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# The absorption of fluids by reinforced and unreinforced resins

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Increases of mass resulting from the absorption of water by a series of plastic laminates reinforced by carbon fibres in woven and unwoven form are reported. The influence of temperature over the range 20 to 60° C and relative humidity over the range 12 to 100% have been studied. Particular attention was paid to the relative magnitudes of absorption through the edges and faces of laminates. Diffusivity corresponding to absorption through the former proved to be significantly higher than that in the out-of-plane direction. The existence of a "reverse thermal effect" has been confirmed and measurements were extended to related material systems and environments, from which a series of comparative observations have been recorded.

## 1. Introduction

The advantages of the high stiffness-to-weight and strength-to-weight ratios of plastics reinforced with carbon and other fibres have led to their increasingly wide use in the aerospace industry. The confidence which may be placed in the operation of components constructed from materials such as these depends upon the extent to which the influence of the environment upon their physical properties is known. The effects of temperature upon the dimensions of carbon fibre reinforced plastics (CFRP) have been studied at some length [1–7] and some of the principal factors governing the thermal expansion characteristics have been identified.

Another important feature of the environment which might be expected to influence the performance of a composite structure is the humidity of the atmosphere in which it operates. Aircraft have to operate in all weathers, when the temperature and humidity vary over wide ranges. The ability of resins and fibres to absorb liquids, particularly water, to varying degrees is known to affect their physical properties [8–10] and this has led to investigations of the absorption characteristics of various resins and composites. One form of CFRP which is finding increasing favour is that in which the fibres are present in the form of a woven fabric. Some of the thermal and mechanical properties of this form of CFRP have formed the subject of earlier investigations in this laboratory [6, 11] and material conforming to this composition has formed the subject around which the programme described in the following account was developed. The investigation was extended to include other materials and liquids which are of interest in the context of aircraft operation.

## 2. The specimens

A summary of the plates from which specimens were prepared is given in Table I. In order to produce Plate 1, carbon fibre cloth consisting of Courtaulds (Coventry) E/XAS fibre woven to a five-shaft satin weave was pre-impregnated with Fothergill and Harvey's (Littleborough) Code 69 resin to a level at which the fibres and resin made up equal parts by weight. Prior to assembly into panels, the cloth prepreg was kept at 90° C for 15 min in an air-circulated oven. After laying up the eight constituent layers of a panel in the standard manner, in which the directions of the warp and weft were alternated from layer to layer and the whole lay-up was symmetrical about the central plane, each side was covered with polytetrafluoroethylene-coated glass cloth and the panel was placed in a matched die steel mould at 140° C. The mould was closed to give constant pressure and maintained in this con-

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TABLE I The subjects of investigation

| Plate number | Fibre identity | Resin matrix | Fibre volume (%) |
|---|---|---|---|
| 1 | E/XAS carbon (Courtaulds) | Code 69 (Fothergill and Harvey) | 67 |
| 2 | HTS (Type II) carbon (Courtaulds) | Fibredux 914 (Ciba-Geigy) | 66 |
| 3 | Kevlar 49 (Du Pont) | DX210 (Shell) | 60 |
| 4 | – | Fibredux 914 (Ciba-Geigy) | 0 |
| 5 | – | Derakane 470/45 (Freeman) | 0 |

dition for 22 min. The temperature was then raised to 170° C and pressure was applied to the mould until it was fully closed, by which time the pressure was approximately 4 MPa. After a period of 2 h the panel was removed from the mould and post-cured at 175° C for 6 h. The mean of fibre volume fractions determined by acid digestion and by weighing and measuring was 67%.

Plate 2 was prepared from Ciba–Geigy pre-impregnated Courtaulds HTS (Type II) carbon fibre in the form of unidirectional prepreg, in which there were nominally $10^4$ fibres per tow. After 18 plies had been laid up in moulds, the resulting plate was placed in a sample bag inside an autoclave. The bag was evacuated and a pressure of 0.2 MPa was applied for 15 min. The plate was then heated to 130° C and left to dwell for 30 min. A pressure of 0.7 MPa was applied to the bag 15 min into the dwell time to remove all the air bubbles. The temperature was then raised to 170° C, at which the plate was cured for 1 h, after which it was allowed to cool to room temperature under pressure. The resulting plate, 2 mm thick, was finally post-cured at 190° C for 4 h.

The Kevlar fibre employed in the production of Plate 3 was held at a temperature of 101° C for 16 h in order to remove moisture before being pre-impregnated with resin. Sheets of prepreg were laid up in a ±45° array within a steel mould, rolling between the addition of successive layers to remove air and applying pressure at intervals to compact the assembly. The block of composite so formed was removed from the mould, which was then pre-heated to 170° C in a press. The temperature of the block was meanwhile raised to 130° C over a period of approximately 1 h in an air controlled oven, where it remained for a further 15 min before being transferred to the mould. The mould was next mounted in the heated press, where the block was cured under closing pressure at a temperature of 170° C over the following 80 min. The block was finally removed from the mould and post-cured for a further 3 h at 170° C.

The block of Fibredux 914 resin (Plate 4) was cured at 140° C for 1 h, followed by 1½ h at 150° C, after which it was post-cured at 190° C for 4 h.

The plate of vinyl ester resin Derakane 470/45 (Plate 5) was prepared according to the formulation of the manufacturers, Freeman Chemicals Ltd (Ellesmere Port), in which a brass mould was employed to produce a sheet from which specimens were subsequently cut.

Specimens employed in the absorption investigations were cut from the plates using diamond-impregnated disc saws. Specimens were generally in batches of four or five, the mean behaviour of a batch being taken as representative of the material. Dimensions varied from one material to another, but specimens were typically 25 mm square and 2 or 3 mm thick. An exception was made in the case of specimens prepared from Plate 3, which were cubic in shape. All the specimens were cleaned with an organic solvent in order to remove any traces of grease, and residual moisture was then removed at 60° C with the aid of a vacuum desiccator or by storing them for some time in the presence of silica gel at room temperature. In order to examine the differences of absorption characteristics in directions parallel and perpendicular to the planes containing the fibres, the faces of some specimens were coated with Apiezon vacuum wax, leaving only the edges exposed, while in others the edges were coated, leaving the faces exposed.

## 3. Experimental details

Table II summarizes the environments in which specimens were conditioned. Relative humidities between 0 and 100% were achieved with the aid of saturated salt solutions, the temperatures of which did not fluctuate by more than 3° C over the period of the experiment. Combinations of salts and humidities were chosen such that the relative humidity was essentially constant over wide ranges of temperature above and below the temperature of the experiment. Before being weighed at intervals, employing a microanalytical

TABLE II The specimens and their environments

| Plate number | Specimen batch designation | Exposed surfaces | Temperature (° C) | Environment (RH = relative humidity) |
|---|---|---|---|---|
| 1 | 1 | Faces | 20 to 25 | RH 12% |
| | 2 | Edges | 20 to 25 | RH 12% |
| | 3 | Faces and edges | 20 to 25 | RH 12% |
| | 4 | Faces | 20 to 25 | RH 76% |
| | 5 | Edges | 20 to 25 | RH 76% |
| | 6 | Faces and edges | 20 to 25 | RH 76% |
| | 7 | Faces | 20 to 25 | Immersed in water |
| | 8 | Edges | 20 to 25 | Immersed in water |
| | 9 | Faces and edges | 20 to 25 | Immersed in petrol |
| | 10 | Faces and edges | 20 to 25 | Immersed in lubricating oil |
| | 11 | Faces | 40 | Immersed in water |
| | 12 | Edges | 40 | Immersed in water |
| | 13 | Faces and edges | 60 | RH 12% |
| | 14 | Faces and edges | 60 | RH 76% |
| | 15 | Faces and edges | 60 | Immersed in water |
| 2 | 16 | Faces and edges | 60 | Immersed in water |
| 3 | 17 | Faces and edges | 20 to 25 | Immersed in water |
| 4 | 18 | Faces and edges | 60 | Immersed in water |
| 5 | 19 | Faces and edges | 60 | Immersed in water |

balance which gave results which were accurate to ± $2 \times 10^{-4}$ g, specimens were wiped with absorbent paper and allowed to dry in the air for approximately 5 min.

## 4. Results and discussions

The weight gains resulting from the exposures are summarized below. These allow one to identify some of the factors which play a significant role in governing the absorption characteristics, and they permit the derivation of time-dependent moisture concentration profiles.

### 4.1. Qualitative comparative observations

### *4.1.1. The influence of direction of entry*

Concentrating on absorption at room temperature, a comparison of the results for Specimens 1, 2 and 3 in Fig. 1 reveals that in the early stages of absorption the increase in mass in the case of Specimens 3 (all of whose faces and edges were exposed) was equal to the combined increase of mass displayed by specimens having either faces only or edges only exposed (Specimens 1 and 2 respectively). As time increases, moisture profiles resulting from entry via edges and faces may be

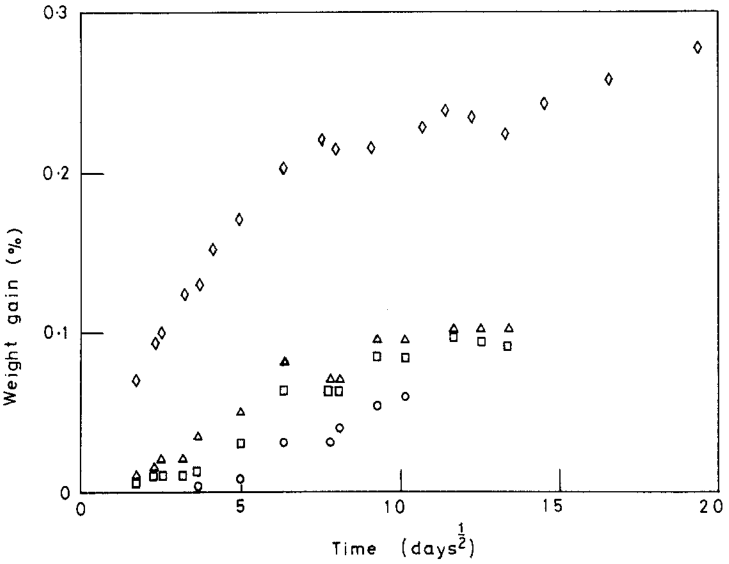

*Figure 1* The weight gain in specimens from Plate 1 resulting from exposure to an atmosphere with a relative humidity of 12%. □ Specimens 1, ○ Specimens 2, △ Specimens 3, ◇ Specimens 13.

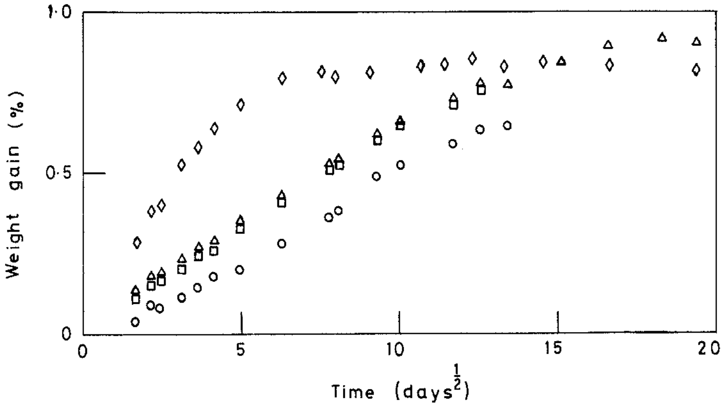

*Figure 2* The weight gain in specimens from Plate 1 resulting from exposure to an atmosphere with a relative humidity of 76%. □ Specimens 4, ○ Specimens 5, △ Specimens 6, ◇ Specimens 14.

expected to meet and, after a sufficiently long time, the results for Specimens 1, 2 and 3 would be expected to meet. Bearing in mind that the area of the faces is approximately five times that of the edges, it is clear from these results that in the early stages absorption per unit area through the edges is much greater than through the faces.

The above results correspond to absorption in an atmosphere having a relative humidity of 12%. Similar remarks apply to the results for Specimens 4, 5 and 6 shown in Fig. 2, where absorption occurred from an atmosphere having a relative humidity of 76%. Support for the relative magnitudes of absorption per unit area via faces and edges is provided by the results for Specimens 7 and 8, displayed in Fig. 3, which correspond to the case of complete immersion in water.

### *4.1.2. The influence of relative humidity*

Comparing the results for Specimens 1 (Fig. 1), 4 (Fig. 2) and 7 (Fig. 3), it is clear that the rate of absorption through the faces increases with the relative humidity of the environment until this takes the form of liquid water, when the rate of absorption falls. A comparison of the results for Specimens 2 (Fig. 1), 5 (Fig. 2) and 8 (Fig. 3) reveals the same trend for absorption through the edges.

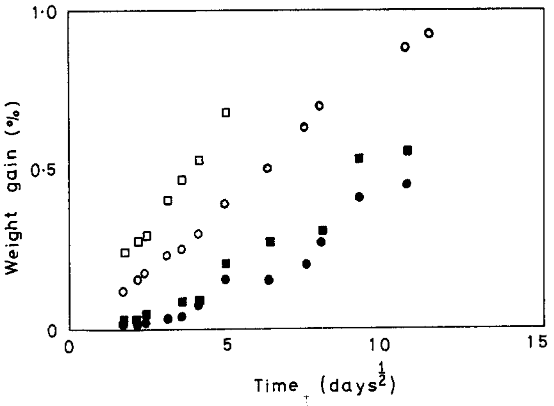

*Figure 3* The weight gain in specimens from Plate I resulting from immersion in water. ■ Specimens 7, ● Specimens 8, □ Specimens 11, ○ Specimens 12.

### *4.1.3. The influence of temperature*

The results discussed so far all refer to absorption at room temperature. Reference to Fig. 1 reveals that the rate of absorption at 60° C through the edges and faces of Specimens 13 was considerably greater than the rate of absorption through the edges and faces of ostensibly similar Specimens 3 at room temperature; both sets of specimens were conditioned in an atmosphere having a relative humidity of 12%. A comparison of the results for Specimens 14 with those for Specimens 6 (Fig. 2) leads to a similar observation when the absorption occurs in an atmosphere with the higher relative humidity of 76%. Turning attention to absorption in water, a comparison of the results for Specimens 7 with those for Specimens 11 and of those for Specimens 8 with those for Specimens 12 (Fig. 3) reveals that increasing the temperature of the water from room temperature to 40° C also leads to an increase in the rate of absorption.

### *4.1.4. The influence of liquid identity*

Alternative mechanisms are believed to exist whereby water molecules may enter resins [12]. These include the occupation of polymer-free volume by the absorbed water molecules, and the disruption of inter-chain hydrogen bonds followed by the formation of new hydrogen bonds between the water molecules and the resin and eventually by diffusion into high-density micelles. Limiting

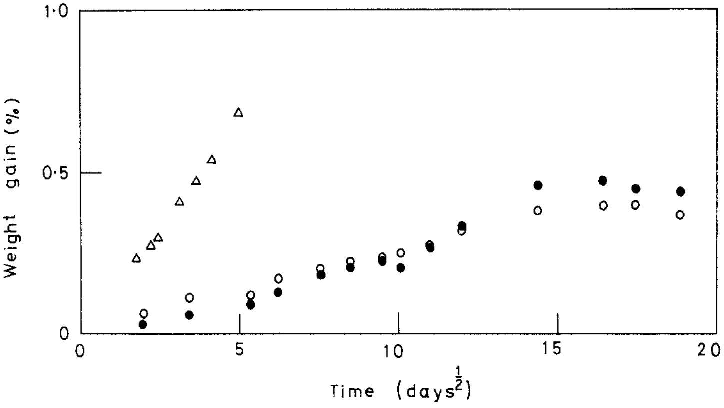

*Figure 4* The weight gain in specimens from Plate 1 resulting from immersion in different liquids at room temperature: △ Specimens 7, ● Specimens 9, ○ Specimens 10.

consideration to diffusion into regions of polymer-free volume, one might expect the efficiency of this process to be affected by molecular size. A comparison of the results for Specimens 7 on the one hand, referring to water molecules entering by the faces only at room temperature, with those for Specimens 9 and 10 on the other (Fig. 4) referring to petrol/oil molecules entering by faces and edges at the same temperature, indicates how much more readily the smaller molecules enter the resin.

### *4.1.5. The influence of composite matrix*

Assuming that the composite matrix is responsible for essentially all the absorption of water by CFRP, the susceptibilities of Code 69 and Fibredux 914 resins to water absorption may be compared employing the results for Plates 1 and 2, which contain almost identical fibre volume fractions. This comparison is made in Fig. 5, employing the results for Specimens 15 and 16 which were completely immersed at 60° C. It is clear that Fibredux 914 resin is more prone to absorb water than Code 69 resin.

### *4.1.6. Additional observations*

It is clear from a comparison of the results for Specimens 18 in Fig. 6 with those for Specimens 16 in Fig. 5 that the earlier statement (that essentially all the water absorbed by CFRP is taken up by the resin matrix) is correct. A comparison of the absorption characteristics of two resin matrices is made in Fig. 6, from which the greater tendency on the part of Fibredux 914 resin to absorb water, compared with the vinyl ester resin Derakane 470/45, is immediately apparent.

Specimens 17, which consist of Kevlar 49 fibre in a matrix of resin DX210, stand esstentially separate and the results for them are presented on their own in Fig. 7. Unlike carbon fibre, Kevlar shows a significant tendency to absorb water and this is reflected in the results for these specimens, which stand distinctly higher than the results for specimens 15 or 16 (Fig. 5), which consist of other typical epoxy resins reinforced with carbon fibre, albeit with somewhat higher fibre volume fractions and at the higher temperature of 60° C.

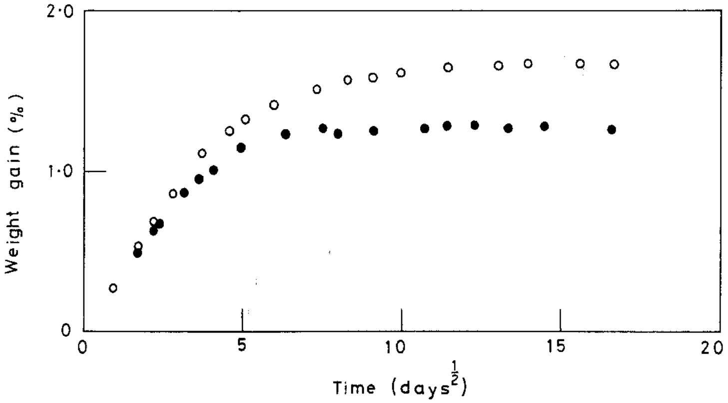

*Figure 5* The weight gain in CFRP specimens from Plates 1 and 2, resulting from immersion in water at 60° C: ● Specimens 15, ○ Specimens 16.

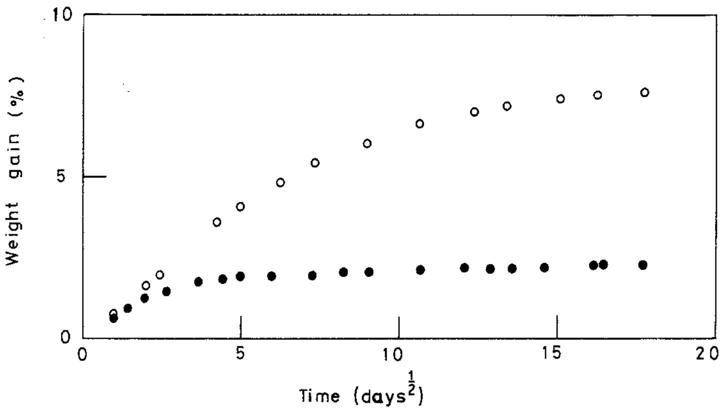

*Figure 6* The weight gain in resin specimens from Plates 4 and 5, resulting from immersion in water at 60° C: ○ Specimens 18, ● Specimens 19.

## 4.2. Variable-temperature absorption

It was shown in Section 4.1.3. that the rate of absorption of water by CFRP was increased by raising the temperature. The observations presented referred to absorption in the pre-saturation region and conformed with established ideas on the sub-

Adamson [12], dealing with the moisture-absorption characteristics of an epoxy resin (Hercules 3501) reported the existence of a "reverse thermal effect" in the saturation region. In a search for a similar effect in the vinyl ester resin Derakane 470/45, we concentrated attention on the five samples comprising Specimens 19, whose condition at the beginning of the experiment is represented by *A* in Fig. 8. When the moisture content had levelled off at around 2%, following immersion in water at 60° C for 64 days, two of the specimens were removed and transferred to water at room temperature (Point *B*). Reference to Fig. 8 will show how the reduction in temperature resulted in an increased capacity for water on the part of the specimens transferred. Returning these two specimens to the bath at 60° C after 80 days at room temperature (*C* to *D*) resulted in a fall of moisture content to a level below that in the three control specimens. With the passage of more time the moisture content rose again, finally approaching that of the control specimens some 60 days later (Point *E* ). In the explanation of his observations on Hercules 3501 resin Adamson [12] drew upon the work of Rehage and Borchard [13] to conclude that water might combine with a glassy polymer in the "frozen" state, that the "freeze-in" heat of the water was liberated, and that as a result the crosslinked mixed phase retained a structure requiring more space which could therefore absorb more water. The observations collected over the region *B*–*C* of the present investigation are in keeping with those of Adamson. Raising the temperature of the specimens back to 60° C presumably raised the amplitudes of atomic/molecular vibration and favoured internal structural modifications which resulted in the expulsion of water molecules, some of which were loosely bonded to resin molecules. The situation corresponding to Point *D* in Fig. 8 is clearly not one of equilibrium, which was slowly restored as Point *E* was approached.

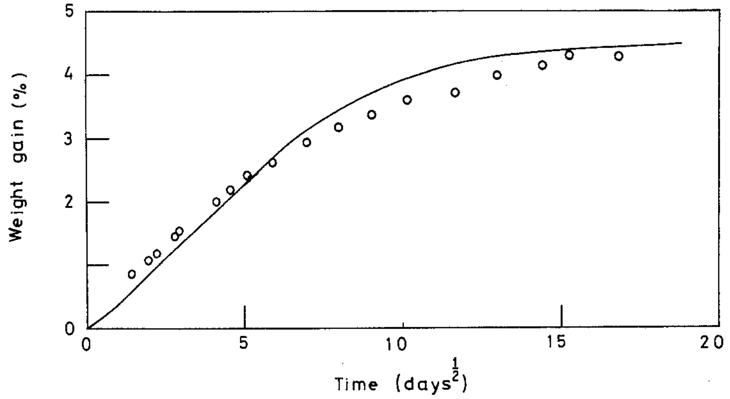

*Figure 7* The weight gain in Specimens 17 resulting from immersion in water at room temperature: ○ primary data, – calculated according to the model of Shen and Springer [14].

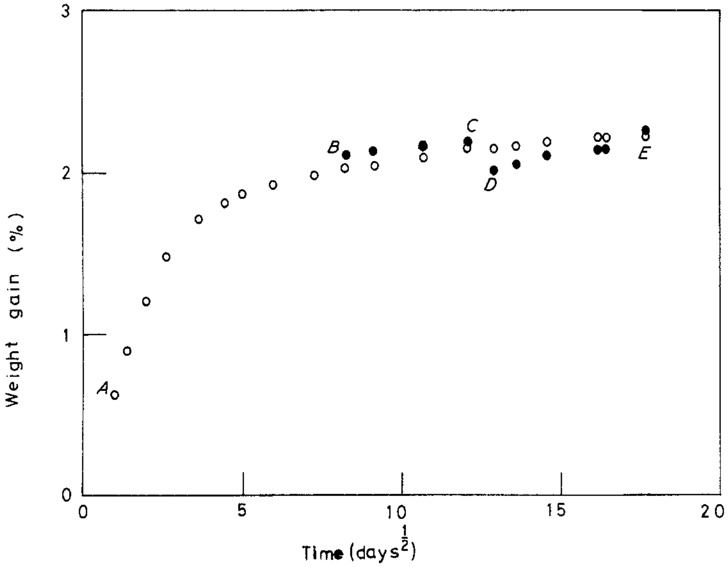

*Figure 8* The "reverse thermal effect" displayed by Specimens 19 (primary data): ○ control specimens in water at 60° C; ● (*B–C*) test specimens transferred to water at 20° C, (*D–E*) same test specimens returned to water at 60° C.

## 4.3. Quantitative comparative observations

After observing that the diffusivity varied very little with moisture content within a material, and that the temperature within a body might generally be taken to be constant, Shen and Springer [14] showed that the diffusion of a fluid into a body could be described by the equation

$$\frac{\partial c}{\partial t} = D_x \frac{\partial^2 c}{\partial x^2}$$

in which $c$ measures the moisture distribution at time $t$ and distance $x$ from the absorbing surface, and $D_x$ is the diffusivity in the $x$ direction.

The analytical technique developed by these authors has been applied to the results of the present investigation, from which the following comparative observations may be made:

1. The diffusivity in an "in-plane" direction is distinctly higher than that in a direction perpendicular to the faces of a composite specimen, i.e. perpendicular to the fibre axes. In the case of humid air the ratio is around 150:1, while in the case of water it is about 40:1.
2. The diffusivities of specimens having all faces exposed lie between values corresponding to "in-plane" and "out-of-plane" directions.
3. The diffusivities of like specimens are raised by increasing the temperature at which the absorption is taking place.
4. Values of the diffusivity and maximum water uptake of CFRP Fibredux 914C exceed those of corresponding CFRP specimens based upon a matrix of Code 69 resin.

In calculating the diffusivities from which conclusions 1 to 3 were drawn it was sometimes necessary to assume a value for the maximum moisture content $M_\mathrm{m}$, consistent with the analytical model employed. In doing this $M_\mathrm{m}$ was assumed to be independent of temperature.

Although the broad features of the present results conformed with expectations based upon the treatment of Shen and Springer [14] there were divergences of detail, and it would be unwise to attach undue significance to absolute numerical results emerging from the analysis. In Fig. 7, for example, the curve calculated according to the analytical treatment is plotted, from which systematic differences between observation and calculation are apparent. Close examination of the results also reveals that approximate proportionality between the rate of moisture uptake and the square root of time sets in after a "lead time" (during which absorption is very low) in specimens exposed to a low humidity at ambient temperature. In relation to the results emerging from the present account, therefore, the treatment has the standing of a useful working model on the basis of which moisture concentration profiles, activation energies, and other physical characteristics of composites and resins may be estimated [15, 16].

## 4.4. Fundamental considerations

Relative humidity provides a measure of the partial pressure of the water vapour in the environment, in terms of the partial pressure at saturation. The pressure applied to the surface of a specimen by water molecules in the atmosphere is governed by the product of the number of molecules striking unit area per second and the momentum communicated by each molecule. Keeping the temperature constant from one experiment to another will keep the momentum distribution of the water molecules constant. Thus, by increasing the partial pressure of the water in the environment while keeping the temperature constant, the rate at which water molecules bombard a specimen surface should be increased, without affecting the momentum distribution among the impinging molecules. On this basis, comparing relative humidities of 12 and 76% at room temperature, we expect the ratio of rates of bombardment to be $12/76 = 1/6.3$. This turns out to be closely similar to the ratio of slopes of the linear regions of the absorption curves for pairs of Specimens 3 and 6, 2 and 5, and 1 and 4 (Figs. 1 and 2) which to the nearest whole numbers are respectively 1/6, 1/7 and 1/7. This direct correspondence between the rate at which molecules are striking the specimen surface and the rate of their absorption presumably favours an explanation in terms of the physical accommodation of water molecules within the free volume of the resin, rather than one based upon the formation of chemical bonds, for this stage of the absorption process.

Comparing results for specimens which have been conditioned at different temperatures is fraught with complications associated with thermal expansion of the specimen. More generally, results of the application of kinetic theory to a humid atmosphere must be subject to reservations. However, using such indications as could be gleaned by employing these ideas, the results for appropriately selected specimens conditioned at 20 and 60° C did not lead to any obvious association of the rate of absorption with the momentum of the impinging molecules.

## 5. Conclusions

In common with the appraisal of a number of other properties of CFRP, observations of the extent to which experimental results concerning fluid absorption conform with the predictions of mathematical models must be qualified by recognizing the influence of structural imperfections in the specimens, deviations from ideality in experimental conditions, and approximations in the models themselves. The present investigation has served to extend earlier observations of the moisture absorption characteristics of resins reinforced with unwoven carbon fibres to the case of carbon fabric reinforced laminates. The work has established the relative importance of absorption through the edges and faces of laminates, and it has illustrated the variability of moisture absorption characteristics among a limited selection of composites and their matrices. An extension of observations such as these, coupled with a refinement of the mathematical analysis of them, may be expected to play a part in the development of purpose-built composites for specific applications.

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