

Influence of the cure cycle upon selected physical properties of a vinyl ester resin

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Detailed observations of volumetric changes which occurred during the cure of a vinyl ester resin system have led to the definition of an alternative cycle which involves the same temperatures as the original cycle but in which the recommended overall time of cure is reduced by some 75%. Flexural and tensile strengths and moduli, thermal expansion characteristics, densities and hygrothermal properties of specimens produced according to each cycle are closely similar. The mechanical properties of the same resin reinforced with glass cloth and prepared according to the two cycles were also closely similar. It is concluded that there is considerable scope for applying observations of the volumetric curing characteristics of a resin system to develop a cycle in which (i) the potential of a given formulation is fully realized and (ii) the product is manufactured as economically as possible.

1. Introduction

The advantages of resin-based composites over metals and alloys for applications in aerospace are well known. Less well known are variations in the degree of cross-linking within the resin matrix, which may result from variations of detail in the cure cycle and which may give rise to variations in the properties of composites containing the resins. Under-curing can result in the product displaying characteristics of creep. Over-curing can result in the product being brittle. Consequently there is a case for optimizing the cure cycle of a resin in order to produce the "best" composite one can from given starting materials. In addition there is a good deal of interest in knowing the minimum time required to produce a composite with physical properties conforming to acceptably high standards. These two reasons, scientific and commercial, provide the background to the present investigation, which was designed to examine the influence of variations of detail of the cure cycle upon selected physical properties of a resin system and composite specimens from which the matrix was formed.

2. Background

2.1. The subject of the investigation

A wide variety of resins and fibres are available to the composite manufacturer [1, 2], the choice in any individual case being governed by the particular requirements of the application. A subject which lent itself to the terms of the present study was the vinyl ester resin system, members of which resemble polyester resins in that they react with styrene to form a

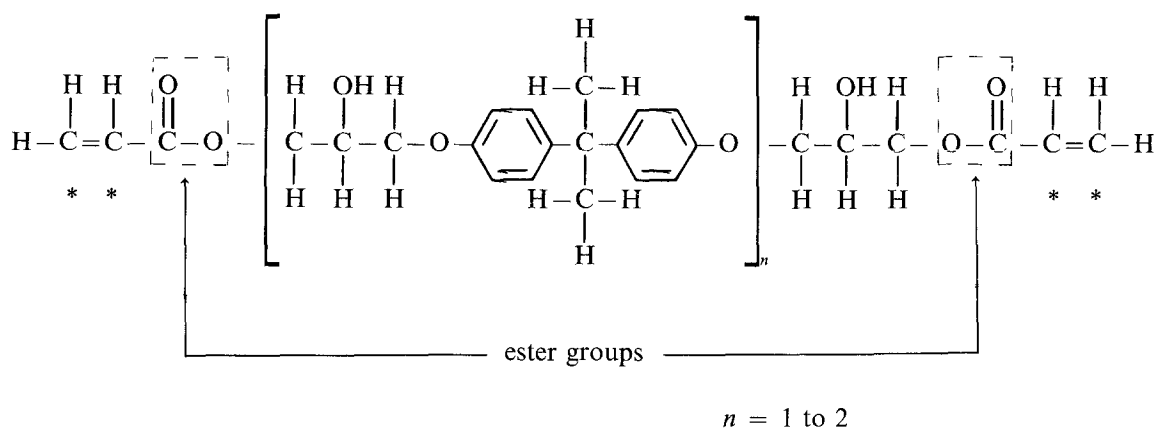
cross-linked structure through addition polymerization, which is promoted by peroxide catalysts. They were introduced some years ago and combine aspects of unsaturated polyester and epoxy chemistry. In most resins used to date there are two ester groups per molecule and two unsaturated groups at each end of the polymer chain. They are usually produced by reaction at each end of a bisphenol A based epoxy resin molecule with a material such as acrylic acid to provide unsaturated sites for cross-linking with monomers such as styrene.

The main advantages claimed for vinyl ester resins are:

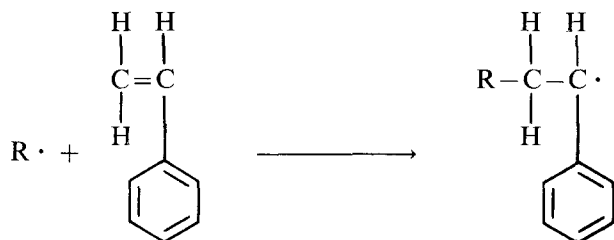
- (i) low molecular weight resins of controlled structure are available;
- (ii) the epoxy backbone with reduced ester groups and terminal unsaturated reactable groups provides improved chemical resistance, high resilience and toughness and a uniformly cured structure with reduced internal stress;
- (iii) the presence of hydroxyl and acrylate groups allows good wetting and adhesion to materials having polar surfaces, such as glass.

The vinyl ester used in this study, Derakane 470-36, was manufactured through the addition reaction of an epoxy resin with an acrylic monomer and diluted with 36% styrene. The molecular structure shown below is characteristic of a vinyl ester polymer chain. The curing involves decomposition of a peroxide to form free radicals which are first used up by reaction with inhibitors contained within the resin, i.e. $I \rightarrow 2R$. The radicals then react at double bond sites of monomer

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and vinyl ester, by taking an electron from the electron-rich bond but leaving an unshared electron at the other end, i.e.



The vinyl ester chains become linked via the styrene monomer, the reaction proceeding through gelation and terminating as all the free radicals react into the thermoset matrix. Accelerators speed up the reaction and a temperature increase from the exothermic reaction and/or post cure increases the molecular mobility and advances the reaction.

Significant differences in the nature of the cross-linked polymer result from using various catalyst systems and cure conditions for the fabrication of reinforced plastic equipment. In practice, for a given resin, the catalyst system, temperature and time of curing are selected according to the following main criteria: desired gel time; working temperature and humidity; effect of the mould as a heat sink; effect of the post cure; details of the exothermic reaction and laminate thickness; mixing errors; coats. Of the several curing systems available for this resin, that based upon methyl ethyl ketone peroxide is most frequently used in fabrication workshops. Several types are available with different active oxygen contents (normally 8 to 11%), the composition playing an important part in the curing. Standard MEKP contains a minimum of 9% active oxygen.

In order to reduce the almost infinite number of curing variables, one catalyst system was selected giving a resin formulation which, according to data provided by the manufacturers, The Dow Chemical Company, had a gelation time of 50 min in 100 g quantities at 23°C. This comprised (in parts by

weight):

vinyl ester resin (Derakane 470-36):	100
standard methyl ethyl ketone peroxide (MEKP):	1.5
cobalt octoate (1% in styrene):	3.0
dimethyl aniline (10% in styrene):	0.5

The cobalt octoate and dimethyl aniline accelerators were used as solutions in styrene, mainly to reduce mixing errors. A proper balance between catalyst (initiator) and accelerators must be maintained, because the accelerator must activate the peroxide catalyst. The wrong ratio would cause incomplete cure, even when the gelation time appeared to be satisfactory. The measurement of levels of residual styrene in the cured resin is a common quality control technique reflecting differences of the resin matrix or degree of cure. This follows because the absence of homopolymerized styrene has been established and it may, therefore, be assumed that any styrene not employed in cross-linking remains as residual monomer. Nevertheless, how these differences relate to important resin properties such as chemical resistance and mechanical properties is a question which frequently arises. The manufacturers advise that the level of peroxide should not influence the gel time dramatically, but the residual styrene (related to the degree of cross-linking) decreases with peroxide level. The heated post-cure is thought to have a major influence on residual styrene, causing it to be driven off, and on polymer cross-link density. Alternatively, encouraging a large temperature rise associated with the exothermic reaction may achieve a better room-temperature cure in the workshop, though this option has associated problems due to the difficulty in controlling the exothermic reaction. Generally the temperature is recognized to be more important than the time of post-cure, but practically any thermal shock must be minimized. Also, due to cost factors, manufacturers do not always employ a post-cure and often facilities are not available to post-cure above 80°C. The time and temperature recommended for cure are flexible, any decrease in post-cure temperature being compensated by an increase in the time the resin is held at that temperature. A post-cure of 6 h at a temperature of 80°C was selected, to follow a period

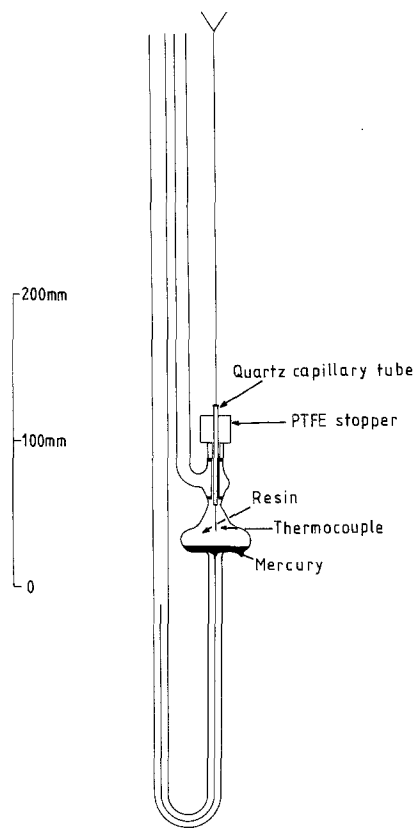


Figure 1 The manometer dilatometer.

of 24 h at room temperature, representing a manufacturer's recommended cure cycle.

2.2. Technological consequences of curing characteristics

The subject of resin flow during the cure of fibre-reinforced composites has captured the attention of a number of workers (e.g. [3]). In practical terms when, for example, making a laminate, the resin would be mixed and some time would elapse while the reinforcement was impregnated, after which the moulding tool would be closed. Some contraction takes place prior to closing the tool so that the loss of volume within the tool is less than the total loss during the curing of the resin. Internal stress will be introduced due to differential contractions of reinforcement and matrix. This will occur between the time when the resin has gelled sufficiently to lock on to the reinforcement and has become an elastic matrix and the time when the matrix is fully cured and the volume reduction is complete and stable. In wet resin moulding a small excess of resin is often used in the tool and this exudes from the edges when pressure is applied. It acts in part as a hydraulic seal and allows resin to flow back when there is a large contraction prior to gel. However, in order to reduce the formation of voids it is desirable to apply the final pressure on to the mould during the onset of gelation. This also helps to keep a maximum volume of resin within the tool at this time. Differential strains within the composite then occur due to the resin curing fully, and the volume reduces. If the cure is carried out at an elevated temperature there is additional strain due to the different rates of contraction on cooling. Consequently, monitoring

volume changes during the cure of the resin, especially in relation to the gel point enables the total contraction after gelation to be determined, hence facilitating the prediction of locked-in stress levels. Cure-cycles generally take many hours; therefore any significant reduction is economically desirable, provided the properties of the "cured" resin are not seriously impaired.

3. Experimental details of the curing process

3.1. Volume changes

Experimental work commenced by employing a dilatometer, of a type described earlier [4]. Experience led to the modified design illustrated in Fig. 1 in which the spine of the PTFE stopper was drilled down its length to accommodate a tight-fitting twin-bore quartz capillary tube, through which thermocouple wires passed. The lower end of the rod was sealed by Ciba-Geigy Araldite Rapid Adhesive and the dimensions were chosen so as to locate the tip of the thermocouple at the centre of the bulb, in intimate contact with the resin. The resin formulation was

- 50 g Derakane 470-36 (manufactured by the Dow Chemical Company)
- 1.5 g Cobalt octoate - 1% in styrene (accelerator)
- 0.25 g Dimethyl aniline - 10% in styrene (accelerator)
- 0.75 g Standard MEKP (catalyst)

After observing the customary preliminaries [4], degassing, etc., the resin was loaded into the dilatometer, air bubbles were removed and the resin was taken through its cure cycle.

3.1.1. Cycle 1

The cycle recommended by the manufacturers, cycle 1, consisted of holding the formulation for 24 h at nominally 20°C, followed by a post-cure at 80°C for a further 6 h. After the constituents of the formulation had been mixed the product was introduced into the manometer dilatometer, which had first been calibrated and which was located within a bath of silicone fluid maintained at 20°C. Volume changes and temperature were recorded over the following 24 h, during which the bath temperature was maintained at 20°C. The temperature was then raised to 80°C; this took approximately an hour, volume changes being recorded at regular intervals during heating and also while the resin was held at the post-cure temperature. At the end of the heated post-cure period the temperature was returned to 20°C by inserting a cooling coil into the bath, the volume and temperature being monitored throughout the whole sequence. The results of the experiment are displayed in Fig. 2. Corrections, amounting to less than 1%, were applied to the results before displaying them in order to allow for dimensional changes of the mercury and the dilatometer.

It was clear from these results that structural modifications were particularly rapid during the early stages of cure and reference to Fig. 3 allows the region

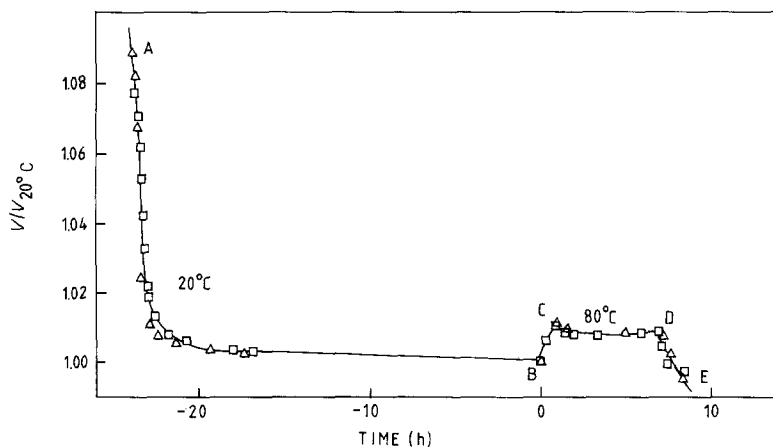


Figure 2 The time dependence of the reduced volume $V/V_{20^\circ\text{C}}$ of Derakane 470-36/MEKP during the curing process. The reference volume of the resin at 20°C and the arbitrary zero of time have been taken at the point B. (\square) Run 1, (Δ) run 2.

of greatest activity to be associated with the peak of the exothermic reaction of the resin. In passing one might note that a subsidiary investigation yielded a time to gelation which was similar to the time to the exothermic reaction peak. Clearly the time taken to reach this critical stage in the cure will be governed by the exact details of the different experimental arrangements. Detailed attention to the foregoing observation led to the conclusion that a substantial fraction of the initial relatively rapid contraction must have occurred after the resin had solidified. This was confirmed by additional experiments undertaken employing bulk mixes of resin from which it became clear that over 50% of the initial total contraction occurred after the resin had solidified. The various observations added up to a picture of a process in which most of the activity took place within an hour of mixing the constituents and this led one to question the need for the period of 24 h at 20°C within the cure cycle.

3.1.2. Cycle 2

Following the above experience it was decided to proceed to the post-cure at 80°C immediately following the exothermic reaction, thus reducing the length of the cure cycle by some 23 h. With this exception, cycle 2 resembled cycle 1. During the course of the investigation small leakages of resin were occasionally encountered in the later stages of cure. In such cases the problem was overcome by duplicating experiments

employing dilatometers with and without thermocouples, traversing cycles in which identity was achieved by an association of times.

3.2. Gelation

Before proceeding to examine the influence of the above variation in cure cycle upon selected physical properties of the product, it was decided to explore the relationship between the temperature of gelation and the temperature of the exothermal peak in more detail, because the manipulation of these temperatures clearly holds out the prospect of exercising some degree of control over the residual stress in the final product.

As cure proceeds in a liquid polymer, a point is reached at which there is an average of one cross-link per molecule. As this stage is approached there is a considerable rise in viscosity and the state of the polymer approaches that of a gel, having the property of elastic recovery from deformation. The present series of experiments was performed employing a "Tecam" gelation timer and associated digital display unit produced by Techne (Cambridge) Ltd and giving results with an accuracy of $\pm 2\%$. The procedure adopted was to bring the temperature of a 100 g sample of resin to the required value by standing the containing cup in a pre-adjusted Tamson TXV40 constant temperature bath for approximately 15 min. The sample was then removed briefly for the addition of

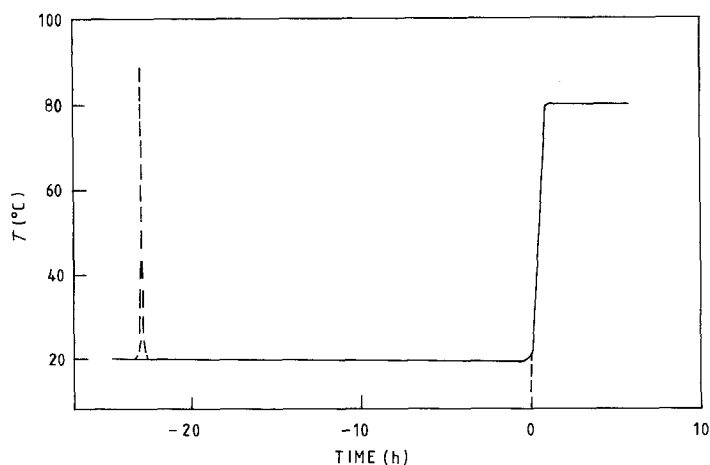


Figure 3 The progress of the early stages of the cure of Derakane 470-36/MEKP resin, referred to the same zero of time as employed in Fig. 2, showing the exothermal temperature. (---) Resin temperature, (—) bath temperature.

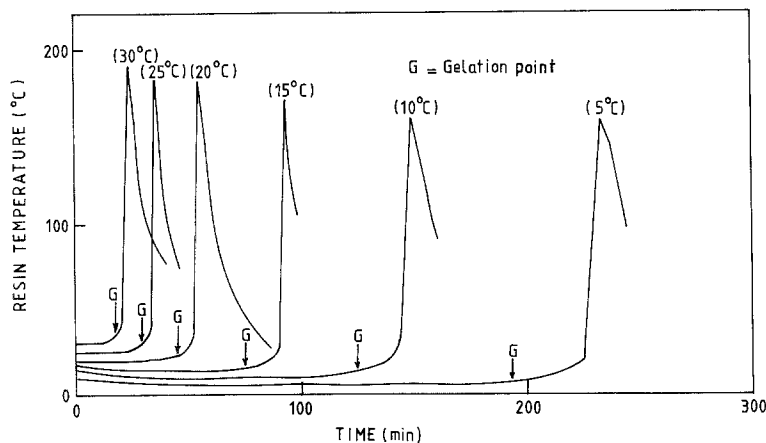


Figure 4 The influence of the curing temperature, shown in parentheses, upon the time into the cycle at which gelation and the exothermic reaction occurred in a 100g mass of Derakane 470-36/MEKP resin.

the curing agents, returned to the bath, the gelation timer plunger and the chromel-alumel thermocouple were inserted and timing commenced.

It is clear from the results of this investigation, summarized in Fig. 4, that gelation always preceded the exothermic reaction. In fact examination revealed that the gelation time, t_g , and the starting temperature, $T(K)$, were related by an empirical equation of the form $t_g = a \exp(b/T)$, while an equation of the same form related the time to the exothermic peak and the starting temperature. The results of subsidiary experiments revealed that the peak temperature achieved in the exothermic reaction increased with the mass of the resin specimen but that a seven-fold increase of specimen mass, from 25 to 175 g, reduced the time to the exothermic peak by only 7 min in 47.

3.3. Viscosity

The viscosity and gel time determine to an important degree the quality of the final composite. This is of particular importance because of the increasingly widespread use of high-performance reinforced plastics in aerospace applications, requiring products of consistently high quality. The emphasis is upon the absence of voids. Sources of voids are commonly either the evolution of gases from retained solvent or trapped air. The former is relevant in the case of a laminate produced using prepreg and may be minimized by the manufacturer. The latter can be reduced to a minimum by careful handling and lay up. A third source is the inability of the resin to always completely fill the spaces between the fibres. Two critical factors

must be considered during the cure:

(i) resin flow out of a laminate (bleed), which depends upon a number of factors such as temperature (a high-temperature cure inevitably produces a marked fall in viscosity) and the pressure applied for consolidation;

(ii) the gel time, which essentially defines the limit beyond which the resin is mechanically unworkable. This point is preceded by a rapid increase in resin viscosity.

If too much resin flows out, voids may result from a resin deficiency whereas after gelation it is too late for mechanical consolidation. This introduces the concept of an optimum time or period during the cure cycle for the application of pressure to give an optimum resin content and degree of consolidation. Against this background it was decided to monitor the variation of viscosity during cure.

Measurements were made using a Ferranti-Shirley cone and plate rotational viscometer, which employed a specimen of volume 0.5 ml. The results were reproducible from run to run, the relationship between shear rate and shear stress displaying a hysteresis effect which is typical of thixotropic materials. The results were used to define an apparent viscosity, the dependence of which upon time was governed by the temperature. Not surprisingly, experience showed that detailed features of the results were influenced by the age of the resin. The results displayed in Fig. 5, which were obtained using fresh resin, correlated well with the results displayed in Fig. 4. In particular the gel points proved to be located in the regions where

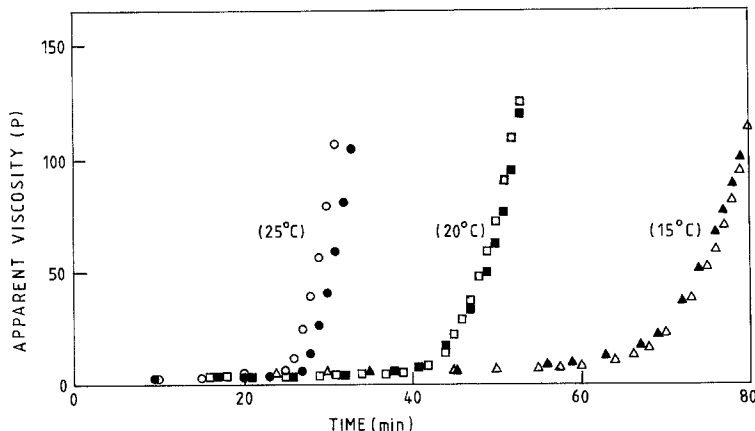


Figure 5 The influence of the curing temperature, shown in parentheses, upon the time dependence of the apparent viscosity of Derakane 470-36/MEKP resin.

TABLE I Results of mechanical tests

	Flexural strength (MPa)	Flexural modulus (10^3 MPa)	Tensile strength (MPa)	Tensile modulus (10^3 MPa)
Cycle 1				
Resin	127 ± 11	3.3 ₂ ± 0.1 ₁	36.0 ₉ ± 14.0 ₀	3.5 ₈ ± 0.3 ₇
Composite	255 ± 15	16.0 ₀ ± 0.6 ₈	163.0 ₇ ± 5.0 ₀	15.1 ₄ ± 0.8 ₇
Cycle 2				
Resin	113 ± 9	3.2 ₄ ± 0.0 ₈	48.0 ₂ ± 10.0 ₂	3.2 ₃ ± 0.1 ₃
Composite	263 ± 19	15.9 ₆ ± 1.0 ₇	187.0 ₁ ± 4.0 ₀	17.3 ₆ ± 0.9 ₄

viscosity was rising rapidly with time. Fig. 5 indicates that critical control is required over the temperature during the early stages of the cure cycle, if the tool is to be closed at the "correct" time required to produce consolidation in a composite component. The relatively small change in the time to the exothermic reaction produced by a large change in the mass of the resin specimen, reported in Section 3.2, suggests that monitoring the time dependence of the viscosity of a small sample of a batch of resin which is to be employed as the matrix of a composite component provides a helpful means of establishing the time at which pressure should be applied in consolidating the component, provided that the two operations are undertaken at the same temperature.

4. Preparation and properties of the solid resin and a composite containing it

It was explained earlier that observations of some of the physical properties of the resin system led the authors to question the length of the 24 h stage of the recommended cure cycle. It was further explained that a second cure cycle had been adopted, cycle 2, in which the post-cure of 6 h at 80°C was initiated immediately after the exothermal peak. The present section forms an account of an investigation of the influence of the reduced cure time upon selected physical properties of specimens cut from plates produced according to the two cycles.

4.1. Preparation of resin and composite plates

Plates of resin required for flexural measurements were cast in a brass mould measuring 170 mm × 170 mm × 4 mm. To facilitate easy removal of the plate, all faces of the mould were separable. Resin was poured into the mould when this was inclined at an angle of about 20° to the vertical, after first being degassed for approximately 5 min, following mixing. The mould was then adjusted to an upright position and placed in a preheated air circulated oven, where the curing took place. When surfaces of cured plates of resin were not both flat over their complete area, specimens measuring 100 mm × 10 mm were cut from the good quality regions of the plate. The shaping of these was finished by hand, employing successively finer grades of emery paper to produce a good surface finish. Resin plates required for the production of specimens for tensile measurements were produced in a similar way to that described

above, except that a mould constructed from 4 mm thick mild steel, measuring 300 mm × 300 mm, was employed on this occasion. Specimens of resin measuring 200 mm × 20 mm were prepared for the tensile measurements; these were waisted to limit failure to a predetermined area well removed from stress concentrations caused by gripping the ends.

Plates of resin reinforced with woven glass cloth were produced with the aid of two flat rectangular aluminium sheets measuring 400 mm × 400 mm × 10 mm. Sheets of glass cloth (P6), cut to size, were laid up in the standard way, resin being applied to successive sheets which were then rolled to remove air bubbles. The top plate was put in position, pressure was applied to close down to stops at the appropriate stage of the cycle through which the assembly was then taken. In this, as in the previous productions, detailed attention was paid to the preparation of mould surfaces and appropriate release agents were employed to facilitate specimen removal. Composite test specimens were prepared in a similar manner to those employed for the resin specimens, specimens for flexural measurements this time measuring 120 mm × 10 mm × 2 mm and specimens for tensile measurements measuring 210 mm × 18.5 mm × 2 mm. The latter were waisted prior to testing, as before. In cutting plates to form specimens it was arranged for the weft direction of the weave to be parallel to the specimen length. During the course of subsequent density determinations it was established that the fibre volume fraction was 45%, the void content was well below 2% and the plates were acceptably uniform in composition over their entire area.

4.2. Mechanical measurements and results

Flexural measurements were conducted upon the resin specimens employing a three-point bending arrangement, attached to a Hounsfield Tensometer. Any specimens which broke outside the central third of the span were discarded and a minimum of five test pieces were used when quoting the averages of the results, which are collected in Table I. The tensile tests upon the resin specimens were undertaken with the aid of a Losenhausen UH6 hydraulic testing rig, fitted with a 0 to 5000 N load cell. Extension of the specimens was measured with the aid of strain gauges attached to them and, as with the specimens studied in the flexural mode of deformation, the results for specimens which failed outside the waisted region were disregarded. The results of the tensile tests are also collected in Table I. These are somewhat lower than anticipated,

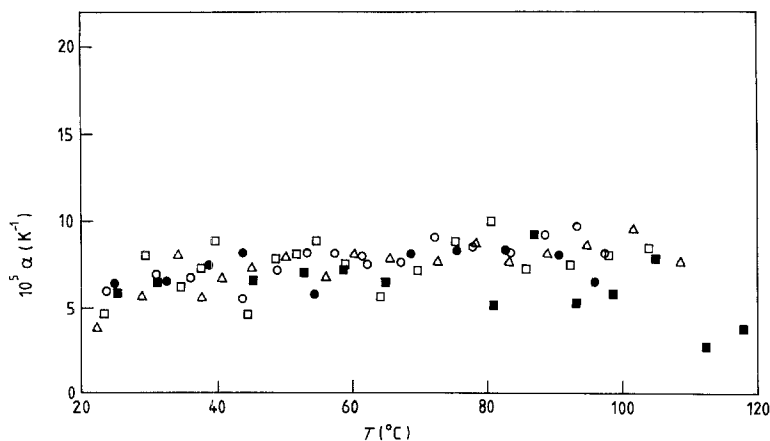


Figure 6 The linear thermal expansion coefficient, α , of Derakane 470-36/MEKP resin: cycle 1: (○) run 1, (□) run 2, (△) run 3; cycle 2: (●) run 1, (■) run 2.

but because the specimens were not cast individually in silicone rubber moulds they are probably more representative of values encountered in the everyday use of components containing the present resin than those produced for exhibition purposes. Tests were conducted upon the composite specimens in the same manner as for the resin specimens and the results of these tests too are collected in Table I. As expected, the strengths and moduli of the fibre-reinforced resin are higher than the corresponding values for the unreinforced resin.

The particularly striking feature of the results for corresponding specimens cured according to the two cycles is their similarity. It is just conceivable that the small reductions in flexural and tensile moduli of the resin, resulting from the reduced curing time of cycle 2, enhance the load transferring capacity of the resin to the fibres of the composite, the tensile strength and modulus of which display increases resulting from the reduced curing time. However, a disadvantage of tensile tests is that a specimen fails at its weakest point and to some extent the results of such tests provide a measure of specimen quality as well as reflecting a fundamental property of the material. The results of three-point bending tests provide an alternative measure of a material's deformation characteristics and the similarity of the flexural strengths and moduli of comparable specimens from the two cycles are probably more significant than small differences in the tensile results.

Failure of resin specimens in flexure was sudden, resulting in the production of several fragments in the region where the load was applied. An examination of photographs of the fracture surfaces of resin specimens which failed in tension, taken with a scanning electron microscope, revealed the existence of regular "tracks" radiating from a point on the specimen surface where failure commenced. These features are both characteristics of brittle materials. Most amorphous materials are brittle and any increase in the degree of ordering, manifested in the production of crystals, enables more deformation to occur before fracture. The present observations are consistent with expectation in this regard, because a high degree of crystallinity is unlikely to occur in a polymer such as Derakane 470-36 due to the lack of symmetry and the bulkiness of side groups of the polymer molecule.

4.3. Thermal expansion characteristics

Specimens for thermal expansion measurements were prepared by mixing 50 g Derakane resin in the manner described earlier and casting in a clean glass test tube, followed by the appropriate curing conditions. Owing to the fact that specimen mass and dimensions were known to have a significant effect upon gelation time and hence also upon time to exothermal peak temperature, a control sample was used, with the hot junction of a chromel/alumel thermocouple situated near its centre. This enabled the exothermal peak to be pinpointed, ensuring that the post-cure for cycle 2 commenced at the correct stage of cure. This method yielded cylindrical specimens of diameter 8 mm and length 57 mm. The thermocouple hot junction was accommodated within a hole drilled half way along the specimen length. Measurements were made using a dilatometer and procedure which have been described elsewhere [5, 6], after first observing the standardization procedure employing copper as the test substance. Because the results turned out to be somewhat higher than anticipated, additional measurements were undertaken, by way of a check, upon specimens prepared according to cycle 1 employing an upgraded form of a Fizeau interferometer dilatometer mentioned elsewhere [7]. These confirmed the correctness of the results taken with the first dilatometer, displayed in Fig. 6, from which it may be discerned:

(i) the linear thermal expansion coefficient, α , rises from approximately $66 \times 10^{-6} \text{K}^{-1}$ at 20°C to approximately $85 \times 10^{-6} \text{K}^{-1}$ at 100°C ;

(ii) the results are reproducible within experimental error from one cycle to another, provided the temperature is not taken too high;

(iii) there is some evidence of softening effects as α falls with increasing temperature beyond approximately 100°C ;

(iv) any differences between the thermal expansion characteristics of specimens prepared according to the two cycles fall within the limits of experimental uncertainty.

4.4. Density

Density provides a measurement from which the absolute value and consistency of the fibre volume fraction and void content of specimens may be monitored.

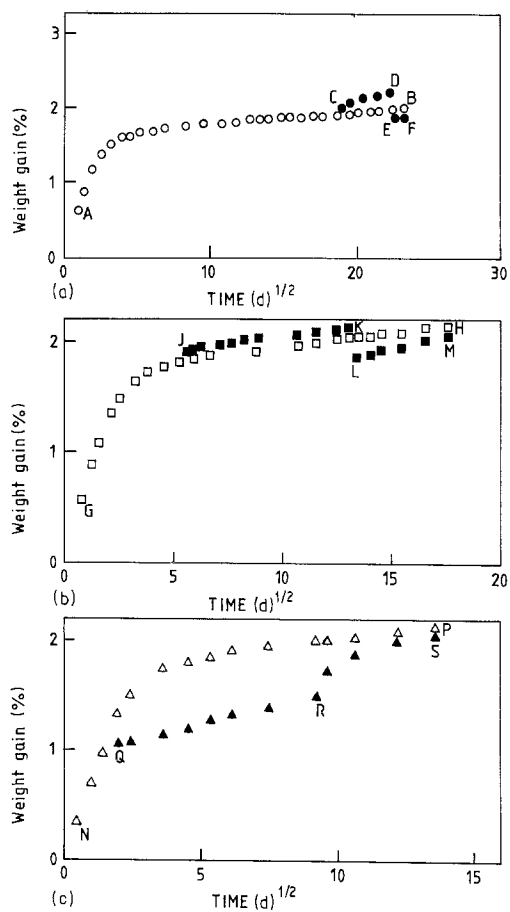


Figure 7 The "reverse thermal effect" displayed by specimens cured according to cycle 1 (primary data): (○) AB, (□) GH, (△) NP control specimens in water at 60°C; (a) (●) test specimens transferred to water at 5°C, (●) EF same test specimens returned to water at 60°C; (b) (■) JK test specimens transferred to water at 5°C, (■) LM same test specimens returned to water at 60°C; (c) (▲) QR test specimens transferred to water at 5°C, (▲) RS same test specimens returned to water at 60°C.

It also provides a means of detecting possible differences of structure between specimens of resin produced according to different cycles.

Specimens of resin were made by mixing 50 g of the constituents in the proportions described previously and casting into clean glass tubes of diameter 10 mm. The tubes were held at 20°C in a constant temperature bath and the temperature was monitored by means of chromel/alumel thermocouples inserted into the resin bulks. Immediately after the exothermal peak temperature had been reached, one tube was transferred to an oven set at 80°C for post cure. The second tube remained at 20°C, the post-cure commencing after a 24 h period had elapsed. The density of each specimen was first measured by weighing in air and distilled water. Surface tension effects proved to be troublesome at the level of precision required and the measurements were repeated employing the specific gravity bottle method, trapped air being removed from the distilled water by a vacuum pump. Consistent results were obtained from repeated measurements, giving a density of $1170 \pm 5 \text{ kg m}^{-3}$ for specimens produced according to cycles 1 and 2, i.e. no difference in density between specimens produced according to the two cycles could be detected.

4.5. Moisture absorption characteristics

During its service lifetime, a composite material consisting of an organic resin matrix reinforced with high-modulus fibres will absorb moisture from its surroundings. In all but exceptional cases this has a detrimental effect upon the physical properties of the composite, particularly at elevated temperatures, limiting the range of working conditions and the useful lifetime over which it might be used with confidence. Against this background it was decided to include moisture absorption characteristics among those physical properties which were open to influence from a change of cure cycle. Some of the main features of the moisture absorption process have been well documented from work conducted in these [8] and other [9] laboratories. For the purpose of the present investigation specimens of unreinforced resin measuring $30 \text{ mm} \times 20 \text{ mm} \times 3.5 \text{ mm}$ were prepared from plates cast in the manner described earlier. Specimens were cleaned using an organic solvent and any residual moisture was removed by drying in a desiccator containing silica gel at 60°C, until the weight became sensibly constant. Batches of four specimens, produced according to each of the two cycles, were subjected to humidities of 12%, 35%, 76%, 100% and some were completely immersed in water. Temperatures of 20 to 25, 40 and 60°C were selected for the study, and specimen weights were recorded at intervals over periods up to 12 months. The customary precautions were observed during the course of this investigation, diffusivities were calculated according to the scheme outlined by Shen and Springer [9], after applying appropriate corrections for edge effects, and maximum moisture contents were recorded. Diffusivities up to approximately $8 \times 10^8 \text{ mm}^2 \text{ sec}^{-1}$ were calculated and moisture levels up to approximately 2% were observed. The dependence of these parameters upon humidity and temperature followed well-established patterns and characteristics of behaviour observed elsewhere [10] were discerned in the present results. The "reverse thermal effect", reported by Adamson [11] and subsequently confirmed by others [8], was seen very clearly. Fig. 7 illustrates the dependence of the sense, i.e. increase or decrease, in which a discontinuous change in the rate of absorption depends upon: (i) the stage in the absorption process at which the temperature is changed suddenly and (ii) the direction in which it is changed.

The temperature dependence of the diffusivities, D , accorded with expectation based upon the theory of activated diffusion, conforming with the Arrhenius equation

$$D = D_0 e^{-E/RT}$$

in which D_0 is the permeability index, E is the activation energy for diffusion and the other terms have their usual meanings. This is illustrated by the graphs in Fig. 8, from which values for the permeability index and activation energy may be deduced. Results for specimens cured according to the two cycles may be seen to be very similar. The equilibrium moisture content was found to be relatively insensitive to temperature, but Fig. 9 shows a plot of equilibrium

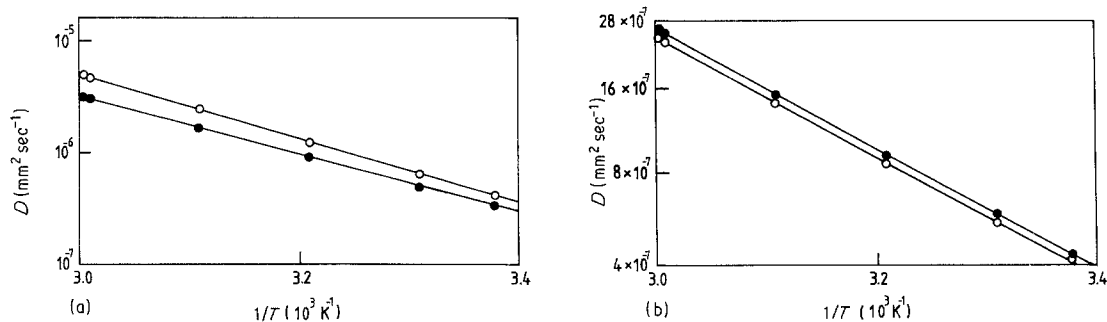


Figure 8 Representative results illustrating the temperature dependence of the diffusivities, D : (a) Specimens exposed to an atmosphere at a relative humidity of 12%, (○) cured according to cycle 1, (●) cured according to cycle 2; (b) Specimens exposed to an atmosphere at a relative humidity of 75%, (○) cured according to cycle 1, (●) cured according to cycle 2.

moisture content, M_m , against relative humidity, H , from which it is clear that these are related by an equation of the form

$$M_m = aH^b$$

where a and b are constants, which accords with earlier observations upon other systems (e.g. [5]). There is no consistent pattern of differential magnitudes of M_m , depending upon the cure cycle employed.

In concluding this account of the hygrothermal characteristics of the two sets of resin specimens it may be mentioned that a mass spectrographic analysis of water in which specimens had been immersed for some time provided evidence of some loss of organic matter from the resins. This point is mentioned for completeness, though it is not considered that the quantity involved was sufficiently large to have any significant effect upon any of the general conclusions which have been drawn.

5. Summary and conclusions

Employing volumetric changes during cure as a means by which structural changes within a resin system might be detected, the post-cure of one formulation of Derakane 470-36/MEKP resin was arranged to commence immediately after the occurrence of the exothermic reaction in the pre-cure. This contrasted with the procedure adopted in the recommended cycle for this resin system, the new cycle producing a reduction in overall cure time by some 75%. The most striking feature of the results of an evaluation of

a range of physical properties of resins produced according to the two cycles is their similarity. A more detailed examination has revealed some minor differences, an appraisal of which suggests that resin produced according to the shorter cycle is the more consolidated of the two. A comprehensive optimization of the curing cycle of a resin system, however desirable, would clearly present a very lengthy task. However, it is clear that modifications to cure cycles based upon observations of volume changes have the potential for reducing the manufacturing time of a product very substantially, without impairing its quality.

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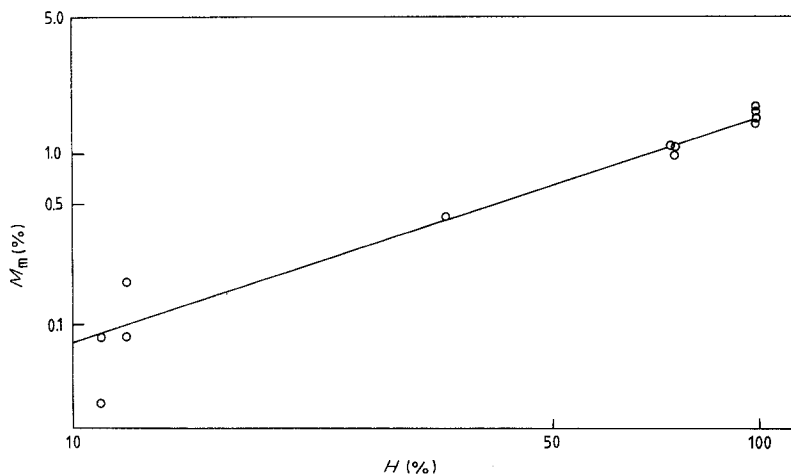


Figure 9 Graph illustrating the dependence of equilibrium moisture level, M_m , upon relative humidity, H .

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