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Environmental ageing of epoxy-based stereolithography parts. Part 1: moisture transport

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Environmental Ageing of Epoxy-Based Stereolithography Parts

Part 1: Moisture transport

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Abstract

It has been shown that current epoxy-based stereolithography materials are highly hygroscopic [1]. However, the diffusion of moisture into these materials and the effect this has on the mechanical performance of manufactured parts has not been thoroughly investigated to date. The first part of this paper will discuss the transport of moisture into representative stereolithography materials and the second part of the paper will describe the effect of the absorbed moisture on mechanical performance. Moisture transport in three different epoxy-based stereolithography materials has been investigated using mass uptake experiments. The results show that anomalous (non-Fickian) diffusion occurs to varying degrees in all three materials, the characteristic uptake appearing to be pseudo-Fickian. Anomalous uptake models based on dual-sorption [2], diffusion-relaxation [3] and a dual-Fickian model were all shown to provide an excellent fit to the data. The effects of relative humidity and sample thickness are also investigated in the paper.

Keywords: Stereolithography, Epoxy Resins, Diffusion, Modelling, Dual Fickian

1. Introduction

Rapid Prototyping (RP) is a group of technologies where physical parts are generated directly from 3-Dimensional Computer Aided Design (3D CAD) models by constructively building them in layers (i.e. additively) [4]. In the past few years, there has been an extended effort to adapt the additive approach to produce end-use parts. This is known as Rapid Manufacturing (RM). The term RM does not suggest that the parts themselves are produced rapidly, but that by using the additive approach straight from the 3D CAD model, the step from design to manufactured part is rapid. This is largely because the tooling used in conventional

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3 manufacturing doesn't need to be designed and manufactured.

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5 Current interest in the use of RP technologies for end-use part manufacture can be largely
6 attributed to the marked development of RP processes and materials in the past decade [5].
7 Despite this, no current RP technology can be truly considered as a manufacturing process as
8 several limitations still exist that impede their wider use as manufacturing systems. Therefore,
9 there is much work to be undertaken to convert the principles of additive manufacturing into
10 viable manufacturing techniques that can be exploited more universally [6]. One of the main
11 areas that needs further investigation is the development and understanding of the materials
12 that can be used in the process. Currently the material properties of parts made by RP
13 processes tend to fail to match those available from conventional manufacturing processes
14 (e.g. injection moulding).
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23 Stereolithography (SL) is one of the most significant RP technologies because of its accuracy
24 and consistency [7]. However, currently, the number of end-use SL parts [8, 9] is limited due
25 to the long-term instability of the parts post-build, especially at high levels of relative
26 humidity [10]. The main objectives of this research are thus: (i) to investigate moisture
27 transport into SL materials, in order to derive a method of predicting the distribution of
28 moisture in a RM component, and (ii) to investigate the effect of the absorbed moisture on the
29 mechanical properties of the material, thus enabling the mechanical performance of the
30 environmentally aged component to be predicted. The first part of the paper is primarily
31 concerned with objective (i) and the second part of the paper addresses objective (ii). The
32 significance of this work is that the methods proposed in the paper can be used to predict how
33 the performance of RM parts will be affected by environmental ageing. This will help
34 designers to use this manufacturing method safely & effectively, and hence support the
35 exploitation of SL as a viable manufacturing technique.
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49 **2. Diffusion Models**

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52 It has been suggested that the kinetics of sorption of moisture in polymers systems is
53 governed by two limiting cases [11], as described below.
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57 Case I (Fickian or diffusion controlled), in which moisture transport is a stochastic process
58 driven by the presence of a concentration gradient. This case predominates in systems where
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1 the penetrant has little hygroelastic effect on the polymer or the rate of diffusion is much less
2 than that of relaxation. In Case I diffusion the weight uptake is initially linear with respect to
3 the square root of time, i.e if the amount sorbed at time t is Kt^n , then n is equal to 0.5.
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7 Case II (relaxation controlled), in which diffusion is more rapid than relaxation.
8 Consequently, there is a discontinuity in concentration between the swollen and unswollen
9 polymer. Initially the discontinuity advances into the polymer with a constant velocity
10 resulting in linear initial uptake of penetrant with respect to time, i.e if the amount absorbed at
11 time t is Kt^n , then n is equal to 1.
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18 In many cases, both the mechanisms described above are present to varying degrees, resulting
19 in anomalous uptake, i.e. n is between 0.5 and 1. Various different forms of anomalous
20 uptake have been identified, as described by Crank [11].
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25 **2.1 Fickian Model**

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28 In this case diffusion can be presented in a quantitative manner by adapting the mathematical
29 equations of heat conduction derived by Fourier in 1822, as shown by Fick in 1855 [11]. The
30 mathematical theory of diffusion is based on the hypothesis that the rate of transfer of a
31 diffusing substance through a unit area of a section is proportional to the concentration
32 gradient measured normal to the section. This hypothesis is presented mathematically by
33 Equation (1), which is usually referred to as Fick's first law.
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$$42 \quad F = -D \frac{\partial c}{\partial x} \quad (1)$$

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45 Where F is the rate of transfer per unit area, c is the concentration of diffusing substance, x is
46 the space coordinate measured normal to the section and D is the diffusion coefficient. The
47 negative sign in Equation 1 is due to the fact that diffusion occurs in the direction opposite to
48 that of increasing concentration.
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54 Considering the total transport of moisture into and out of a two dimensional differential
55 element, the rate of change of moisture with time can be obtained by Fick's second law,
56 which is shown in Equation (2) [11].
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$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \quad (2)$$

The solution to equation (2) for the case of a plane sheet where the region x ($-b < x < b$), C_t the concentration at time t and C_∞ when saturated is given by Equation (3) [11].

$$\frac{C_t}{C_\infty} = \left[1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} e^{\left\{ \frac{-D(2n+1)^2 \pi^2 t}{4b^2} \right\}} \cos \frac{(2n+1)\pi x}{2b} \right] \quad (3)$$

Equation (3) can be integrated with respect to x to determine the total mass of water absorbed at time t . If M_t indicates the mass of the total amount of penetrant absorbed at time t and M_∞ is the mass at saturation, then:

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} e^{\left[\frac{-D(2n+1)^2 \pi^2 t}{4b^2} \right]} \quad (4)$$

Fickian diffusion, as described in the equations above, is unable to accurately represent the anomalous uptake behaviour often seen in the sorption of moisture in polymers. Many models for anomalous uptake have been proposed. In the main, these can be classified as either “diffusion-relaxation” or “dual-uptake” models. Examples of both types of model have been investigated in this paper and these are described in the following sections.

2.2 Diffusion-Relaxation Model

These models are concerned with moisture transport when both Case I and Case II mechanisms are present [12-16]. Berens and Hopfenberg [3] assumed that the net penetrant uptake could be empirically separated into two parts, a Fickian diffusion controlled uptake and a polymer relaxation controlled uptake, with the latter being a first order function of the concentration difference. The equation for mass uptake using Berens and Hopfenbergs model is shown below.

$$M_t = M_{D\infty} \left[1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} e^{\left[\frac{-D(2n+1)^2 \pi^2 t}{4l^2} \right]} \right] + \sum_i M_{R\infty,i} [1 - e^{-\Omega_i t}] \quad (5)$$

Where, M_t is the total mass at time t , $M_{D\infty}$ is the equilibrium amount of sorption in the un-relaxed polymer. $M_{R\infty,i}$ and Ω_i are the equilibrium sorption owing to the relaxation process and the relaxation rate constant, respectively, for the i^{th} relaxation process. Berens and Hopfenberg [3] showed that in general only one or two relaxation terms are required to provide a good fit to the experimental data.

2.3 Dual-Sorption Model

Dual-sorption models are based on the premise that whilst some penetrant molecules diffuse normally in the polymer matrix, others will be affected by polymer-penetrant interactions or micro-void filling [17-19]. Carter and Kibler [2] addressed this problem in terms of the probability that a water molecule may react with a polymer molecule. Their model is based on the theory that moisture in a polymer network can be either bound or free. The probability that a free water molecule becomes bound is γ and the probability that a bound water molecule is emitted from the bound site and becomes mobile is β . The local weight fraction reaches equilibrium, M_i , when the number of free molecules per unit volume, n , and the number of bound molecules per unit volume, N , approach values such that Equation (6) is satisfied.

$$\gamma n = \beta N \quad (6)$$

When γ and β are small compared to K , the moisture uptake is described by Equation (7).

$$\frac{M_t}{M_\infty} = 1 - \frac{\gamma}{\gamma + \beta} e^{-\beta t} - \frac{8\beta}{\pi^2(\gamma + \beta)} \sum_0^\infty \frac{1}{(2n+1)^2} e^{-K(2n+1)^2 t} \quad (7)$$

Where $K = \pi^2 D/l^2$

2.3 Dual-Fickian Model

Loh et al [20] proposed a dual-uptake model based on the summation of two Fickian diffusion models. Physically this can be interpreted as two different uptake processes operating in parallel, both of which are adequately described by Fickian diffusion. This model was seen to accurately represent anomalous moisture transport in an epoxy-based material exposed to

different levels of humidity. Both of the Fickian diffusion models are based on equation (4), with separate diffusion coefficients (D_1 and D_2) and saturation levels ($M_{1\infty}$ and $M_{2\infty}$), respectively. The equation for mass uptake using the dual Fickian model is hence:

$$\frac{M_t}{M_\infty} = M_{1\infty} \left[1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} e^{\left[\frac{-D_1(2n+1)^2 \pi^2 t}{4b^2} \right]} \right] + M_{2\infty} \left[1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} e^{\left[\frac{-D_2(2n+1)^2 \pi^2 t}{4b^2} \right]} \right] \quad (8)$$

At low concentrations, Equation (4) can be simplified to Equation (9) and this was used to determine one of the diffusion coefficients (D_1). This is justifiable because at low concentrations Fick's law is obeyed, indicating that one of the diffusion processes is dominant in this region.

$$\frac{M_t}{M_\infty} = \frac{4}{b} \left[\frac{D_1 \cdot t}{\pi} \right]^{1/2} \quad (9)$$

3. Experimental Methodology

3.1 Comparison of moisture uptake in different SL resins

Three different materials were tested (Accura SI40 by 3D Systems, SL7560 and SL7580 by Huntsman) and samples of each material were manufactured using an SLA 7000 stereolithography machine by 3D Systems. The materials were chosen for their varying evolution within the field of Rapid Prototyping and Rapid Manufacturing. Whilst all were state of the art at the time of the investigation, the SI40 material is predominantly aimed at a prototyping market whereas SL7580 and its predecessor SL7560 were chosen for their supposed potential for manufacturing end-use parts and because, anecdotally, they were considered to be less hygroscopic than traditional SL materials. As with the majority of commercial stereolithography resins, all the materials investigated are predominantly epoxy-based but also include other constituents such as photo-initiators (to start the polymerisation

1 process upon exposure to light) and acrylic (to speed up the initial polymerisation to create
2 stable parts during build) amongst other, often proprietary, components.
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5 Samples were manufactured in a flat orientation to ensure ease of specimen removal. The
6 sample dimensions were 60x60x1mm, as recommended in ISO 62 [21]. A Mettler Toledo
7 digital scale with an accuracy of 0.1mg was used to weigh the samples before the drying
8 stage. After manufacture, the samples were dried in an oven for 24 hours at 50°C and then
9 transferred to a desiccator to cool to room temperature. The samples were kept in the
10 dessicator and weighed periodically until the mass was constant. 956 hours were taken to
11 completely dry the samples
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20 Once completely dried, samples of each material were fully immersed in deionised water at a
21 constant temperature of 20°C. Specimens were extracted at 4, 8, 12, 20, 32, 44, 68 and 92hrs,
22 and then at time intervals of 24hrs. On extraction, surface water was removed with a clean,
23 dry cloth, and each sample was weighed to the nearest 0.1mg. This was completed within 1
24 minute of removing it from the water. This process was repeated until moisture saturation was
25 reached, as indicated by a constant weight
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32 A graphical plot of water uptake (M_t/M_∞) against (\sqrt{t}/b) was made for each material, where
33 M_t indicates the mass of the total amount of penetrant absorbed at time t ; M_∞ is the
34 corresponding mass at saturation and b is the specimen thickness. The commercial
35 mathematical programming package “Mathcad” was used to obtain the best fit diffusion
36 parameters for the experimental results by using least square curve fitting technique.
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44 **3.2 Effect of sample thickness and relative humidity on water absorption**

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46 SL7580 resin was used for these experiments and samples were produced with two sample
47 thicknesses (1 and 2mm), the other dimensions remaining as described in 3.1. After drying the
48 samples, they were stored at four different humidity levels. The samples were conditioned in
49 sealed glass containers that were kept at a constant temperature (50°C ±1). The humidity
50 inside the containers was controlled by the use of chemical salts. The salts used were
51 Potassium Fluoride, Magnesium Nitrate, Potassium Iodide and Potassium Chloride, to
52 provide relative humidities of 20.8%, 45.5%, 64.5% and 81.7% respectively.
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Specimens were extracted at 4, 8, 12, 16, 20, 24, 32 and 48hrs, and then at time intervals of 24hrs, and weighed to the nearest 0.1mg. The conditioning process took 312 hours to ensure that saturation had been reached for the four specified humidity conditions.

4. Results

4.1 Comparison of moisture uptake in different SL resins

A comparison of water uptake in the three different epoxy-based SL resins can be seen in Figure 1, which plots the relation between water uptake (M_t , wt%) and (\sqrt{t}/b) , where M_t is the weight percentage of absorbed water at time t and b is the specimen thickness. The experimental points shown are the average of readings from three samples for each material, with a standard deviation of not more than 2%. This plot is chosen as it produces an initial straight line in the case of Fickian diffusion, as can be seen by studying Equation 9. It can be seen in Figure 1 that the initial slope of the uptake curves is similar for the SI40 and SL7580 resins but less steep for the SL7560 and that the equilibrium quantity of water absorbed varies significantly. It is also noticeable that the equilibrium amount of water absorbed is quite high in all cases, varying from 4.96 weight % for the SL7580 to 7.22 weight % for the SI40. This difference has a significant effect on the diffusion coefficient, as shown in Figure 2, which re-plots the data in terms of the fractional water uptake (M_t/M_∞), allowing the initial slope of the curve to be directly related to the Fickian diffusion coefficient, in accordance with Equation (9). It would thus be expected from Figure 2 that the SI40 and SL7560 resins would have similar Fickian diffusion coefficients but that of the SL7580 resin would be significantly greater. A final observation from Figures 1 and 2 is that the curves appear to take the form of a Fickian uptake curve. This aspect of the investigation has confirmed the extent of the hygroscopy in SL materials. Additionally, though it is clear that there is an improvement in terms of the amount of water diffusion found in the SL7580 material compared to SI40, the level of absorbed moisture is still rather high and, therefore, must bring into question its viability for end-use part manufacture stated applications.

Figures 3 to 5 show the results of fitting the Fickian diffusion model (Equation 4) to the experimental data. It is obvious from this that although the equation adequately fits the early stages of water uptake, it provides a poor fit to the data above 50-70% of the equilibrium uptake. It can also be seen that the poorest fit is seen in the case of the SI40 resin, which was also the material that absorbed the most moisture. This type of moisture uptake, that has a

1 Fickian-like shape but approaches equilibrium more slowly than predicted by the Fickian
2 model, is sometimes termed pseudo-Fickian behaviour [11] and is quite common in epoxy
3 resins [22-23]. There is also a hint of sigmoidal behaviour in the data, although this can't be
4 considered significant with respect to the experimental accuracy. The Fickian diffusion
5 constants used in the model fitting are given in Table 1.
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10 Figures 6 to 8 show the results of fitting Berens and Hopfenbergs [3] diffusion relaxation
11 model, as given in Equation 5, to the experimental data. It is obvious that this provides a far
12 better fit to the data and has no problem modelling the pseudo-Fickian behaviour. The curves
13 shown in these figures are with one relaxation term, however, there was no improvement in
14 the curve fitting when two relaxation terms were used. The constants used in fitting the
15 diffusion-relaxation model to the data are shown in Table 2.
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23 Figures 9 to 11 and 12 to 14 show the results of fitting the dual-sorption and dual-Fickian
24 models to the experimental data respectively and it can be seen that the results are very
25 similar to those with the diffusion-relaxation model. The constants used in the dual-sorption
26 and dual-Fickian model fitting are given in Tables 3 and 4, respectively.
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32 It is interesting to see then, that the pseudo-Fickian behaviour seen in these materials can be
33 represented perfectly well by a number of models with very different mechanistic
34 backgrounds and, without further evidence of the actual mechanisms occurring, one model
35 can be used as well as another to model water uptake in these materials. The dual-Fickian
36 model is interesting in this respect as Loh et al [20] have shown that is quite straightforward
37 to implement this model in a finite element based coupled stress-diffusion analysis. This
38 method of analysis would enable the ageing behaviour of RM components of virtually any
39 geometry and boundary condition to be accurately modelled.
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48 **4.2 Effect of sample thickness and relative humidity on water absorption**

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51 The results from the mass uptake tests for SL7580 resin conditioned at 50°C and four different
52 relative humidities for 1mm and 2mm thick samples are presented in Figures 15 and 16. The
53 results look Fickian/pseudo-Fickian and it can be seen that there is an obvious relationship
54 between the relative humidity and the equilibrium mass uptake. The equilibrium quantity of a
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diluent within a polymer, c_d , can related to the environmental activity of the diluent, a_d , using Henry's law [24].

$$c_d = ka_d \quad (10)$$

Where k is Henry's law constant. In the case of moisture absorption, the environmental activity equates to relative humidity and this relationship is explored in Figures 17 and 18. It is obvious from these figures that Henry's law is not applicable to the current system. This is not surprising as Henry's law doesn't allow for polymer-penetrant interaction and is generally only applicable at low concentrations or in systems in which the penetrant and polymer have little affinity for each other. An improvement on Henry's law is the Flory-Huggins model [25], which takes into account the large difference in size between the polymer and penetrant molecules and interactions between the two.

$$\ln a_d = \ln V_d + \left(1 - \frac{v_d}{v_p}\right)V_p + \chi_d V_p^2 \quad (11)$$

Where the subscripts 'd' and 'p' refer to the diluent and polymer respectively, V is volume fractions, v is molar volume and χ_d is a polymer-penetrant interaction term. As the molar volume of the polymer is generally much greater than that of the penetrant, equation (11) can be simplified to:

$$\ln a_d = \ln V_d + V_p + \chi_d V \quad (12)$$

χ_d was found by fitting a straight line to a plot of $(\ln a_d - \ln V_d - V_p)$ against V_p^2 and has a value of 1.2; this value was then substituted in equation (12) to create the Flory-Huggins plots seen in Figure 17 and 18. It can be seen that this equation fits the experimental data far better than Henry's law. Further advances on Flory-Huggins theory include the substitution of a concentration dependent interaction term [26] and dual absorption models [27, 28] that add a Langmuir adsorption term to account for preferential sorption sites. However, exploring these more complex models is of doubtful use in the present work given that the Flory-Huggins equation fits the experimental data as well as can be expected within the experimental scatter.

The effect of sample thickness on moisture uptake is illustrated in Figures 19-22. A best-fit Fickian absorption curve is included in the figures in order to evaluate the effect of thickness

and relative humidity on anomalous behaviour. The material constants used in the Fickian curve fits are given in Table 5. From these figures and table, a number of facts are apparent. Firstly, it can be seen in the figures that in most cases the behaviour appears to be pseudo-Fickian rather than true Fickian, with the most nearly Fickian behaviour being observed at the lowest environmental activity, namely 20.8% relative humidity. It can be seen from both the figures and table that the diffusion constant is significantly higher for the thicker samples. This is further evidence of non-Fickian behaviour and has been observed by previous investigators [29, 30]. One suggestion for this phenomenon is that the concentration in the outer layer of the polymer does not reach saturation instantaneously but is time dependent [31]. This would have a more significant impact on thinner samples and would result in the lower uptake rates observed. An alternative explanation is that the coupling of diffusion and relaxation effects can produce thickness effects [32]. This can be explored via the Deborah number (DEB) that defines the relative rates of diffusion and relaxation.

$$\text{DEB} = \frac{\lambda}{\theta} \quad (13)$$

Where λ is the characteristic relaxation time of the system and θ is the characteristic diffusion time. A DEB value much greater or smaller than unity indicates the domination of relaxation or diffusion processes, respectively, whereas DEB close to unity indicates a coupling of relaxation and diffusion effects. Sample thickness, h , can be related to the characteristic diffusion time by:

$$\theta = \frac{h^2}{D} \quad (14)$$

And hence, from (13) and (14):

$$\text{DEB} = \frac{\lambda D}{h^2} \quad (15)$$

It can thus be seen from Equation (15) that coupling of diffusion and relaxation would result in the increased values of D observed in the thicker samples.

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It can also be seen from Table 4 that the equilibrium moisture content is higher in the thinner samples, although this trend is far less significant than that seen for the diffusion constant. It is also worth noting that there is no obvious relationship between relative humidity and the diffusion constant.

5. Conclusions

The absorption of moisture in three resins that are being considered for the rapid manufacturing of parts using the stereolithography process has been investigated. It was found that the diffusion rates and equilibrium moisture contents varied widely between the resins but that in all cases significant quantities of moisture were absorbed, which would be expected to impact the mechanical performance of manufactured parts. Anomalous (i.e. non-Fickian) moisture absorption was seen, with the moisture uptake plots being similar to Fickian, but with a more gradual approach to equilibrium. This is termed pseudo-Fickian behaviour. Three anomalous uptake models, a diffusion-relaxation model, a dual-sorption model and a dual-Fickian model, were all seen to fit the experimental data well, despite of being based on different mechanisms.

Equilibrium moisture uptake was seen to be strongly dependent on the relative humidity of the conditioning environment. The relationship between relative humidity and equilibrium moisture content was seen to fit the Flory-Huggins model that includes a penetrant-polymer interaction term. The diffusion constant was seen to be dependent on sample thickness, which is a further indication of non-Fickian behaviour, and this was related to possible diffusion-relaxation effects.

This work has demonstrated that the epoxy resins in the investigation exhibit significant moisture uptake and that this can be successfully modelled using a variety of anomalous moisture uptake models. The ability to predict the moisture distribution in the manufactured parts is an important first step in being able to predict the effect of in-service ageing on the mechanical performance of the parts. The second step is to relate the moisture content with the mechanical properties of the materials and this step is considered in Part 2 of this paper.

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Table 1.

	D (m ² s ⁻¹)	M _∞ (wt.%)
Accura SI40	1.22x 10 ⁻¹²	7.22
SL7560	1 x 10 ⁻¹²	5.88
SL7580	3.3 x 10 ⁻¹²	4.96

Table 2.

	D (m ² s ⁻¹)	M _{D∞} (wt.%)	Ω	M _{R∞} (wt.%)
Accura SI40	0.541 x 10 ⁻¹²	1.444	10 ⁻¹⁴	5.776
SL7560	0.638 x 10 ⁻¹²	1.176	10 ⁻¹⁴	4.704
SL7580	3.21 x 10 ⁻¹²	0.992	10 ⁻¹⁴	3.968

Table 3.

	D (m ² s ⁻¹)	γ (s ⁻¹)	β (s ⁻¹)
Accura SI40	2.8 x 10 ⁻¹³	10 ⁻⁶	0.09
SL7560	2.29 x 10 ⁻¹³	10 ⁻⁶	0.09
SL7580	7.4 x 10 ⁻¹³	10 ⁻⁶	0.09

Table 4.

	D ₁ (m ² s ⁻¹)	M _{1∞} (wt.%)	D ₂ (m ² s ⁻¹)	M _{2∞} (wt.%)
Accura SI40	1.2 x 10 ⁻¹²	2.888	1.1 x 10 ⁻¹²	4.332
SL7560	1.01 x 10 ⁻¹²	2.352	0.9 x 10 ⁻¹²	3.528
SL7580	8.4 x 10 ⁻¹²	0.992	2.1 x 10 ⁻¹²	3.968

Table 5.

Sample thickness	Relative Humidity	D (m ² s ⁻¹)	M _∞ (wt.%)
1 mm	20.8 %	4.38 x 10 ⁻¹²	0.398
	45.5 %	3.0 x 10 ⁻¹²	1.046
	64.5 %	3.93 x 10 ⁻¹²	1.898
2 mm	81.7 %	3.93 x 10 ⁻¹²	2.562
	20.8 %	11.5 x 10 ⁻¹²	0.353
	45.5 %	6.67 x 10 ⁻¹²	0.860
	64.5 %	5.32 x 10 ⁻¹²	1.737
	81.7 %	6.79 x 10 ⁻¹²	2.435

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2 **Tables Caption:**
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5 Table 1: Fickian diffusion constants (1mm thick samples immersed at 20°C).
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8 Table 2: Diffusion-relaxation model constants (1mm thick samples immersed at 20°C).
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11 Table 3: Dual-sorption model constants (1mm thick samples immersed at 20°C).
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14 Table 4: Dual-Fickian model constants (1mm thick samples immersed at 20°C).
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17 Table 5: Effect of sample thickness and relative humidity (SL7580 at 50°C).
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21 **Figures Caption:**
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25 Figure 1: Comparison of water uptake in different SL resins as a function of weight
26 percentage of moisture (M_t , wt. %).
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29 Figure 2: Comparison of water uptake in different SL resins as a function of fractional
30 moisture uptake (M_t/M_∞).
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33 Figure 3: Fitting of Fickian diffusion model to experiment results for Accura SI40.
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36 Figure 4: Fitting of Fickian diffusion model to experiment results for SL7560.
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39 Figure 5: Fitting of Fickian diffusion model to experiment results for SL7580.
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42 Figure 6: Fitting of diffusion-relaxation model to experiment results of Accura SI40.
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45 Figure 7: Fitting of diffusion-relaxation model to experiment results of SL7560.
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48 Figure 8: Fitting of diffusion-relaxation model to experiment results of SL7580.
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51 Figure 9: Fitting of dual-Sorption model to experiment results for Accura SI40.
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54 Figure 10: Fitting of dual-Sorption model to experiment results for SL7560.
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57 Figure 11: Fitting of dual-Sorption model to experiment results for SL7580.
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60 Figure 12: Fitting of dual-Fickian model to experiment results for Accura SI40.
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63 Figure 13: Fitting of dual-Fickian model to experiment results for SL7560.
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- Figure 14: Fitting of dual-Fickian model to experiment results for SL7580.
Figure 15: Effect of relative humidity (R.H.) on moisture uptake at 50°C for 1mm thick SL7580 samples.
Figure 16: Effect of relative humidity (R.H.) on moisture uptake at 50°C for 2mm thick SL7580 samples.
Figure 17: Relationship between relative humidity and sorption equilibria for 1mm thick SL7580 samples.
Figure 18: Relationship between relative humidity and sorption equilibria for 2mm thick SL7580 samples.
Figure 19: Fitting of Fickian model to experiment results for SL7580 samples conditioned at 50°C at 20.8% RH.
Figure 20: Fitting of Fickian model to experiment results for SL7580 samples conditioned at 50°C at 45.5% RH.
Figure 21: Fitting of Fickian model to experiment results for SL7580 samples conditioned at 50°C at 64.5% RH.
Figure 22: Fitting of Fickian model to experiment results for SL7580 samples conditioned at 50°C at 81.7% RH.

Plastics, Rubber and Composites

Ref. No.: PRCME 2800

Title: Environmental Ageing of Epoxy-Based Stereolithography Parts; Part1: Moisture transport

Dear Mr. Xiao L. Wang

Please find below the referees comments (in bold) and our responses.

Regards,

Kazim Altaf

This is generally of high quality, well written and well described. My only comment is the units - D values are given in cm²/s, clearly not SI.

Units have now been changed to SI throughout the paper.











































