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Annealing effects in epoxy resins examined by a refined density-gradient technique

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An aqueous density-gradient column was used to study annealing effects in a series of epoxy resins. The crosslinking densities were varied via the monomer composition. The height of the specimens floating in the column was observed to change linearly with the square root of time during several days. The corresponding total density change typically amounts to 6 kg m^{-3}, or 0.6%. By back-extrapolating the sample heights to time zero, accurate density values, uninfluenced by liquid absorption and other confounding effects, may be determined. Analysis of variance shows a residual error of 0.1 kg m^{-3}, or 0.01%, for the means of three specimens. Consistent density increases, ranging from 0.11 to 0.17%, were shown to occur upon annealing of the cured resins. The differences between samples of varying crosslinking densities were found to be significant.

1. Introduction

1.1. Volume relaxation, annealing and physical ageing

The concept of free volume, characteristic for glassy amorphous solids, was first developed in the context of transport processes [1]. Despite its qualitative nature, it has been very useful in explaining many phenomena [2], like e.g. the slow changes occurring when a glassy polymer is kept at temperatures moderately below its glass transition temperature (T_g). These have been summarized under the term "physical ageing" by Struik [3]. This author was one of the few who correlated specific volume changes (amounting to less than 0.1%, measured by mercury dilatometry) with changes of thermomechanical properties. Below T_g, large increases in relaxation times are associated with very small volume changes. The discrepancies he found may be interpreted by imagining a distribution of free volume among "pockets" of various sizes [1]. A minimum size would be required to allow self-diffusion of polymer chains, and thus relaxation.

Physical ageing of polymers that are crosslinked, especially epoxy resins, has gained interest very recently [4, 5] in the context of the prediction of long-term reliability of adhesives and composite materials with or without applied load. The role of crosslink density, or its inverse quantity, segment length between crosslinks, in these slow changes is still rather uncertain. Lee and McKenna [4] found a slight increase, with crosslink density, of the time required to "age into structural equilibrium" at temperatures just below T_g. Since in general the picture is complicated by concurrent chemical reaction on one hand, and by the lack of a crystalline (or even a liquid) reference state on the other, treatments have been largely phenomenological. Accurate density measurements thus appear useful for more fundamental interpretation of the ageing phenomenon.

As an illustration of our density extrapolation method, the present work reports densities at 23 °C of a series of model epoxy systems with varying crosslink density, and the effect of annealing the samples at slowly descending temperatures. The corresponding mechanical properties have been published elsewhere [6].

1.2. Aspects of density measurement

The determination of density is part of routine polymer characterization [7]. The methods available most noticeably differ with regard to the size and perfection of the sample required, the demands on time and equipment, and the factors influencing accuracy and/or resolution. Techniques based either on pycnometry (measurement of displaced liquid volume) or buoyancy (the Archimedes principle) are probably the most widespread. They share the requirement of a certain minimum sample size for a given degree of accuracy. A density-gradient column [8–10] was first used in the polymer field by Boyer *et al.* [11] to follow the crystallization of PVC on a time-scale of 20 min. The method is based on measuring the equilibrium height of samples suspended in a liquid with a stable gradient of density in the vertical direction. Besides the high potential resolution attainable (linearity even improves with shallower gradients), this method offers the advantage of a large number of small individual samples that can be followed practically simultaneously. Spatial density variations may thus be explored by cutting up a block of material [12]. Individual samples floating within the column may readily be identified if they are given distinctive shapes (Fig. 1). Over the years the method, used mostly for the determination of crystallinity in thermoplasts, has been improved in many respects, so that an accuracy of 0.2 mg cm^{-3} or better, i.e. a significant fourth decimal place in density, is claimed [10]. However, Boyer

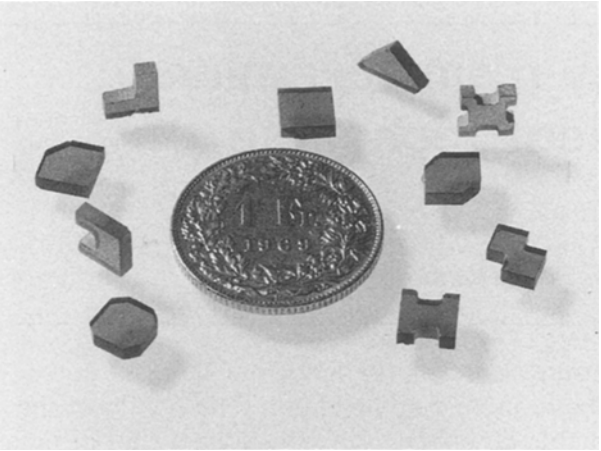

Figure 1 Typical size and distinctive shapes of thermoset samples for use with a density gradient column.

et al. [11] already noted the possible bias introduced by attack of the suspending fluid on, or slow wetting of, the samples.

In this paper we present a method to overcome this type of limitation and thereby to expand the field of application of the density-gradient technique, as exemplified by annealing effects in a series of epoxy resins.

The approach taken by the present work is to eliminate the time factor by taking a number of readings and back-extrapolating to zero time, exploiting the observed linear dependency of sample position on the square root of time. At the same time, the uncertainties due to the limited height resolution are averaged out.

2. Experimental procedure

2.1. Materials

The five types of solid examined here resulted from stoichiometric polyaddition of bisphenol A, 2, 2-di(4-hydroxyphenyl)-propane (BA), with a polyglycidyl compound of bisphenol A (PGCBA, average functionality 3.45 epoxy groups per molecule), and diglycidylether of bisphenol A (DGBA) in various proportions. The catalyst was 2-ethyl-4-methyl-imidazol (0.1 wt %). This chemistry, described in more detail elsewhere [6], resembles that of widely used encapsulation compounds. It allows wide variation of crosslink density with minimal changes of other molecular properties (non-covalent interactions); e.g. the calculated concentration of phenyl rings in the solid varies from 6.7 to 7.0 mol kg^{-1} between the end members A and E of the series. Completeness of cure was checked by differential scanning calorimetry (DSC) and infrared spectrophotometry.

The crosslink densities of the five systems, denoted by the molecular mass between crosslinks M_c, determined from the modulus in the rubbery region [6], are listed in Table I. Sample A is thus the most densely crosslinked network, while sample E at least theoretically represents a thermoplast.

TABLE I Composition and crosslink densities of samples

Sample	BA (wt %)	DGBA (wt %)	PGCBA (wt %)	M_c (kg mol^{-1})
A	45.4	0	54.6	0.327
B	42.7	29.3	27.9	0.693
C	41.3	44.1	14.6	1.090
D	40.6	52.0	7.4	2.70
E	39.8	60.2	0	–

2.2. Thermal treatment of samples

Cast specimens of the five resin systems were post-cured for 1 h at 180 °C. Samples of each system were then divided into two groups: half were quenched immediately in liquid nitrogen, the other half were annealed by cooling through the glass transition region from 120 to 72 °C at a rate of 0.25 °C/h^{-1}.

2.3. Density gradient technique

2.3.1. General considerations

After being put into the gradient column at height z_0, a sample needs a certain time to descend to its equilibrium position z_∞, where the gravity force is cancelled by buoyancy. Using Stokes' law, it may be shown that this occurs exponentially:

$$z = z_\infty + (z_0 - z_\infty)\exp\left(-\frac{2ga^2\delta}{9\eta}t\right) \qquad (1)$$

a being the sample radius, δ the density gradient and η the viscosity of the suspending liquid. With a typical aqueous gradient of 125 kg m^{-4}, a particle of 1 mm radius takes about 23 s to approach the equilibrium position from a distance of 0.5 m to within its own radius. Recovery of the gradient from small disturbances caused by the introduction of the sample may take a little longer. Any further changes of position of the specimen are caused by changes in its relative density. Possible causes include non-equilibrium structure of the solid, release of trapped air (since the column liquid is degassed, it is able to dissolve air bubbles), or interaction with the suspending liquid, e.g. selective absorption of solvent.

Deterioration of the linear density gradient, on the other hand, which begins at the ends of the column, was discussed by Oster and Yamamoto [13]. With appropriate temperature stabilization, it only starts to become noticeable after about 40 days.

2.3.2. Calibration

Degassed aqueous potassium iodide solutions were used to establish a gradient of 125 kg m^{-4}. The water jacket of the commercial six-column apparatus (Mk II, Daventest Ltd, Welwyn Garden City, UK) is thermostatted at 23 ± 0.1 °C. The glass calibration floats purchased from the same firm are stated as of ± 0.1 kg m^{-3} accuracy. Since, in an equilibrated gradient column, the diffusion law precludes random deviations from linearity [7], such persisting deviations as are observed must be due to calibration errors. This fact was confirmed, (a) by the reproducibility of the deviations of individual floats on repeat column fillings and (b) by recalibration of floats. To reduce this source of error, a linear regression of the reference floats' positions against their stated density values was computed (after several days equilibration time, on the same day as the samples were put on to the column) and used to estimate the sample densities from the measured sample heights. Heights of reference floats and of samples were read with a cathetometer to the nearest 0.5 mm. The useful column height is about 750 mm. In the present study, the maximum deviation of a reference float from its calculated position amounted to 2.5 mm, and the standard error of the density estimation from the regression line was $\pm 0.3\,\mathrm{kg\,m^{-3}}$. No systematic trend in the residuals of this regression was present.

2.3.3. Measurement

Three specimens of each material, measuring 2–3 mm, were put on to the same column within a few minutes. The final positions of our polymer samples were situated near the centre of the gradient.

Since systematic changes in height of the samples were noticed over a period of several days, readings were taken at known time intervals after sample introduction. In order to obtain densities of the original dry samples, the plots of about 12 sample height readings versus square root of time were back-extrapolated to time zero. Initial points deviating from the straight line were omitted from the regression. In the present work, the only such deviation was due to a small air bubble.

3. Results and discussion

3.1. Density determination

Height changes were found, in the vast majority of cases, to be linearly proportional to the square root of time. Some examples are shown in Fig. 2. This is easily explained by solvent diffusion into the samples [14]. With a sample radius of 1 mm and a diffusion coefficient of $10^{-12}\,\mathrm{m^2\,s^{-1}}$ for water in epoxy resins, the diffusional time constant is around 280 days, so that our measurement periods are amply within the "$t^{1/2}$ region", meaning that only a thin surface layer is saturated by the liquid. Measured heights that deviated from the $t^{1/2}$ law were found to be influenced by air bubbles, cracks in the samples etc. (Fig. 2a). After dissolution of the air, even such samples moved linearly with the square root of time. All the correlation coefficients of the regression lines were in excess of 0.995, the standard errors of the back-extrapolated heights ranging from 0.3 to 0.5 mm.

The slopes of regression lines (height versus square

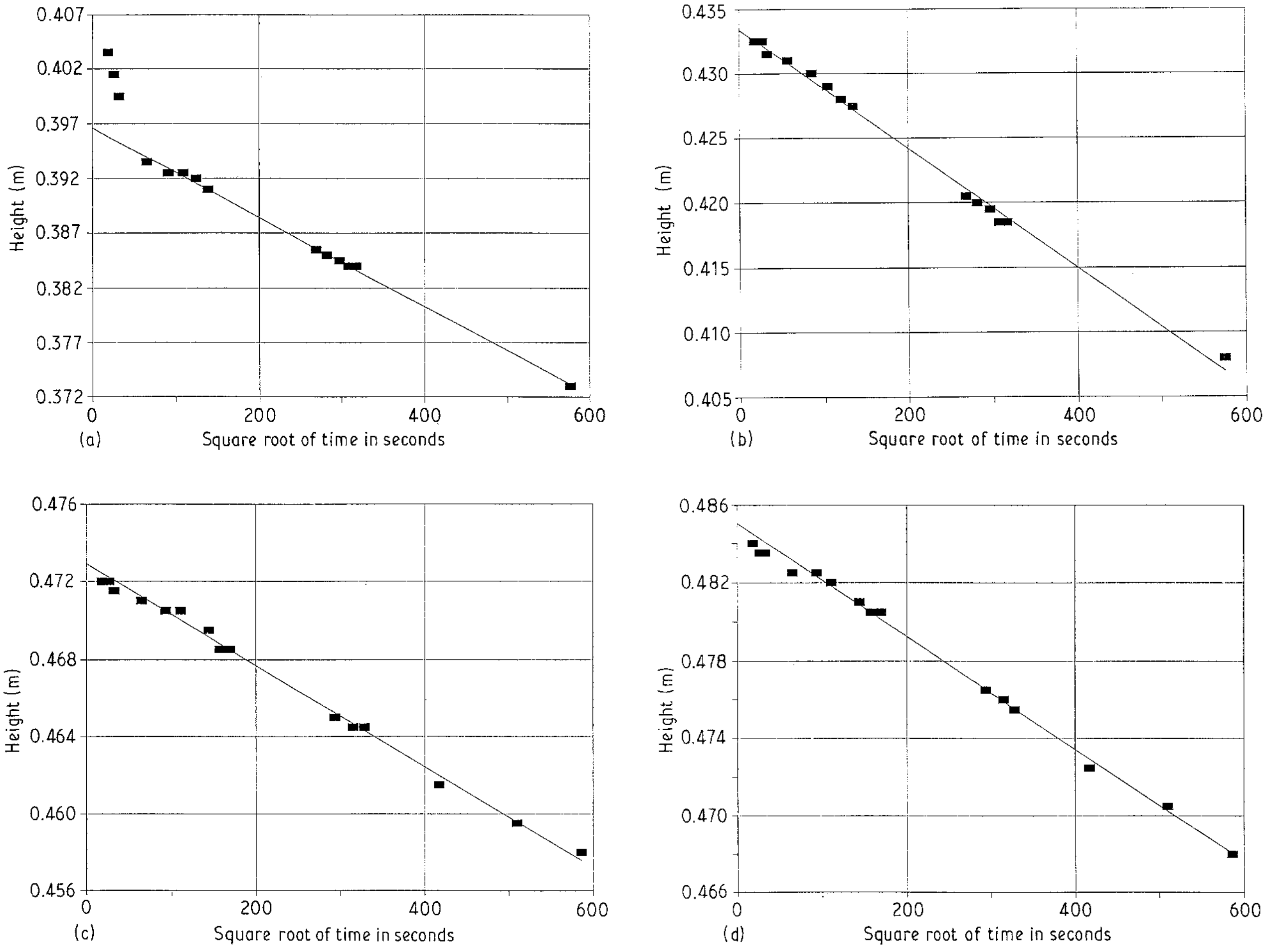

Figure 2 Movement of specimens in density gradient column: height plotted against the square root of time with linear regression line. (a) Resin system A, quenched, initially with adhering air bubble, correlation coefficient $R = 0.9989$. (b) System B, annealed, $R = 0.9969$. (c) System D, quenched, $R = 0.9983$. (d) System D, annealed, $R = 0.9976$.

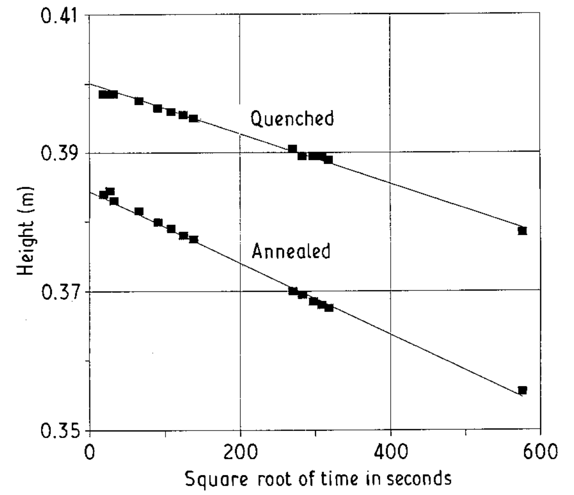

Figure 3 Influence of annealing on temporal variation of sample heights: quenched (upper line) and annealed specimens of system A.

TABLE II Density of quenched and annealed samples

System	Average density ($kg\,m^{-3}$)	Std error ($kg\,m^{-3}$)	95% confidence interval
Annealed specimens			
A	1197.2	0.23	1197.0–1197.4
B	1190.8	0.03	1190.6–1191.0
C	1187.2	0.10	1187.0–1187.4
D	1186.0	0.10	1185.8–1186.2
E	1184.1	0.09	1183.9–1184.3
Quenched specimens			
A	1195.2	0.12	1195.0–1195.4
B	1188.9	0.09	1188.7–1189.1
C	1185.8	0	1185.6–1186.0
D	1184.4	0.03	1184.2–1184.6
E	1182.7	0.03	1182.5–1182.9

root of time) obtained from annealed samples tended to be slightly steeper than those of quenched specimens, as illustrated in Fig. 3. Since the value of the slope is influenced by the sample size and shape, it will not be discussed quantitatively here. The observation nevertheless suggests novel possibilities of performing sensitive comparative studies of water diffusivity and swelling using density gradient columns.

Considering Fig. 3, it may also be appreciated that the systematic annealing effects borne out by the extrapolation method might have been obscured completely by reading of sample heights at arbitrary times. Most reports in the literature are conspicuously vague about the actual time the samples spent in the column before readings were taken.

3.2. Influence of crosslink density and annealing:

The densities computed from the back-extrapolated heights of all the 30 individual specimens were subjected to analysis of variance (STATGRAPHICS software, STSC Inc., USA). The effects of the resin system ($p < 0.001$), and annealing ($p < 0.001$) were highly significant. The density averages (three samples per cell), and the various measures of uncertainty resulting from this analysis, are listed in Table II.

It should be noted that the uncertainties of Table II include (a) spatial density fluctuations among "identical" specimens originating from a cast sheet, (b) uncertainty of height reading due to finite specimen size and parallax and (c) errors due to local gradient disturbance by specimens. They are thus a useful measure of the relative accuracy of the method. Errors (b) and (c) are reduced by the extrapolation of multiple readings to zero time. On the other hand, the error bands do not include calibration errors of the column, which are discussed in section 2.3.

The interaction between the resin system and annealing factors was also significant ($p = 0.01$). This indicates that the relative extent of density change caused by the present annealing procedure depends on the resin structure. Absolute and relative density differences between quenched and annealed specimens of the various resin systems are listed in Table III, together with reciprocal values of the molecular mass between crosslinks, taken from Fischer [6].

The relative orders of magnitude of (a) density variation among samples, (b) annealing effects and (c) experimental uncertainties (95% confidence intervals) are further illustrated in Fig. 4. The relative density changes are plotted against reciprocal crosslink density in Fig. 5. The correlation coefficient of the linear regression is 0.85. It just fails to reach significance at the 5% level. Further experiments are therefore required to verify the suggested monotonous dependency of annealing effects on crosslink density. The significant interaction derived from the analysis of variance (see above) indicates that the density measurements themselves are sufficiently precise to reveal such a relationship, but processing parameters other than nominal composition of the resin systems are bound to introduce additional fluctuations at this level of accuracy.

Given the single thermal treatment schedule applied to the samples of the present study, either an increase or a decrease of the annealing effect with crosslink density could probably be explained. While all the samples, before quenching, were heated well above their T_g, and probably attained equilibrium there, the corresponding amount of free volume also depends on the temperature at which the original crosslinking took place. It is known that the free volume of thermosets increases at higher gelation temperatures. While in the case of thermoplasts (cf. sample E) no "disorder" (i.e. imperfect intermolecular fitting) may be permanently incorporated at this stage, the potential for such incorporation increases with crosslink density. No conclusions in this respect may be drawn from the varying absolute densities of the samples, since the variation in chemical composition, though small, should be able to account for those.

The structure at the lower temperature after annealing, on the other hand, was certainly far from equilibrium (cf. [4]), and the relative degree of relaxation was determined by kinetic as well as thermodyn-

TABLE III Crosslink density and annealing effects

System	Annealing effects			
	$1/M_c$	Absolute	Relative (%)	
	(kg mol^{-1})	(kg m^{-3})	Observed	Regression
A	3.06	2.0	0.170	0.173
B	1.44	1.9	0.159	0.144
C	0.92	1.4	0.118	0.135
D	0.46	1.6	0.137	0.126
E	0	1.3	0.112	0.118

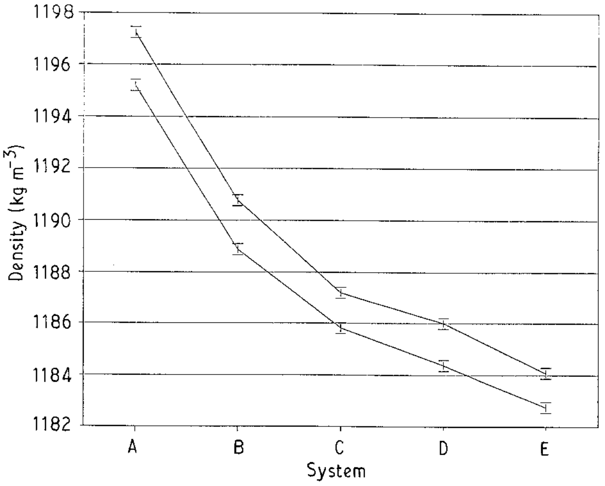

Figure 4 Densities, extrapolated to time zero, of annealed (upper line) and quenched (lower line) samples of five resin systems with crosslink densities decreasing from left to right. Temperature 23 °C. Error bars indicate 95% confidence intervals.

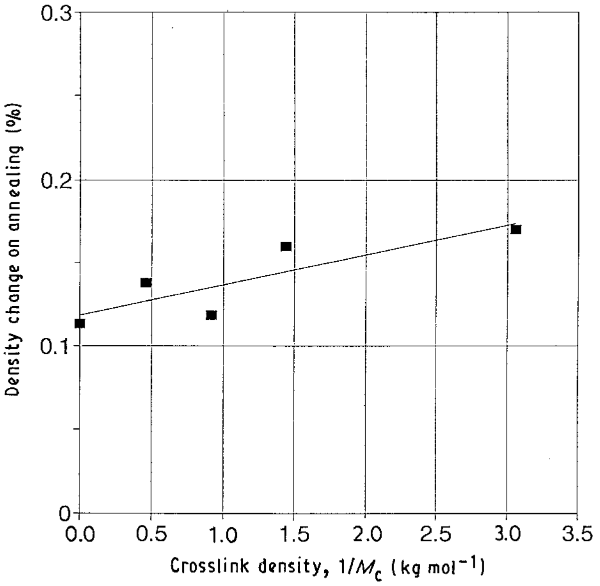

Figure 5 Relative density changes of the five resin systems upon annealing, plotted against the reciprocal of molecular mass between crosslinks.

amic factors. Given the fixed temperature range of cooling, the time spent in a "relaxing" state varied among the systems. Experiments using different annealing schedules would be required to elucidate this point.

Very recently, Won Ho Jo and Kyoung Jin Ko [15] reported a study of physical ageing, including density determinations by gradient column, on a series of five amine-cured epoxy systems, the composition (and presumably, the crosslink density) having been varied via the amine/epoxy ratio. The authors used annealing at constant temperature, fixed for each system at 20 °C below the respective glass transition temperature. Notwithstanding these different conditions, their graph of density versus mixing ratio suggests a maximum annealing effect (nearly 0.4%) at the 1:1 stoichiometry, where the highest crosslink density is expected, in accordance with our results.

4. Conclusions

The relative accuracy of the density-gradient column method, applied to polymers, is considerably increased by making use of the systematic time dependency of the specimen heights. Since many small samples may be observed simultaneously, the method appears well suited to examine treatment effects or preparative variants resulting in minute density changes. The method is also applicable to filled thermosets, e.g. to study the spatial homogeneity of filler distribution, as was shown by similar work using columns with heavy organic liquids [16].

Density determination of a series of model thermosets has revealed significant variations in the decrease of free volume on annealing. While there was a suggestive increase of this annealing effect with crosslink density, it did not quite reach statistical significance, probably due to confounding factors inherent to thermoset sample preparation.

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