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Curing characteristics of a composite matrix

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The account describes investigations into the variations of specific volume and viscosity of a typical high-performance epoxy resin during various time–temperature cycles. The work was undertaken primarily to provide additional background information relating to the nature and causes of "fibre kinking" which has been observed in laminates comprising epoxy–carbon composite. The investigation has quantified certain characteristics of the resin which are presumed to be major contributory factors in the occurrence of fibre kinking. It is concluded that a simple solution to the general problem cannot be identified, although some possibilities are discussed for individual cases.

1. Introduction

The origin of this investigation lies in the observation of "fibre kinks" which were first noted in carbon fibre–epoxy (CFRP) laminates manufactured by British Aerospace plc (Warton). The occurrence of this phenomenon does not appear to be restricted to a specific matrix/fibre type although for the purposes of this study a single system was investigated.

The kinks were only observed in the 0° plies of laminates in the 0°, +/−45° family but had proved to be significant in that they appeared to be the cause of considerable reductions in laminate strength. Full details of the phenomenon have been given elsewhere [1].

It was initially suggested that two aspects of material behaviour might prove to be critical for the formation of kinks in the fibres:

(i) the variation of density (resin shrinkage) during cure, and

(ii) the variation of resin viscosity during cure (with associated effects on the fibre–matrix interactions).

The investigation described was undertaken with a view to gaining information about both effects, in order to secure a better understanding of the formation of kinks and, if possible, to suggest methods of avoiding the problem.

2. Experimental details

2.1. Temperature–time-dependent volume changes

Volume thermal expansion measurements were made using the glass dilatometer shown in Fig. 1. The dilatometer consisted of a precision-bore capillary attached to a bulb with a threaded opening at the bottom. The opening was sealed with a Viton O-ring and a flat glass plate held in place by a silicone rubber washer and plastic screw cap. This arrangement was necessary to facilitate introduction of the resin into the bulb.

The principle of operation was to introduce a specimen of resin into the bulb via the opening at the bottom, to seal the bottom end, fill the system up to a fiduciary mark on the capillary tube with silicone fluid and support the assembly in a bath containing silicone fluid. This rather complex arrangement was necessitated by the high viscosity of the resin, which prevented its introduction via the capillary. Varying the temperature of the bath appropriately allowed the specimen of resin to be taken through a curing cycle. The bath was provided with a window through which the liquid level in the capillary tube could be monitored using a travelling microscope which read to 0.01 mm. A thermocouple was positioned adjacent to the dilatometer in the bath fluid. It was not conveniently possible to introduce a thermocouple into the dilatometer during the investigation of the resin, because the thermocouple would have displaced an unknown volume of fluid. The temperature gradient across the dilatometer wall was determined in a separate experiment. This depended upon the heat-up rate and allowance was made for it in the subsequent calculations.

The measurements were preceded by first calibrating the dilatometer with mercury, and then taking it through a similar temperature excursion in which it contained silicone fluid only. This allowed the volume change of the resin to be calculated during the progress of the curing cycle. In order to avoid any trapped air, the dilatometer was always filled under vacuum.

2.1.1. Preparatory work

Dilatometers were chemically cleaned prior to use, and before experiments could be undertaken it had to be established that there was no significant chemical reaction between silicone fluid and resin over the

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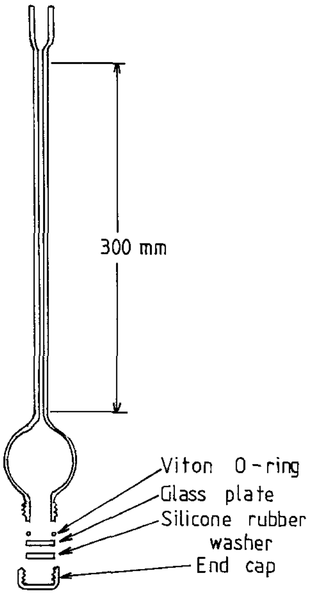

Figure 1 The dilatometer.

temperature range of the experiments. This was achieved in a subsidiary experiment, by immersing a sample of resin in silicone fluid and taking it through the curing cycle. The sample was observed to gain in weight by 0.6%. No obvious chemical reaction took place and the influence of such a gain in weight, which probably had a physical rather than chemical origin, was not considered to be sufficiently serious to merit a radical change of method from that planned and described. Heating a sample of resin through the curing cycle in an oven, in a further subsidiary experiment, resulted in a weight loss of approximately 0.6%. This was attributed to a loss of volatiles and in the light of this result samples were pumped for 36 h at 40° C before being cycled.

By way of a further precaution, the uniformity of the capillary bore was checked at the outset to each experiment. The dilatometer was rigorously tested for the development of leaks during excursions through simulated curing cycles in the early stages and a leak-tight system was finally achieved by employing the combination of a Viton O-ring and silicone rubber washer, which compensated for the effects of differential thermal expansion of the components. Taking account of the various experimental uncertainties it was concluded that the reduced volume V/V_r of a specimen, where V is the volume at temperature T and V_r is the volume at some reference temperature, could be determined to 0.2%. Taking account of the weight changes described above, the results taken during the course of an experiment should be reliable in an absolute sense to between 1 and 2%, and in a comparative sense over restricted ranges of temperature to better than this.

2.2. Temperature–time-dependent viscosity changes

Viscosity measurements were made on a Ferranti–Shirley cone and plate viscometer. A controlled temperature bath supplied oil to the sample plate and enabled viscosity to be measured either with increasing temperature or isothermally. Machine constants were verified using standard oils prior to embarking upon the investigations.

TABLE I The curing cycles

Cycle No.	Details
1	Raise temperature from 55° C to 175° C at a rate of approximately 2 deg min^{-1}. Dwell at 175° C for 1 h. Cool to 55° C at a rate less than 4 deg min^{-1}.
2	Raise temperature from 55° C to 120° C at a rate of approximately 2 deg min^{-1}. Dwell at 120° C for 3 h. Raise temperature from 120° C to 175° C at a rate of approximately 2 deg min^{-1}. Dwell at 175° C for 1 h. Cool to 55° C at a rate less than 4 deg min^{-1}.
3	Raise temperature from 55° C to 120° C at a rate of approximately 0.4 deg min^{-1}. Dwell at 120° C for 2 h. Raise temperature from 120° C to 135° C at a rate of approximately 0.4 deg min^{-1}. Dwell at 135° C for 1 h. Raise temperature from 135° C to 175° C at a rate of approximately 0.4 deg min^{-1}. Dwell at 175° C for 1 h. Cool to 55° C at a rate less than 4 deg min^{-1}.
4	Raise temperature from 55° C to 120° C at a rate of approximately 2 deg min^{-1}. Dwell at 120° C for 3 h. Raise temperature from 120° C to 175° C at a rate of approximately 2 deg min^{-1}. Dwell at 175° C for 1 h. Cool to 55° C at a rate less than 4 deg min^{-1}.
5	Raise temperature at a rate of approximately 0.35 deg min^{-1} to a temperature of 140° C (see text for further details).

3. Results

The original intention was to measure changes of resin density and viscosity over the same cure cycles as those employed in curing composite panels. However, since catastrophic exothermal reactions sometimes occur when the resin cures it proved to be necessary to work through a variety of programmes, in which there was some common ground with composite curing cycles.

3.1. Temperature–time-dependent volume changes

The complete programme of cycles contemplated for the volumetric work using pure resin is collected in Table I. Because of runaway exothermal reactions which occurred during the early stages of the investigation, an attempt was made to undertake volumetric measurements using prepreg, in which it was hoped that the carbon fibres would act as a heat sink. Problems associated with the evaporation of volatiles caused experimental difficulties and the complications associated with the derivation of fundamental information concerning the resin from the results, which was relevant to an understanding of fibre kinking, led to the abandonment of this approach. Comments upon the progress made with the cycles employed with the pure resin are collected below.

3.1.1. Cycle 1

A catastrophic exothermal reaction occurred at a temperature of 150° C, preventing further observations.

3.1.2. Cycle 2

Although this cycle is employed in composite

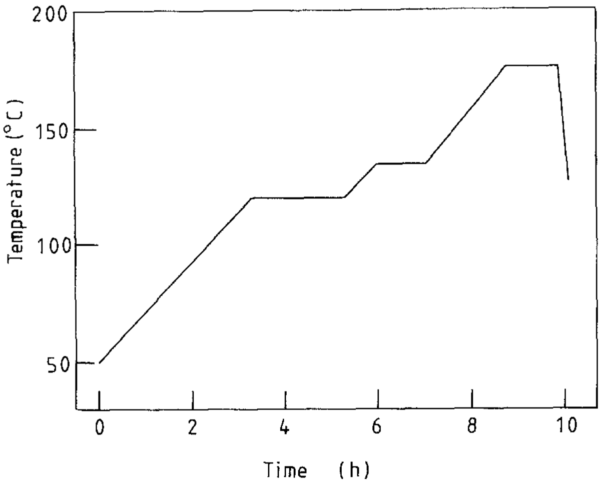

Figure 2 Cycle 3.

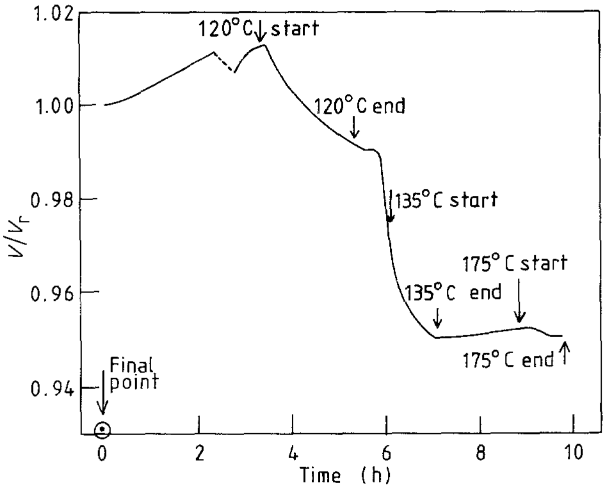

Figure 3 The time dependence of the reduced volume during Cycle 3.

fabrication, it was not pursued in the context of the present programme because of the experience described in Section 3.1.1.

3.1.3. Cycle 3

Employing Cycle 3, illustrated in Fig. 2, the time-dependent values of V/V_r shown in Fig. 3 were evaluated. Fig. 4 shows a corresponding plot against temperature in which the final volume was calculated from a knowledge of the thermal expansion characteristics of the resin deduced by Parker *et al.* [2]. Expansion was observed up to 120° C, immediately before which there was a small contraction. Bubbles were observed to be evolved from the resin and the contraction may be associated with this expulsion of gas. A significant contraction occurred during the dwell at 120° C and this was followed by an even larger contraction as the temperature was raised to 135° C. Presumably the bulk of the crosslinking was occurring over this region. The rise to 175° C was accompanied by a small expansion, implying that most of the crosslinking had occurred, and this seemed to be confirmed by the small contraction which occurred during the dwell at 175° C.

3.1.4. Cycle 4

Employing Cycle 4, illustrated in Fig. 5, resulted in the observations which are recorded in Figs 6 and 7. The lower part of Fig. 7 was calculated from thermal expansion results for the solid resin reported earlier [2], in the same way as the lower part of Fig. 4. This cycle is of particular interest since, apart from the exclusion of variations in the pressure applied to the specimen in a particular sequence within the cycle, it resembles one of the cure cycles employed in the manufacture of composite panels from the prepreg. During the rise of temperature to 120° C gas was released, and this may be the cause of the irregular shape of the initial part of the curve shown in Fig. 7. Gas continued to be produced during the dwell at 120° C. It is noticeable that the contraction during the 175° C dwell was considerably greater in Cycle 4 than it was is Cycle 3. Bearing in mind that the heat treatment preceding the 175° C dwell was more extensive in Cycle 3 than it was in Cycle 4, the resin was presumably more completely cured in the former case before entering the 175° C dwell. Related to these observations it is interesting to contrast the shapes of the curves in the 120° C and 175° C regions. In the 120° C case the rate of volume diminution increases with the passage of time. This may be partly because the centres from which crosslinking is initiated are increasing in number, but partly because of the gas which was expelled during the 120° C dwell. In the 175° C region, however, the shape is concave upwards in the manner observed in other resin systems [3], suggesting that the

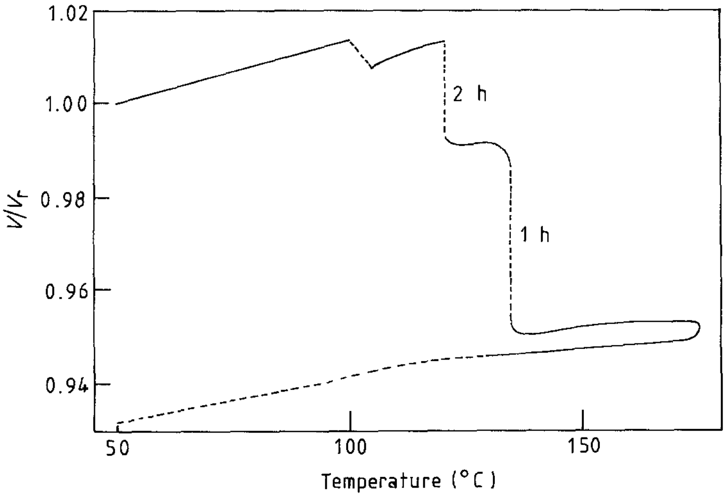

Figure 4 The temperature dependence of the reduced volume during Cycle 3. The lower part of this graph was calculated from the earlier thermal expansion results of Parker *et al.* [2].

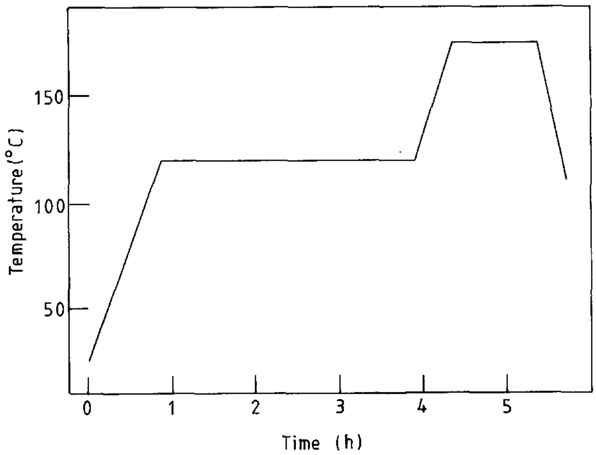

Figure 5 Cycle 4.

rate of formation of crosslinks was diminishing as the curing advanced. It is also noticeable that the overall volume contraction in Cycle 3 was somewhat greater than that in Cycle 4. Associating this contraction with the more extensive heat treatment leads one to conjecture that the product from Cycle 3 was probably more completely cured than that resulting from Cycle 4.

3.1.5. Cycle 5

In an attempt to evolve a programme in which the resin might be cured without suffering any shrinkage, the temperature was raised at the rate of 0.35 deg min^{-1} without interruption. The results of this treatment are displayed in Figs 8 and 9. During the heat-up phase large bubbles were observed to emerge from the resin. The greatest evolution of gas occurred at 60° C and the result was a drop in the liquid level in the capillary. The later stages of heating proceeded without further visible evolution of gas. At approximately 140° C a catastrophic exothermal reaction occurred, preventing further observations.

3.2. Temperature–time-dependent viscosity changes

At room temperature the viscosity of the resin was too high to be measured with the viscometer. As the temperature was raised the resin flowed and the viscosity first fell with increasing time and temperature, as shown in Figs 10 and 11. As the curing process advanced, the number of crosslinks apparently increased and the viscosity rose above a temperature around 140° C, until it finally reached a level beyond the range of the instrument. A comparison of the results of a second exploratory run, displayed in Figs 12 and 13, shows that by increasing the rate of rise of temperature the broad features of the variation are preserved, but corresponding qualitative features appear in shorter times. On the other hand the viscosities at corresponding temperatures are higher in the advanced stages of the slower cycle than in the cycle corresponding to Figs 12 and 13, presumably because of the more advanced state of the cure. Figs 14 and 15 refer to a cycle in which the influence of a dwell time of 1 h at 120° C may be seen very clearly. The increasing viscosity over this hour presumably results from the growing number of crosslinks.

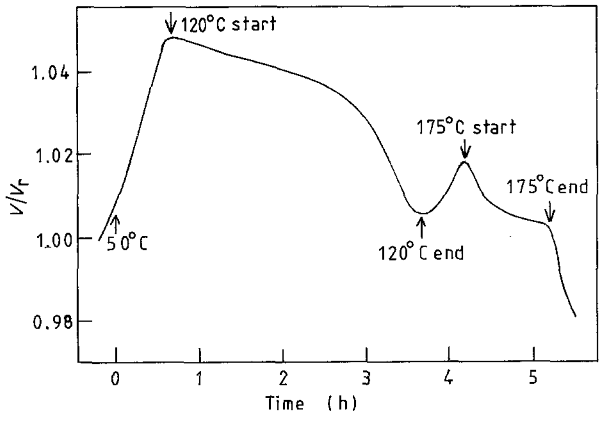

Figure 6 The time dependence of the reduced volume during Cycle 4.

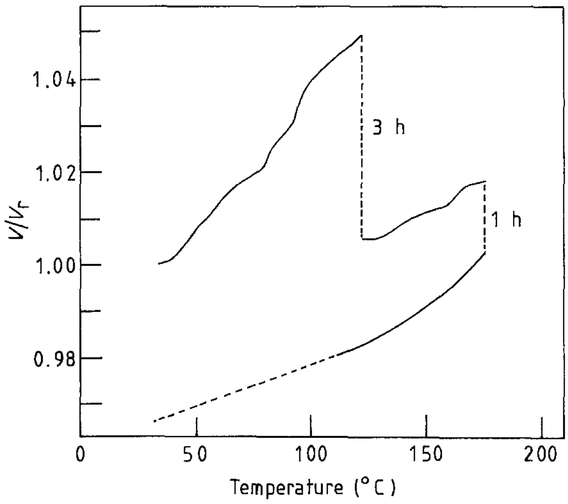

Figure 7 The temperature dependence of the reduced volume during Cycle 4. The lower part of this graph was calculated from the earlier thermal expansion results of Parker *et al.* [2].

The results displayed in Figs 16 and 17 are particularly interesting because the temperature–time sequence is closely similar to the early stages of Cycle 4 which, as explained earlier, corresponds to a cycle employed in curing the composite, apart from the absence of a sequence of pressure changes. Comparing these results with those displayed in Figs 6 and 7, which refer to the volumetric results for Cycle 4, one

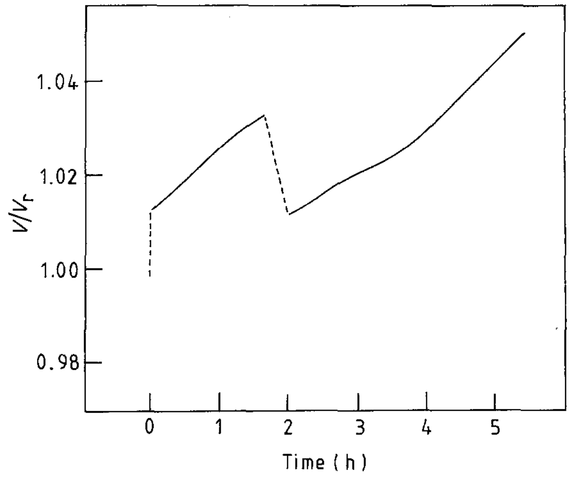

Figure 8 The time dependence of the reduced volume during Cycle 5.

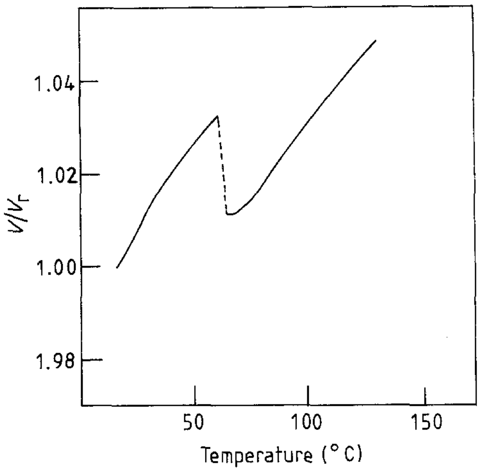

Figure 9 The temperature dependence of the reduced volume during Cycle 5.

may observe that the rise of temperature to 120° C was accompanied by an increase in the volume of the resin and by a fall in its viscosity. During the 120° C dwell the viscosity rose essentially linearly on the logarithmic plot of Fig. 16, which corresponds to an increasingly rapid increase in viscosity with time as the dwell proceeded. This is consistent with the increasing rate of fall of volume with time shown in Fig. 6 and is presumably associated with an increase in the rate of crosslink formation. Further heating to 175° C caused an increase in viscosity as the curing advanced.

4. Discussion

The investigation has served to highlight the mechanisms which appear to dominate the processes which occur within the resin at different stages of its thermal history. As the temperature is raised from ambient the resulting thermal expansion is accompanied by a fall in viscosity, which is presumably caused principally by the enhanced thermal vibrations of the molecules. The predominant process in this heat-up region is therefore essentially physical. During the dwell at 120° C the hardener and monomer begin to react and cause the formation of crosslinks.

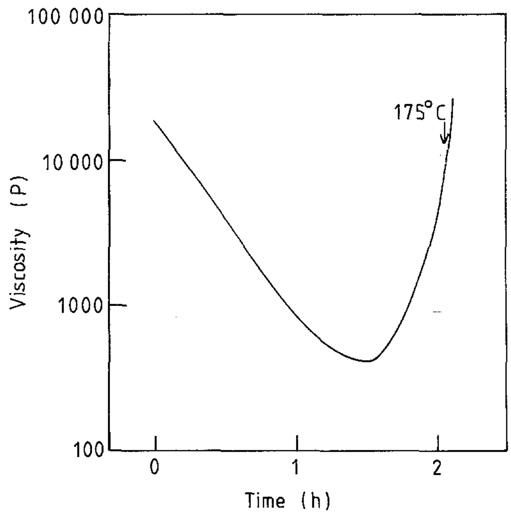

Figure 10 The variation of viscosity with time during Exploratory Temperature Excursion 1. 1P = 0.1 Pa sec.

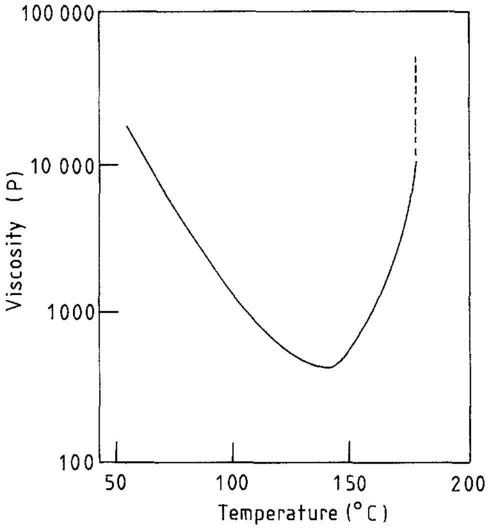

Figure 11 The variation of viscosity with temperature during Exploratory Temperature Excursion 1. 1P = 0.1 Pa sec.

Associated with this process there is a reduction of volume and an increase in viscosity, which corresponds to the reduced mobility of the larger molecules. During these first two stages of a cycle experience shows that there is a tendency for volatiles to leave the resin in the form of gas. As time proceeds and the temperature is raised further, the rate of reaction increases and a catastrophic exothermal reaction may occur and destroy the product. Indeed, as explained earlier, it was this experience that led to the slow initial heat-up rate adopted in Cycle 3 [4]. A comparison of Figs 4 and 7 indicates that it is possible to change the temperature at which the majority of the volume reduction takes place by altering the cure cycle. Whereas Figs 11, 13, 15 and 17 indicate that the viscosity seems to be less influenced by variations in the cure cycle, a dramatic rise occurs at approximately 175° C each time for the cycles investigated here. This observation should be qualified by noting that the viscosity is plotted on a logarithmic scale and large variations of viscosity are taking place at lower temperatures. Also it is not known in what range of

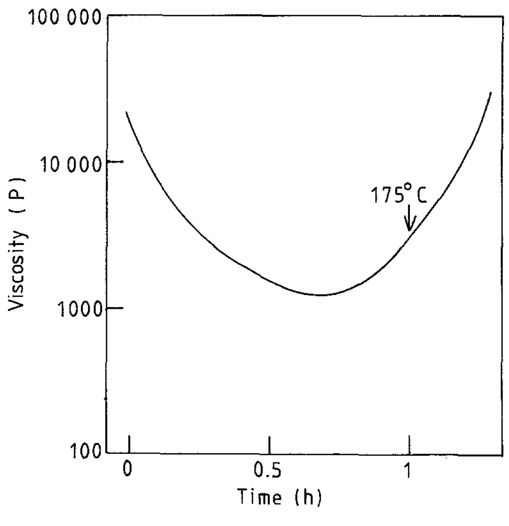

Figure 12 The variation of viscosity with time during Exploratory Temperature Excursion 2. 1P = 0.1 Pa sec.

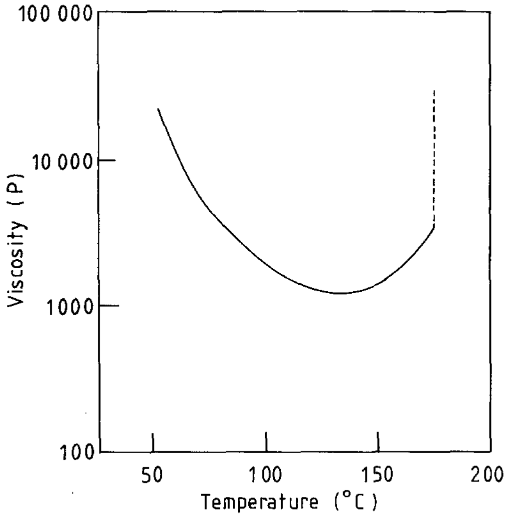

Figure 13 The variation of viscosity with temperature during Exploratory Temperature Excursion 2. 1P = 0.1 Pa sec.

viscosity the resin is able to impart sufficient load into the fibres to cause a kink, while remaining sufficiently mobile to allow the kinks to form.

It is difficult to say when curing is complete on the basis of observations made in this investigation. Observations upon another resin system [5] have shown that the principal mechanical properties of resins are not always particularly sensitive to details of the state of cure. On the other hand, evidence of creep has been reported [6] in incompletely cured specimens of the resin. Perhaps the best conclusion to draw in this connection is that for many practical purposes curing is essentially complete after the second dwell of 1 h at 175° C (Cycle 4), while a post-cure at 190° C for 4 h produces a more stable product. The latter point is added for completeness, though it is not immediately relevant to the problem of fibre kinking, which is observed in specimens which have not been post-cured.

5. Conclusions

It is difficult to draw unambiguous conclusions concerning the formation of kinks in the fibres of composites from observations made during the course of the present investigation. However, it is possible to make some observations which are relevant to the problem and to suggest possible ways forward.

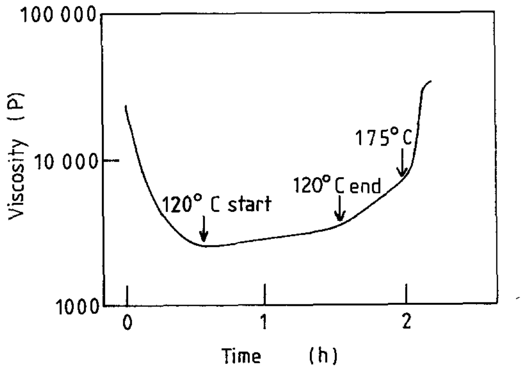

Figure 14 The variation of viscosity with time during Exploratory Temperature Excursion 3. 1P = 0.1 Pa sec.

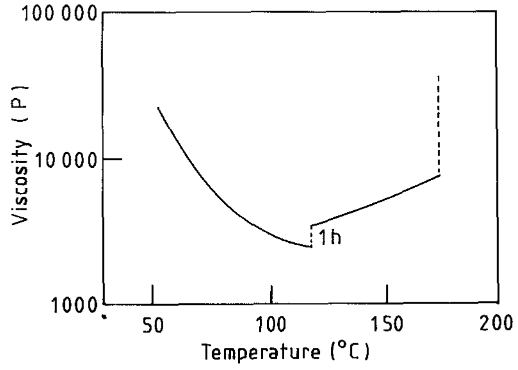

Figure 15 The variation of viscosity with temperature during Exploratory Temperature Excursion 3. 1P = 0.1 Pa sec.

Some earlier investigators have thought in terms of the resin matrix "locking on" to the fibres at some stage in the thermal history of the composite, beyond which stresses were presumed to arise due to the differential contraction of the components as the product cooled to ambient. The results of the present investigation have not contributed any further evidence for a unique point at which such a process might occur. It is implicit, however, that a fibre–matrix interaction must occur at some stage in the processing cycle although this must be sufficiently early for the resin to be "fluid". (It would be difficult to imagine how the matrix could accommodate the movement associated with the growth of a fibre kink if the matrix was in the solid cured state.) It seems realistic to consider the matrix becoming more viscous as the cure cycle advances, rather than changing phase at a unique point. During dwell periods the matrix contracts due to the density increase associated with the progress of the change of composition. A combination of these processes, coupled with an assumed associated improved adhesion between fibre and matrix, will undoubtedly produce a strain within the fibres. Movements in the matrix perpendicular to the fibre axis might be accommodated simply by translation of the fibre positions, but in the fibre direction longitudinal strains will develop within the filaments. The compressive strains resulting from net contractions of the matrix resin may, under certain circumstances, be relieved by local areas of filament buckling. The geometry of the (0°, +/−45°) lay-up, coupled with the application of pressure perpendicular to the faces

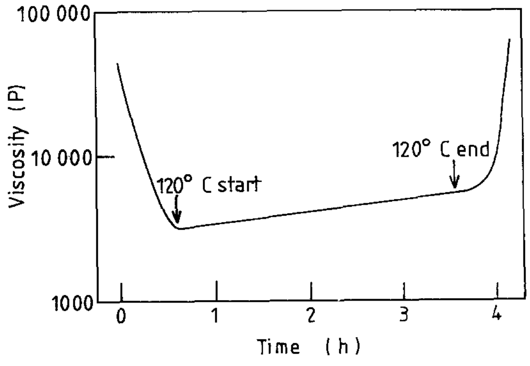

Figure 16 The variation of viscosity with time during the early stages of Cycle 4. 1P = 0.1 Pa sec.

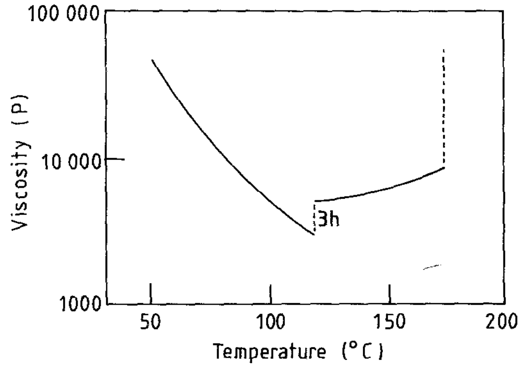

Figure 17 The variation of viscosity with temperature during the early stages of Cycle 4. 1P = 0.1 Pa sec.

of a panel during its fabrication, favours the above sequence of events. It is not difficult to envisage bodily movements of the +/−45° fibres which would allow the resin contraction to be accommodated; indeed, attention has been drawn to the related shearing movements of fibres in cross-plies resulting from thermal expansion [7]. It is also clear that the panel dimension in the fibre direction must exceed a certain minimum value for kinks to occur, since the smaller overall deformations developed in shorter panels may be sustained by the fibres without buckling. Such a minimum dimension has already been identified [1].

The resin liberates a large quantity of heat when it cures, which raises its temperature and accelerates the curing process. It is possible that some regions of a panel cure more rapidly than others, because of local variations in fibre/resin ratio which arise from the use of tows of fibres in the production of composites. Consequently there may be some relatively rigid regions which are contracting and imposing stress on the fibres, whilst other regions are still fluid enough to allow fibre buckling to occur. Clearly the details of the kinking process will be governed by factors such as fibre modulus in relation to resin modulus, fibre volume fraction, fibre diameter and the temperature dependences of the resin viscosity and specific volume, to name but a few.

Currently the solution to the problem is limited to avoiding those lay-ups and aspect ratios which theory suggests and practice have proved to result in the formation of kinks. It would appear from the initial theory [1] that the inclusion of as little as 5% of 90° plies within a lay-up should be sufficient to constrain the deformations which lead to kink formation in epoxy-based systems; however, this leads to a reduction in the performance of the composite. As kinks are only found in the 0° plies in the 0, +/−45° family of laminates, the use of 0° plies on the outside of the lay-up facilitates the non-destructive detection of fibre kinks. This is not possible when the 0° layers are within the laminate, a condition which is frequently required by design practice.

In the longer term further development may offer possible solutions based upon cure cycles in which the bulk of the resin contraction occurs when the viscosity is low, so that fibre–matrix shear conditions are not conducive to kink formation. It is doubtful whether the length of such a cycle would be commercially acceptable. However, it may be possible to develop low-temperature catalysts in order to reduce the length of the curing cycle.

Realistically, it is doubtful whether a simple and universal solution to the kinking problem will be found in the short term. In some instances the occurrence of kinks (and the associated strength reduction) could be considered as an intrinsic material property. It seems likely that other solutions will be established for individual cases by trading off one physical property against another. A long-term general solution might finally emerge from combined efforts within science, engineering and design.

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