Environmental ageing of epoxy-based stereolithography parts. Part 2: effect of absorbed moisture on mechanical properties

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Environmental Ageing of Epoxy-Based Stereolithography Parts
Part 2: Effect of absorbed moisture on Mechanical Properties

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Abstract

The first part of this paper demonstrated how the quasi-Fickian moisture uptake exhibited by stereolithography resins could be modelled. This part outlines the effect of moisture absorption on the mechanical properties of one of the materials. Fickian and dual-Fickian diffusion models, using both analytical and FEA techniques were used to model the moisture uptake in aged samples. Uniaxial tensile testing of dog-bone samples revealed a decrease in elastic modulus and yield stress and an increase in strain to failure with increased moisture content. A model has been developed to predict the change in stiffness of aged samples over time. The results produced from this model show a good correlation to the experimental data and FEA predictions. It is proposed that FEA based coupled stress-diffusion analysis methods can be used to predict the effect of moisture on the mechanical performance of parts made by SL when used in service.

Keywords: Stereolithography, Diffusion, Mechanical properties, Dual Fickian, Stiffness, FEA

1. Introduction

Stereolithography (SL) is one of the main rapid prototyping (RP) processes currently being considered for the manufacture of end-use parts, owing to its accuracy and consistency [1]. Materials used in the SL process are termed photo-polymers and they are primarily cured using ultra-violet (UV) light sources [2]. The majority of current SL resins are thermosetting polymers, such as epoxies and acrylates, with the addition of a light-curing agent (photo-initiator). The latter is also known as a hardener as it causes phase conversion and subsequent material polymerisation (solidification) when exposed to UV radiation [3].

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Currently, the SL process is only used to produce end-use parts for limited applications [4,5]. This can partly be attributed to the instability of current SL materials at high levels of relative humidity [6]. Hence, in order to increase the applications of SL as a manufacturing process, materials more suited to a wide variety of end-use applications must be developed. One of the material aspects that requires significant development is the environmental stability of the SL materials post-build, and in order to achieve this, the mechanism of water diffusion into different SL materials should be investigated. In Part 1 of this paper [7], water diffusion into various SL Epoxy-based materials was found to be anomalous and different methods of modelling this behaviour were investigated.

In polymer matrices, moisture absorption can lead to a wide range of effects, both reversible and irreversible. These effects include; plasticization by weakening of the intermolecular interactions among the functional groups of the chains [8,9], de-bonding at filler-matrix interfaces [10-12], leaching of un-reacted functional groups [13], structural damage such as micro-cavities or crazes [14,15] and chemical degradation of the polymer matrix due to hydrolysis and oxidation [14]. The effect of absorbed moisture on the glass transition temperature \((T_g)\) of polymers has been investigated by Moy et. al. [16] and Ivanova et. al. [9] and the effect on mechanical properties has been investigated by Kasturiarachchi and Pritchard [12], Lawrence et. al. [17] and Butkus et. al. [18]. It was seen in this work that both \(T_g\) and the mechanical properties of polymers can be significantly affected by humidity. Hamid [19] and Al Andrady [20] showed that moisture can have various effects on polymers. One is a chemical influence, attributed to the hydrolysis of unstable bonds. Another is physical, which is due to the breakdown of bonds in the polymer network, leading to swelling and softening of the material. A further influence is that water increases degradation involving the generation of free radicals or other reactive species that can react with other chemical factors. Ritter et. al. [21] and Salmon et. al. [22] showed that water acts as a plasticizer as well as a reactant. Long-term exposure causes a decrease in the molecular weight of polymers due to chain scission (breaking of the cross-links that form the chains in the polymer network) [23] and this will weaken the mechanical properties [24].

It is clear from the literature, therefore, that absorbed moisture can affect the mechanical properties of polymers through many mechanisms and, as Part 1 of this paper demonstrated, there is significant moisture absorption in SL materials. The next steps in this investigation are to characterise the effect of this absorbed moisture on material properties and develop a
model to predict the changes in the mechanical performance of RM structures on aging. This is achieved by modelling the moisture concentration in specimens using Fickian and dual-Fickian models with both analytical and finite element analysis (FEA) methods. The moisture concentration is then correlated with the Young’s modulus, enabling the stiffness of the structure to be modelled as a function of the predicted moisture uptake.

2. Relationship between absorbed moisture and mechanical properties

2.1 Diffusion

It has been suggested that the kinetics of sorption of moisture in polymers systems is governed by two limiting cases [7]; Fickian, or diffusion controlled, and relaxation controlled. The solution to Fick’s second law for the case of a plane sheet where the region x (−b < x < b) has concentration \( C_t \) at any time \( t \) and \( C_\infty \) when saturated is given by Equation (1):

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

(1)

For a dual-Fickian model, based on the summation of two Fickian diffusion models, operating in parallel the normalised concentration is given by:

\[
C_t = [1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} \left\{ \frac{-D_1(2n+1)^2 \pi^2 t}{4b^2} \right\} \cos \left( \frac{(2n+1)\pi x}{2b} \right)]C_\infty +
\]

(2)

\[
[1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} \left\{ \frac{-D_2(2n+1)^2 \pi^2 t}{4b^2} \right\} \cos \left( \frac{(2n+1)\pi x}{2b} \right)]C_\infty
\]

Equation (1) 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 \( M_\infty \) is the mass at saturation, then:
\[
\frac{M_t}{M_\infty} = 1 - \sum_{n = 0}^{\infty} \frac{8}{(2n + 1)^2 \pi^2} e^{-\frac{D(2n + 1)^2 \pi^2 t}{4b^2}} \]  

(3)

The equation for mass uptake using the dual Fickian model, with separate diffusion coefficients \(D_1\) and \(D_2\) and saturation levels \(M_{1\infty}\) and \(M_{2\infty}\), respectively is hence:

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

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

(4)

2.2 Proposed relationship between elastic modulus and moisture concentration

As moisture is absorbed, the concentration at a specific point within the specimen increases with time and this reduces the value of Young’s Modulus \((E)\), which gradually varies from the dry modulus \((E_d)\) to the saturated modulus \((E_s)\). It is proposed that Young’s Modulus \((E)\) varies with the concentration \((C)\) according to Equation (5):

\[
E_t = E_d - \left[ \frac{C_t}{C_\infty} (E_d - E_s) \right] \]  

(5)

Where \(E_t\) is the Young’s Modulus at time \(t\). This linear relationship may be rather simplistic but has the advantage of only requiring the values of dry and saturated moduli. For Fickian diffusion, Equation (1) can be substituted in Equation (5), to yield:

\[
E_t = E_d - \left[ 1 - \frac{4}{\pi} \sum_{n = 0}^{\infty} (-1)^n e^{-\frac{D(2n + 1)^2 \pi^2 t}{4b^2}} \cos \left( \frac{(2n + 1)\pi x}{2b} \right) \right] (E_d - E_s) \]  

(6)

Similarly for dual-Fickian uptake, Equation (2) can be substituted in Equation (5), to yield:
2.3 Analytical model to predict stiffness

Stiffness $S$, is a useful measure of mechanical performance as it relates deformation to applied load.

\[ S = \frac{P}{\delta} \]  

(8)

Where $P$ is the force applied to the specimen and $\delta$ is the deflection. When the Young’s Modulus ($E$) and cross-sectional area ($A$) of a specimen are uniform, the stiffness can be calculated according to Equation (9):

\[ S = \frac{EA}{L} \]  

(9)

where $L$ is the length of the specimen. If the Young’s modulus, $E$, varies in the $x$ and $z$ directions but there is no variation in $E$ along the length then stiffness is given by:

\[ S = \frac{1}{L} \int_{0}^{w} \int_{0}^{b} E(x,z) \, dx \, dz \]  

(10)

This equation is applicable in the case of a sample exposed to moisture where length, $L$, is much greater than width, $w$, and thickness, $b$, as moisture transport in the $y$ direction has little effect away from the sample ends and it can be assumed that there is no variation in $E$ in the length direction. If the sample is designed such that the width is significantly greater than the thickness, moisture transport in the $z$ direction can also be ignored and it may be assumed that the Young’s modulus varies in the $x$ direction only, and hence:
$$S = \frac{wb}{L} \int_0^L E(x) \, dx$$  \hspace{1cm} (11)$$

Substituting Equation (6) in Equation (11) and integrating gives the following solution:

$$S_t = \frac{wb}{L} \left[ E_d - \left( \left[ 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} e^{-\frac{D(2n+1)^2 \pi^2 t}{4b^2}} \right] \left( E_d - E_s \right) \right) \right]$$ \hspace{1cm} (12)

Where \( S_t \) is the stiffness at time \( t \), \( w \) is the width and \( b \) the thickness of the specimen. For dual- Fickian diffusion, Equation (12) can be extended to include the two parallel Fickian stages as:

$$S_t = \frac{wb}{L} \left[ E_d - \left( \left[ 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} e^{-\frac{D_1(2n+1)^2 \pi^2 t}{4b^2}} \right] \left( E_d - E_s \right) \right) \right] + \left[ \left[ 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} e^{-\frac{D_2(2n+1)^2 \pi^2 t}{4b^2}} \right] \left( E_d - E_s \right) \right]$$ \hspace{1cm} (13)

3. **Experiments**

The polymer investigated in the present study is an epoxy based resin SL-7580. The samples were manufactured in a flat orientation using an SLA7000 stereo-lithography machine from 3D Systems with 1mm, 2mm & 4mm thicknesses. Environmental conditioning of samples was carried out under the following environments.

(i) Fully immersed in deionised water at 20°C
(ii) 20.8% RH at 50°C
(iii)45.5% RH at 50°C
(iv)64.5% RH at 50°C
(v) 81.7% RH at 50°C
Where RH is relative humidity. In order to control the humidity, the chemical salts; Potassium Fluoride, Magnesium Nitrate, Potassium Iodide and Potassium Chloride were used to give 20.8%, 45.5%, 64.5% and 81.7% RH respectively.

3.1 Moisture uptake

Moisture uptake samples with 1mm and 2mm thickness were manufactured with dimensions of 60x60 mm, as recommended in ISO 62 [25] and shown in Figure 1. A Mettler Toledo digital scale with an accuracy of 0.1mg was used to weigh the samples before drying in an oven for 24 hours at 50°C and then transferring to a desiccator to cool to room temperature. The samples were kept in the desiccator and weighed periodically until the mass was constant. Once completely dried, five samples of each thickness were immersed in deionised water at 20°C, while the remaining samples, Five samples of 2mm thickness were conditioned at each of the constant % RH environments at a temperature of 50°C. Specimens were extracted at 4, 8, 12, 20, 32, 44, 68 and 92hrs, and then at time intervals of 24hrs. On extraction of immersed samples, surface water was removed with a clean, dry cloth, and each sample was weighed to the nearest 0.1mg. This was completed within 1 minute of removal from the water. The conditioning process was continued for 312 hours.

The moisture uptake data was fitted to equations 3 & 4 using the commercial mathematical programming package Mathcad, developed by PTC, by using the least square curve fitting technique available in the software. The best fit values of D, D1 and D2 [7] obtained through curve fitting are given in Tables 1-4. These values were substituted in equations 1 and 2 to predict moisture concentration profiles for different time intervals.

3.2 Effect of moisture on mechanical properties

In order to observe the effect of moisture uptake on the mechanical properties of the SL7580, tensile tests were carried out. The specimens were built in an edge orientation to avoid build failure owing to the small thickness of the samples. Tensile testing samples of 2mm thickness, were manufactured for each environmental condition, with the dimensions as specified in ISO 527-1 & 2 [26, 27], as shown in Figure 1. The drying process for these samples was the same as that described in Section 3.1. Tensile testing was performed using a Zwick Z030 tensile testing machine with a 10kN load cell, 25mm gauge length bi-axial extensometer and at a constant displacement rate of 2mm/min. Samples, 4mm thick, were also immersed in water at
20°C for 52 weeks and tensile tests were performed at 4 week intervals to find the effect of moisture uptake on modulus and stiffness. This data was used in the analytical models developed in Section 2 to determine the relationships between modulus & concentration and stiffness and moisture uptake.

### 4.0 Finite Element Analysis

Numerical techniques, such as finite element modelling (FEM) have advanced considerably in recent years and the availability of multi-physics solvers has made FEM an ideal choice for diffusion modelling and coupled hygro-mechanical analysis. A coupled stress-diffusion FEA analysis [28] has previously been used to study the stress and moisture distribution in adhesive joints and a good agreement between experimental and FEA modelling was reported. In this work a finite element based approach is used to model the diffusion and mechanical stresses in SL 7580 using the commercial FEA software Marc from MSC Software Corporation. In MSC Marc software there is no direct option for moisture transport analysis, however, diffusion can be analysed by adapting the mathematical equations of heat conduction, derived by Fourier, as described by Crank [29].

The FEA method has the ability to analyse the transient moisture diffusion response using the single and dual Fickian models discussed previously. The dual Fickian model was implemented by combining the FE nodal moisture concentrations of two separate Fickian diffusion analyses. FEA can be undertaken in terms of the normalised moisture concentration i.e. with respect to the boundary condition applied to the edges of the model. These boundaries are assumed instantaneously saturated at the exposed edges.

Advances in computer hardware and software now make it practical for analyses to account for the effects of two or more interacting physical phenomena together; termed coupled FEA, or performing one physical phenomenon first and taking its result as the initial boundary condition for the second physical analyses; termed sequential FEA. In this paper, the results from Fickian and dual Fickian diffusion analyses have subsequently been used as the initial conditions for the mechanical analyses.

Eight noded quadrilateral continuum elements with an average element size of 0.063x0.063 mm for the moisture uptake models and 0.20x0.08 mm for the tensile test models were used, as shown in Figure. 2. Values of coefficient of diffusion for the diffusion analyses were taken
from Tables 1-4. In order to introduce moisture dependant material properties, a table was defined to provide the relation between elastic modulus and moisture concentration for the mechanical analysis. One end of the tensile test sample was restricted against movement in all directions and at the other end a tensile force was applied. Another table was defined to give the relationship between load and time to control the analysis.

5. Results & Discussion

5.1 Modelling of moisture concentration

A comparison of normalised moisture concentration from Fickian and dual-Fickian models, using both analytical and FEA techniques is shown in Figure 3 & 4 for immersed samples. The plots show that concentration increases with time and varies through the sample thickness. Almost full saturation of the samples has been reached after 48 hours conditioning. It can be seen that there is a good correlation between the analytical and FEA results for both diffusion models, with the FEA predicting slightly lower concentrations.

The Fickian and dual-Fickian models result in similar concentration profiles, with the Fickian model predicting higher concentrations, particularly at 20 hrs conditioning. This trend can be explained by observing the mass uptake plots shown in Figure 5 & 6. It can be seen that the dual-Fickian model correlates very well with the experimental data whilst the Fickian model over-predicts the moisture contents, particularly in the time period corresponding to the greatest over-prediction seen in the concentration profiles. Similar behaviour has also been reported by other researchers [30].

Figure 7 & 8 shows normalised moisture concentration profiles for 2mm thick samples conditioned at various relative humidities at t = 8 and 48 hours respectively. Constants used in the calculation for various %RH conditions are listed in Table 3 and 4. The curves for both Fickian and dual-Fickian models result in similar concentration profiles, with the Fickian model, again predicting higher concentrations. FEA results correlate well with the analytical model, with FEA predicting slightly lower concentrations for both models. Figure 9 shows a plot of logarithmic values for saturated moisture concentration at various %RH conditions for samples conditioned at different %RH at 50°C. The trend of the plot supports a logarithmic power relation between saturated concentration and %RH.

5.2 Modelling of elastic modulus profiles
As elastic modulus, $E$, is dependent on moisture concentration, then a variable moisture concentration in a sample, as seen in Figures 3, 4, 7 & 8, will result in a variation in $E$ of the samples. Equations (6) and (7) were used to calculate the elastic modulus profiles at various times. The values of $E$ for dry and saturated samples determined from tensile tests are given in Table 5. Figure 10 shows the predicted change in $E$ after $t = 10, 20$ & $30$ hours for both Fickian and dual Fickian models for 2mm thick samples immersed in deionised water. Results obtained for the Fickian and dual Fickian models are quite close to each other, with less than 2% variation. The variable decrease in the value of modulus can be attributed to an increase in the concentration at a specific point as a result of the non-uniform moisture absorption causing plasticisation [31]. Figures 11 and 12 further support this argument where modulus profiles have been plotted for different relative humidities, after 10 and 30 hours conditioning, respectively. It can be seen that RH below 50% has relatively little effect on $E$ whereas samples immersed in water or at 81.7%RH see a significant degradation. Figure 13 shows a plot of $E$ as a function of moisture concentration, the error bars indicating ± 1% standard deviation. The plot indicates a linear relationship and hence fully supports the linear model proposed in Equation (5).

### 5.3 Relationship between stiffness and moisture uptake

Stiffness is a material property exhibiting resistance to deformation under an applied load and hence prediction of stiffness against environment degradation is important for designing the service life of any object. Figure 14 shows the relationship between stiffness and saturated moisture content of 2mm thick samples at various relative humidity conditions. The stiffness was calculated from Equation (9) by substituting dry and saturated modulus calculated from tensile tests. Standard deviations and mean values of stiffness are plotted against saturated moisture uptake. The plot shows a linear decrease in stiffness with increased moisture content.

Equation (13) was used to predict the change in stiffness of 2mm samples using the dual-Fickian model at various %RH conditions at 50°C. The same relationship was determined using FEA and it can be seen in Figure 15 that there is a good agreement with the analytical method. The plots in Figure 15 show that stiffness decreases with increased moisture uptake with time, as expected. It can be seen that the stiffness decreases sharply initially, which can
be contributed to the rapid moisture uptake in the initial stages, resulting in decreased mechanical strength due to plasticisation.

Additionally, tensile tests were performed on a monthly basis on 4mm thick tensile test samples that were stored at 20°C in water for a year. The experimental data was used to calculate the change in stiffness with conditioning time, as shown in Figure 16. The experimental plot show that the stiffness decreases with an increase in moisture uptake, which is consistent with previous work [24, 31]. It can be seen in Figure 16 that the stiffness model and FEA agree well with each other and provide a good fit to the experimental data. There is a discontinuity in the experimental data around 75 days. Although possibly a real effect, this is more likely an artefact of the testing. The fit of the models to the experimental data would be better if this was removed.

6. Summary & conclusions

This paper describes the effect of absorbed moisture on the mechanical properties of a representative stereolithography resin, typical of the type proposed for use in rapid manufactured parts. The work included an experimental investigation, the development of an analytical model and the application of coupled moisture-mechanical finite element analysis. Diffusion coefficients calculated from Part 1 of the paper were used to predict moisture concentration profiles through the thickness of samples using two analytical models and FEA. The FEA and analytical methods agreed well and the difference in results from Fickian and dual Fickian uptake models illustrated the pseudo-Fickian behaviour of the material, highlighted in part 1 of the paper. It was seen that as the amount of absorbed moisture increased, the modulus of elasticity of the material decreased, as discussed in previous work [30-32].

Analytical models were developed to predict spatial and temporal changes in the value of the elastic modulus resulting from increasing moisture concentration. Models based on Both Fickian and dual Fickian models were shown to give similar results. An analytical model was also developed to predict changes in stiffness with increasing moisture uptake. The model was seen to fit well with experimental data. Results showed that as the moisture concentration increases it decreases elastic modulus and as stiffness is proportional to elastic modulus hence it decreases it as well in same proportion linearly.
This work has demonstrated that current epoxy resins proposed for stereolithography based rapid manufacturing are highly hygroscopic and that the mechanical performance of manufactured parts using these materials will vary as a function of the absorbed moisture. This clearly needs to be taken into account when designing parts. This paper, together with part 1, presents a relatively straightforward way that this can be achieved to a good degree of accuracy.

7. References


### Table 1:

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Tables Caption:

Table 1: Fickian model constants for 2mm and 1mm SL 7580 samples fully immersed in water at 20°C.

Table 2: Dual-Fickian model constants for 2mm and 1mm SL 7580 samples fully immersed in water at 20°C.

Table 3: Fickian model constants for 2mm thick SL 7580 samples at various relative humidity conditions and at 50°C.

Table 4: Dual-Fickian model constants for 2mm thick SL 7580 samples at various relative humidity conditions and at 50°C.

Figures Caption:

Figure 1: Schematic showing dimensions of moisture uptake samples and tensile test samples (thickness = 1mm and 2mm).

Figure 2: Typical finite element meshes.

Figure 3: Normalised moisture concentration profile through 1mm thick samples immersed in de-ionised water at 20°C.

Figure 4: Normalised moisture concentration profile through 2mm thick samples immersed in de-ionised water at 20°C.

Figure 5: Experimental, Fickian and dual-Fickian models curves for 1mm thick samples immersed in de-ionised water at 20°C.

Figure 6: Experimental, Fickian and dual-Fickian models curves for 2mm thick samples immersed in de-ionised water at 20°C.

Figure 7: Normalised moisture concentration profile through 2mm thick samples after 8 hours under various relative humidity conditions.

Figure 8: Normalised moisture concentration profile through 2mm thick samples after 48 hours under various relative humidity conditions.

Figure 9: Logarithmic values of moisture concentration at various %RH for 2mm thick samples at 50°C.
Figure 10: Change in elastic modulus with moisture over time for 2mm thick sample immersed in water.

Figure 11: Changes in elastic modulus with moisture over time through 2mm thick samples stored under various relative humidity conditions after 10 hours’ time.

Figure 12: Changes in elastic modulus with moisture over time through 2mm thick samples stored under various relative humidity conditions after 30 hours’ time.

Figure 13: Modulus of elasticity as function of moisture concentration for 2mm thick samples at 50°C.

Figure 14: Change in stiffness with increased moisture content under various %RH for 2mm thick samples at 50°C.

Figure 15: Change in stiffness with time of 2mm thick SL7580 sample at constant temperature of 50°C under various %RH conditions.

Figure 16: Change in stiffness with increasing moisture uptake for 4mm thick tensile test samples as function of time.
Dear Mr. Xiao L. Wang

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

Regards,

Kazim Altaf

This is an interesting paper of high quality. Minor comments: Are all the figures 10-13 necessary? Just a point to consider.

Figure 12 has been removed but we believe the remaining figures are necessary.

Equation (10) relies on there being no variation in E along the specimen length. This is entirely reasonable, but perhaps should be made explicit.

The text pertaining to Equation (10) has now been expanded to clarify this point, as given below.

“where L is the length of the specimen. If the Young’s modulus, E, varies in the x and z directions but there is no variation in E along the length then stiffness is given by:

\[ S = \frac{1}{L} \int \int E(x,z).dx.dz \]  

This equation is applicable in the case of a sample exposed to moisture where length, L, is much greater than width, w, and thickness, b, as moisture transport in the y direction has little effect away from the sample ends and it can be assumed that there is no variation in E in the length direction. If the sample is designed such that the width is significantly greater than the thickness, moisture transport in the z direction can also be ignored and it may be assumed that the Young’s modulus varies in the x direction only, and hence:”
Non-colour figure
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