determine the Simha–Somcynsky free volume function of polymers during long-term isothermal physical ageing from the positron lifetime spectrum. Finally, changes in the ESR spectra of nitroxide spin probes dispersed in polymers during physical ageing have

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[*] Dedicated to Professor Walther Burchard on the occasion of his 60th birthday

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0032-3861/90/050812-06

been described[26,27]. Numerical connections between the decrease in rotational correlation time and the ageing free volume function have been identified[26].

These studies suggest that it should be possible to establish quantitative comparisons and connections between free volume parameters as measured by spectroscopic probes, and time–temperature dependences of other material properties of amorphous polymers. Indeed, recent experimental studies in our laboratory[28] have established a close correlation between the time evolution of the fluorescence emission of the probe Auramine O dispersed in polyvinylacetate, and viscoelastic shift parameters for stress relaxation during isothermal physical ageing. We note a major problem in comparing different free volume-dependent properties of glassy polymers, i.e. the requirement of establishing identical thermal histories. It is thus advantageous to utilize the same polymer sample, hence avoiding the possibility of specimen-dependent variations in glass transition temperature.

In this paper, we report experimental studies of the time evolution of the emission intensity of two fluorescence probes dispersed in fully-cured epoxy adhesives during isothermal annealing below T_g following a rapid quench from the equilibrium melt. These data are compared with the corresponding variation in the viscoelastic shift parameters which characterize ageing of the shear stress relaxation of the same polymer sample. The fluorescent probes are randomly dispersed into the polymer at small concentrations, and are then excited by irradiation with photons of appropriate wavelength. The excited probes return to their ground state either by fluorescing or by dissipating the excitation by friction or momentum transfer to the matrix, a process termed internal conversion. If the probe is free to rotate or vibrate it is more likely to return to its ground state by internal conversion. If, on the other hand, those motions are severely hindered, the probe is more likely to emit a photon, i.e. fluoresce. Thus, the mobility of a probe should be directly related to the free volume around it. Loutfy[16] has suggested an expression describing the fluorescence intensity, namely:

$$F = F_0 \exp(V_m/bV_f) \qquad (1)$$

where V_m is a critical volume required for radiationless de-excitation of the probe and V_f is the free volume per mole of polymer. F is the fluorescence intensity, F_0 the fluorescence intensity of unhindered probes and b is a system-dependent constant. Equation (1) is qualitatively consistent with experimental observation that the fluorescence quantum yield of larger probes in polymeric matrices is larger than that of smaller probes, and is inversely related to the matrix free volume.

EXPERIMENTAL

Fluorescence spectroscopy

Fluorescence measurements were performed as previously described[29], using an Aminco–Bowman spectrofluorimeter, with the capability of generating corrected spectra via the ratio method using a reference photomultiplier tube (PMT). A digital microvoltmeter was employed to monitor the output of the PMTs, and a thermocouple inserted directly into the sample was used to monitor the sample temperature. To avoid photodegradation of the probe during experiments over extended periods of time, a mechanical shutter was installed to enable intermittent illumination of the sample. Using a custom-made sample cell holder, temperature regulation to ±0.1°C was achieved. The fluorescent probes used in this study were 1,3-bis-1-pyrene propane (BPP) and 1,(4-dimethylaminophenyl)-6-phenyl-1,3,5-hexatriene (DMA-DPH) obtained from Molecular Probes Inc. (Junction City, OR, USA). BPP is an excimer-forming probe. However, dispersed in a glassy epoxy matrix, the excimer formation is essentially zero[29]. The monomer emission of BPP and the emission of DMA-DPH each show substantial intensity enhancement in vitreous media via changes in internal conversion[29].

Table 1 Glass transition temperatures of DAB/HA/EPON 828 epoxy system as a function of the weight ratio of DAB to HA

DAB (g)	HA (g)	EPON 828 (g)	T_g (°C)
0.115	0.0	1.0	115
0.086	0.066	1.0	95
0.065	0.113	1.0	85
0.023	0.211	1.0	60
0.0	0.264	1.0	50

For this work the chemistry of the EPON 828 epoxy system (Shell Chemical Co., Houston, TX, USA) was selected to constrain the glass transition temperature of the fully-cured epoxy to the range of 60–80°C. This is accomplished by combination of di- and tetra-functional hardeners, hexylamine (HA) and 1,4-diamino-butane (DAB) (*Table 1*). Curing of the epoxy hardener system is accomplished in two stages. First, the mixture is cured at room temperature for 12 h, with subsequent final curing at $T = T_g + 10°C$ for at least 1 h. Curing slightly above the ultimate T_g ensures complete conversion without chemical degradation. Glass transition temperatures were determined using a Perkin–Elmer DSC-7. All samples were run initially at a heating rate of 20°C min^{-1} for the first scan and the reported T_g values are derived from a second scan at 10°C min^{-1}. Liquid epoxy mixtures were cured directly in standard aluminium d.s.c. pans.

Epoxy samples for fluorescence studies during isothermal annealing below T_g were polymerized directly in cylindrical sample cells with a 5.5 mm internal diameter. Temperatures were determined to ±0.1°C by means of a thermocouple inserted directly into the epoxy resin prior to polymerization, which was then cured in place. The samples were annealed at $T_g + 20°C$ for 30 min to allow for complete volume equilibration. The spectrometer chamber was pre-heated to the temperature of the physical ageing studies. The doped epoxy samples were transferred quickly from the annealing oven to the spectrometer. Thermal equilibration took place within 3 min.

Stress relaxation measurements

Momentary stress relaxation curves during isothermal physical ageing were performed using the Rheometrics RMS-800 dynamical mechanical spectrometer. Epoxy samples were cast as rectangular bars of dimension 3 mm x 12 mm x 45 mm from silicone rubber moulds. The sample was mounted in the spectrometer using standard accessories with the sample fixture enclosed within an oven that allows temperature control. The oven maintains constant temperature by preheating a stream of dry nitrogen gas forced into the oven chamber. Accuracy of the oven set temperature was verified by bonding a thermocouple directly to the epoxy bar and measuring the temperature with a digital thermocouple. Oven response is fast enough to allow annealing of the sample above T_g *in situ* with subsequent quenching to $T < T_g$. Equilibrium is established in approximately 10 min.

Time dependent shear stress relaxation $G(t)$ data were collected at specified ageing times during isothermal annealing, following a quench from above to below T_g. Adopting the method outlined by Struik[1], a step strain of 0.1% was applied to the sample and maintained for a time period of less than 10% of the total ageing time. There are two important consequences of this procedure. First the choice of a 0.1% strain is well within the linear viscoelastic region for these epoxy samples and second, the restriction of measurement times to less than 10% of the ageing time assures that effects of physical ageing during data collection will be negligible. The instrument automatically calculates the time dependent shear stress following a step in strain using specified information on the sample geometry and calibrated voltages from torque on the transducer.

RESULTS

Fluorescence measurements

In *Figure 1* we show fluorescence intensities, F, during isothermal physical ageing for the probe BPP dispersed in a fully-cured DAB/HA/EPON 828 epoxy with $T_g = 66°C$. Quenches were performed at three different temperatures, $T_g - 21°C$, $T_g - 31°C$, and $T_g - 40°C$. By displaying the intensity data as ratios to a suitable reference state we can compare the results at different ageing temperatures. The reference state selected is the intensity, F_{10}, at ageing time $t_a = 10$ min. *Figure 1* shows that, at each temperature, the fluorescence intensity increases during ageing, consistent with a decrease in radiationless de-excitation of the probe as the free volume of the polymeric matrix decreases (equation (1)). It is also evident from *Figure 1* that the deeper the quench, the larger the overall magnitude of the fluorescence recovery. This observation is also consistent with equation (1) since the deeper the sample is quenched below T_g, the larger is the excess free volume over the equilibrium free volume at that temperature. Thus, the driving force for recovery will be greater the further the sample is removed from equilibrium. This manifests itself in the recovery curves as a greater initial slope, and a larger overall magnitude of change in free volume and hence in the ratio F/F_{10}. A similar behaviour is evident in *Figure 2* for the ageing time evolution of the emission from DMA-DPH in a DAB/HA/EPON 828 epoxy of $T_g = 67°C$ at quench temperature $T_g - 9°C$, $T_g - 14°C$ and $T_g - 23°C$.

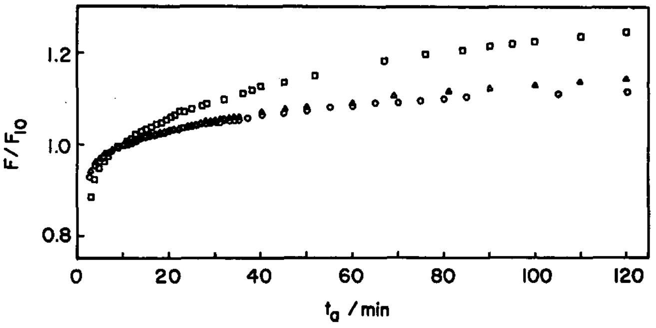

Figure 1 Increase of fluorescence intensity of BPP dispersed in an Epon 828/DAB/HA epoxy with $T_g = 66°C$ during isothermal physical ageing at indicated quench depths. □, $T_g - 40°C$; △, $T_g - 31°C$; ○, $T_g - 21°C$. Intensity data are scaled to a reference intensity at an ageing time $t_a = 10$ min

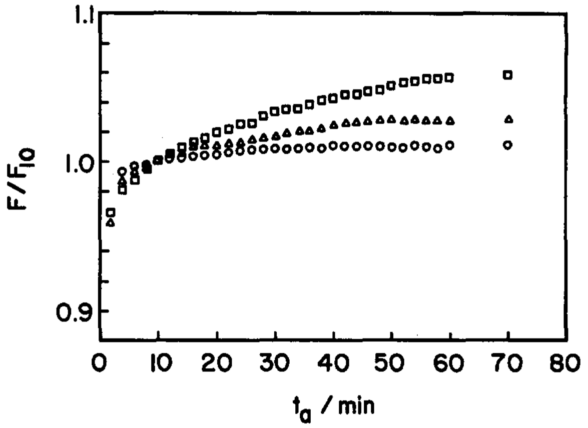

Figure 2 Increase of fluorescence intensity of DMA-DPH dispersed in an Epon 828/DAB/HA epoxy sample with $T_g = 67°C$ during isothermal physical ageing at indicated quench depths. □, $T_g - 23°C$; △, $T_g - 14°C$; ○, $T_g - 9°C$. Intensity data are scaled to a reference intensity at an ageing time $t_a = 10$ min

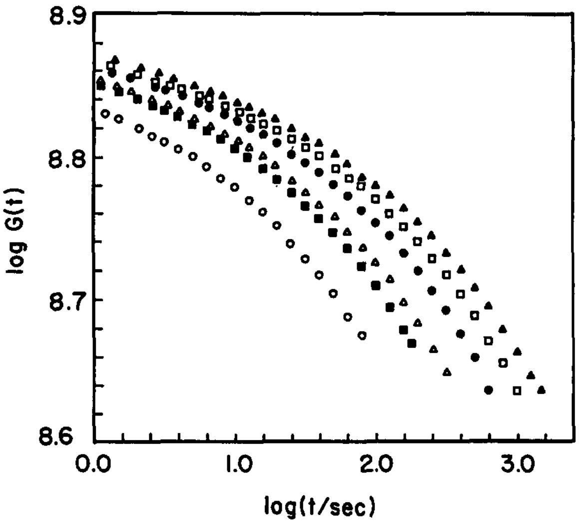

Figure 3 Momentary shear stress relaxation $G(t)$ for different ageing times during isothermal annealing of an Epon 828/DAB/HA sample with $T_g = 60°C$, quenched to $T_g - 21°C$. $t_a\,\mathrm{min}^{-1} = 15$ (○); 30 (■); 60 (△); 120 (●); 180 (□); 240 (▲)

Stress relaxation measurements

Physical ageing of the shear stress relaxation function for a DAB/HA/EPON 828 epoxy with $T_g = 60°C$, quenched to $T_g - 21°C$ is shown in *Figure 3*. It demonstrates that with increasing ageing time the momentary shear stress relaxation curves shift to longer relaxation times. Clearly, the shape of the relaxation curves is similar, and the curves are shifted along the logarithmic loading time scale as volume relaxation occurs during isothermal annealing below T_g. Following the procedure of Struik[1], we can evaluate the increase in mechanical relaxation times, $t_0(t_a)$, from the $G(t)$ curves by vertical and horizontal shifts, and superposition on a suitably chosen master curve. The shift procedure can be performed manually using a light box and it was found that the shifts appear to be purely horizontal within experimental errors. Following Booij and Palmen[30], we choose a function of the form:

$$G(t)=G_0\left(\frac{t}{t_0}\right)^b \exp-\left(\frac{t}{t_0}\right)^a \qquad (2)$$

where G_0 is the instantaneous modulus, t_0 is a characteristic mechanical relaxation time, t is time, and a and b are constants which can be evaluated numerically, using the ZXSSQ software package from the IMSL subroutine library on a VAX 11-780 mainframe computer. ZXSSQ is a finite difference, Levenberg–Marquardt routine for solving non-linear least squares problems. A master curve is then constructed as shown in *Figure 4*. Once the constants a and b are known for the master curve, the individual ageing curves are fitted to two parameters G_0 and t_0 (see *Table 2*). In principle, a slight increase in G_0 is expected due to densification of the material, but *Table 1* indicates this is too small to detect. The mechanical relaxation times $t_0(t_a)$ characteristic of each momentary stress relaxation curve are thus established, and the viscoelastic shift factors $a(t_a)$ can be defined in terms of a suitably chosen reference state:

$$\log a=\log\left(\frac{t_0}{t_{0,\mathrm{ref}}}\right) \qquad (3)$$

for a given value of t_a.

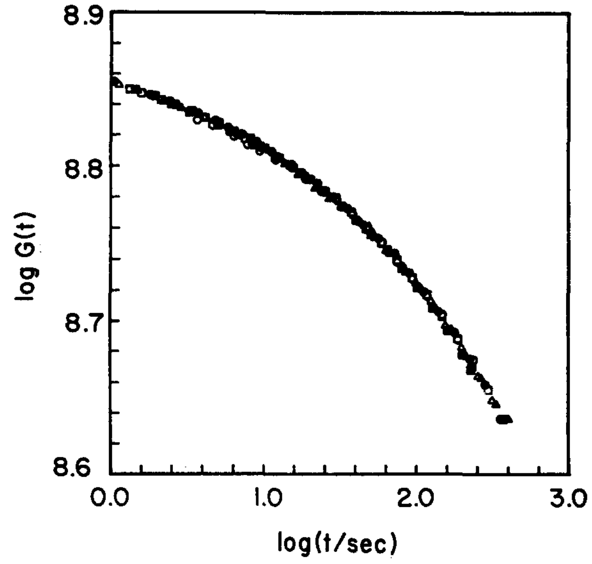

Figure 4 Master curve of shear stress relaxation data in *Figure 3*, constructed via horizontal shifts and superposition on the $G(t)$ record, at a reference time of $t_a=60$ min. Symbols as in *Figure 3*

Table 2 Shear stress relaxation parameters for a DAB/HA/EPON 828 epoxy of $T_g=60°C$

t_a (min)	t_0 (sec)	G_0 (Pa)	a	b
15	703	7.85×10^8	0.313	−0.0014
30	1374	7.96×10^8	0.313	−0.0014
60	1855	7.94×10^8	0.313	−0.0014
120	3245	7.96×10^8	0.313	−0.0014
180	5062	7.91×10^8	0.313	−0.0014
240	7062	7.93×10^8	0.313	−0.0014

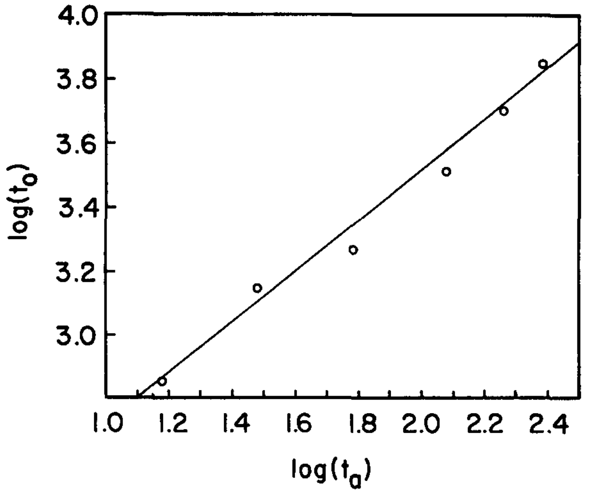

Figure 5 Plot of the mechanical relaxation times t_0 from the shear stress relaxation data of *Table 2*, as a function of ageing time. The straight line corresponds to an ageing rate $\mu=\mathrm{d}\log t_0/\mathrm{d}\log t_a=0.8$

In *Figure 5*, we plot $\log t_0(t_a)$ for the stress relaxation data summarized in *Figures 3* and *4*. Consistent with previous observations[1,31], *Figure 5* shows the ageing rate $\mu=d\log t_0/d\log t_a$ to be approximately constant and close to unity.

DISCUSSION

Previous analyses of the correlation between volume recovery and viscoelastic temperature shift factor[4,5] were performed in terms of the function $h(P, T, t_a)$, mentioned in the Introduction. The lack of PVT and volume recovery data for the present systems prevents the introduction of this function here. In order to facilitate the comparison of mechanical relaxation times, t_0, with the fluorescence results, we proceed in terms of free volume quantities of the type $V-V_m$. Thus, based on Loutfy's arguments, we express the fluorescence intensity F of our two probes by equation (1). Accordingly the emission intensities corresponding to free volume states 1 and 2 are related by:

$$\ln(F_1/F_2)=\frac{V_m}{b}\left[\frac{1}{V_{fs1}}-\frac{1}{V_{fs2}}\right] \qquad (4)$$

Let the free volume V_{fsi} of state i be defined as V_i-V_m. Eliminating in equation (4) V_m by the characteristic volumes for states 1 and 2 respectively, leads to:

$$\ln(F_1/F_2)=\frac{1}{b}\left[\frac{1}{f_{s1}}-\frac{1}{f_{s2}}\right] \qquad (5)$$

with the free volume fraction f_{si} equal to V_{fsi}/V_i. Equations (4) and (5) are to be compared with an analogous Doolittle equation for the mechanical relaxation times in stress relaxation. Accordingly we have:

$$\ln(t_{01}/t_{02})=(V^*/B)\left(\frac{1}{V_{fm1}}-\frac{1}{V_{fm2}}\right) \qquad (6)$$

where V^* is a characteristic volume required for mechanical relaxation, and $V_{fm}=V-V^*$ is the free volume pertinent for the process. Defining again free volume fractions, one obtains:

$$\ln(t_{01}/t_{02})=\frac{1}{B}\left[\frac{1}{f_{\mathrm{m1}}}-\frac{1}{f_{\mathrm{m2}}}\right] \qquad (7)$$

Writing $\lambda=(V-V^*)/(V-V_{\mathrm{m}})=f_{\mathrm{m}}/f_{\mathrm{s}}$, and comparing equations (5) and (7), the final result is:

$$\ln(t_{01}/t_{02})=\frac{b}{B\lambda}\ln(F_1/F_2) \qquad (8)$$

λ is a positive constant which is introduced to account for the possibility that, because of its finite size, the probe may sample a more restricted region of the free volume distribution than that which determines the stress relaxation behaviour. Taking state 2 as the reference state, we can write:

$$\ln(t_0/t_{0,\mathrm{ref}})=\frac{b}{B\lambda}\ln(F_1/F_{2,\mathrm{ref}}) \qquad (9)$$

This equation suggests a linear correlation between an ageing shift parameter for mechanical relaxation and a similar quantity for fluorescence emission of a probe embedded in a glassy polymer, provided identical thermal histories are involved. Now, it is well known[1,30], and illustrated in *Figure 5*, that the ageing rate $\mu=\mathrm{d}\log t_0(t_{\mathrm{a}})/\mathrm{d}\log t_{\mathrm{a}}$ is usually constant and of order unity, provided the ageing temperature is sufficiently far below T_{g}. This behaviour has been rationalized by Struik[1], using free volume arguments. Based on an equation of the form of equation (6), and provided the values of the free volume parameter $f(t_{\mathrm{a}})$ are sufficiently far removed from both the initial and final states, i.e. $f(0)\gg f(t_{\mathrm{a}})\gg f(\infty)$, it can be shown that $\mu\lesssim 1.0$. It is therefore apparent that according to equation (9) $\mathrm{d}\log(F_1/F_{\mathrm{ref}})/\mathrm{d}(\log t_{\mathrm{a}})$ should also be constant under these circumstances. Thus, in *Figures 6* and *7* we exhibit, respectively, the fluorescence data of BBP and DMA-DPH from *Figures 1* and *2* as plots of $\log(F/F_{10})$ *versus* $\log t_{\mathrm{a}}$. Clearly, the fluorescence ageing shift parameters are consistent with $\mathrm{d}\log(F/F_{10})/\mathrm{d}\log t_{\mathrm{a}}=$constant, particularly so for deeper quenches. Deviations from linearity are seen in the shallower quenches at longer ageing times. These arise mainly from the large experimental uncertainties, since the small incremental fluorescence changes at large t_{a} test the limits of instrumental stability. It is also noteworthy that the fluorescence ageing rate $\mathrm{d}\log(F/F_{10})/\mathrm{d}\log t_{\mathrm{a}}$ increases with increasing quench depth, consistent with free volume arguments given above.

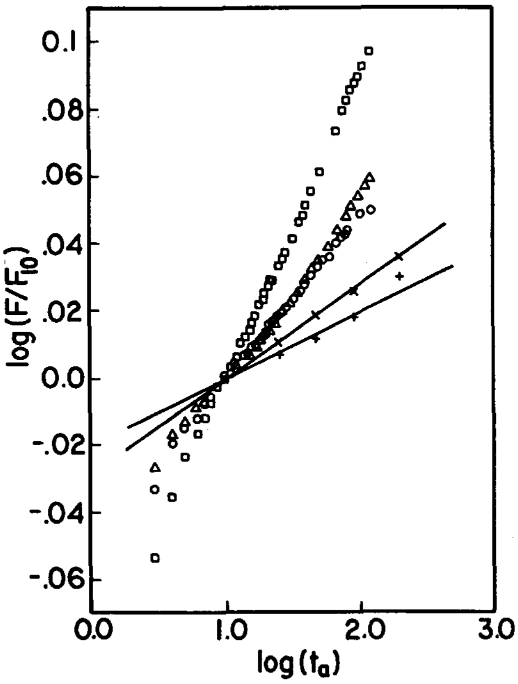

Figure 6 Intensity data of *Figure 1* plotted as $\log(F/F_{10})$ vs. $\log(t_{\mathrm{a}})$, illustrating linear dependence of the spectroscopic shift factor on log ageing time. Straight lines show corresponding behaviour earlier reported (Ref. 28) for Auramine 0 dispersed in polyvinylacetate ($T_{\mathrm{g}}=35°\mathrm{C}$) at quench temperatures $T_{\mathrm{g}}-10°\mathrm{C}$ and $T_{\mathrm{g}}-15°\mathrm{C}$. □, Epoxy, $T_{\mathrm{g}}-40°\mathrm{C}$; △, epoxy, $T_{\mathrm{g}}-31°\mathrm{C}$; ○, epoxy, $T_{\mathrm{g}}-21°\mathrm{C}$; ×, PVAc, $T_{\mathrm{g}}-15°\mathrm{C}$; +, PVAc, $T_{\mathrm{g}}-10°\mathrm{C}$

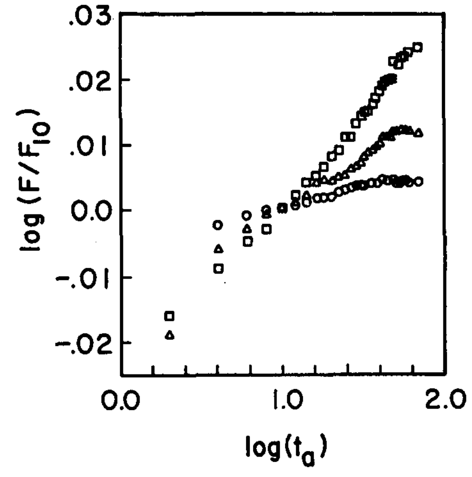

Figure 7 Intensity data of *Figure 2* plotted as $\log(F/F_{10})$ vs. $\log(t_{\mathrm{a}})$, illustrating linear dependence of the spectroscopic shift factor on log ageing time. □, $T_{\mathrm{g}}-23°\mathrm{C}$; △, $T_{\mathrm{g}}-14°\mathrm{C}$; ○, $T_{\mathrm{g}}-9°\mathrm{C}$

Our results for BPP and DMA-DPH are consistent with earlier data of Meyer *et al.*[28] for the fluorescence probe Auramine O, dispersed in vitreous polyvinylacetate (PVAc). Indeed in *Figure 6* we present lines derived from Meyer's results which also show a constant $\mathrm{d}(\log F/F_{10})/\mathrm{d}\log t_{\mathrm{a}}$, increasing with depth of quench. An alternative test of equation (9) is to plot $\log(F/F_{\mathrm{ref}})$ *versus* $\log(t_0/t_{0,\mathrm{ref}})$ for a sample of specified and identical T_{g}. For experimental reasons it was not practicable to obtain samples of identical T_{g}s for the two sets of experiments. Instead, comparisons were carried out for samples of similar T_{g}s at corresponding temperatures $T_{\mathrm{g}}-\Delta$. Examples are seen in *Figure 8* for the two probes with $\Delta=21°\mathrm{C}$. Clearly, the experimental data are in accord with equation (9). Since the slopes of the fits to each data set differ, it follows that λ and/or b are, not unexpectedly, different for the two probes.

CONCLUSIONS

In the initial stages of the isothermal ageing process of a polymer the fluorescence emission intensity, F, of the probes BPP and DMA-DPH dispersed in the epoxy matrix shows a substantial time-dependent increase. This is qualitatively consistent with expectation based on a decrease in internal conversion due to the relaxation of the matrix free volume. The ageing time dependence

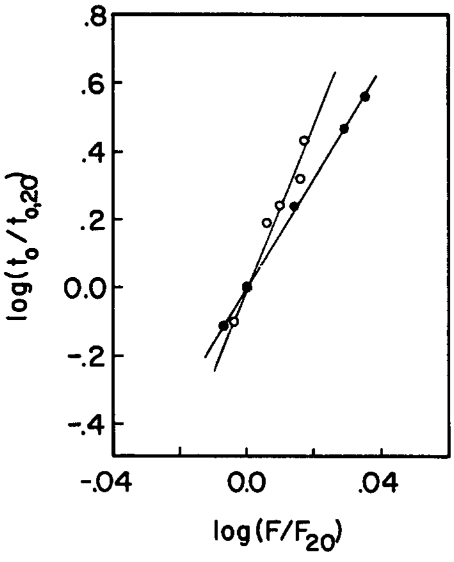

Figure 8 Relation between viscoelastic and fluorescent shift parameters for isothermal ageing of an Epon 828/DAB/HA epoxy at T_g-21°C: ○, BPP fluorescence; ●, DMA-DPH fluorescence. Reference time $t_a=20$ min

appears to follow closely the experimental law:

$$d \log F/d \log t_a = k \qquad (10)$$

where k is a constant which increases with the depth of the quench below T_g. This behaviour is consistent with the application of free volume arguments to the equation of Loutfy[15] (equation (1)). Fluorescence measurements show promise as a spectroscopic probe for changes in free volume in amorphous polymers during physical ageing.

ACKNOWLEDGEMENTS

We thank the Center for Coatings, Adhesives and Sealants at CWRU, and the National Science Foundation, Polymers Program (Award DMR 85-04372) for support of this work. We are also indebted to Professor H. Ishida for use of the Rheometrics Mechanical Spectrometer.

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