Moisture Absorption and Swelling of Nylatron GS-51-13

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# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABSTRACT</td>
<td>5-6</td>
</tr>
<tr>
<td>INTRODUCTION</td>
<td>7</td>
</tr>
<tr>
<td>EXPERIMENTAL</td>
<td>8</td>
</tr>
<tr>
<td>DIFFUSION EQUATION</td>
<td>9</td>
</tr>
<tr>
<td>RESULTS</td>
<td>10</td>
</tr>
<tr>
<td>SUMMARY</td>
<td>13</td>
</tr>
<tr>
<td>ACKNOWLEDGEMENTS</td>
<td>13</td>
</tr>
<tr>
<td>REFERENCES</td>
<td>14</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>15</td>
</tr>
<tr>
<td>Figure 1</td>
<td>16</td>
</tr>
<tr>
<td>Figure 2</td>
<td>17</td>
</tr>
<tr>
<td>Figure 3</td>
<td>18</td>
</tr>
<tr>
<td>Figure 4</td>
<td>19</td>
</tr>
<tr>
<td>Figure 5</td>
<td>20</td>
</tr>
<tr>
<td>Figure 6</td>
<td>21</td>
</tr>
<tr>
<td>Figure 7</td>
<td>22</td>
</tr>
<tr>
<td>Figure 8</td>
<td>23</td>
</tr>
<tr>
<td>Figure 9</td>
<td>24</td>
</tr>
<tr>
<td>Figure 10</td>
<td>25</td>
</tr>
<tr>
<td>Figure 11</td>
<td>26</td>
</tr>
<tr>
<td>Figure 12</td>
<td>27</td>
</tr>
<tr>
<td>DISTRIBUTION</td>
<td>28</td>
</tr>
</tbody>
</table>
MOISTURE ABSORPTION AND SWELLING OF NYLATRON GS-51-13

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ABSTRACT

The moisture absorption and swelling properties of Nylatron GS-51-13 detent wheels have been characterized at high humidity and at several temperatures. Thickness changes of the parts were found to be linearly related to the amount of water uptake. Diffusion theory was used to analyze the data. The parts were modeled as hollow right circular cylinders and the diffusion equation was solved for this geometry. Diffusion was found to be Fickian with the effective diffusion constants, \( D \) (in \( \text{cm}^2/\text{s} \)), given by the Arrhenius equation, \( D = 4.23 \exp(-6740/T) \), where \( T \) is the absolute temperature. The activation energy is 13.4 kcal/mole. Since the parts deviate slightly from the model geometry, the effective diffusion constants contain a geometrical factor. However, by varying the cylinder dimensions, it was estimated that the effective diffusion constants for the parts are within 20% of the true Nylatron material properties. From the foregoing work, a model was developed to predict dimensional changes in the parts as a function of environmental conditions.
INTRODUCTION

In the design of a mechanical component, a major concern is dimensional stability with respect to environmental conditions. Thermal expansion at elevated temperatures, for example, must be considered to ensure that the part will remain within tolerances and perform reliably. For parts made of polymeric materials, the greatest source of dimensional instability is often swelling of the polymer due to absorption of water. Under environments likely to be encountered, the dimensional changes resulting from moisture absorption may be an order of magnitude larger than the effects of temperature alone. This report shows that if the relationship between moisture absorption and swelling is known, the theory of diffusion can be used to predict dimensional changes as a function of time, temperature and relative humidity.

In this study, the swelling of Nylatron GS-51-13 (40% glass filled nylon 6,6 with MoS2 powder as a dry lubricant) due to water absorption is analyzed. Nylatron finds application in parts such as dry bearings and gears. The geometry of a typical part is given in Fig. 1. The moisture absorption and swelling characteristics of the parts themselves were examined under a variety of conditions and a linear relationship was found between the amount of moisture uptake and the extent of swelling. By modeling the part as a hollow right circular cylinder, effective diffusion constants for water in Nylatron were determined. These, in turn, serve as a basis for predicting dimensional changes. While the diffusion constants
exhibit internal consistency, they contain contributions due to the component's deviation from the model geometry. It is estimated, however, that they are within 20% of the true Nylatron material properties.

EXPERIMENTAL

The parts were dried by vacuum baking at 80°C for 72 hrs after which three parts each were immersed in distilled water (100% relative humidity) at 21°C, 50°C and 71°C. The parts were periodically removed from the water, cooled, dried, weighed and had their thickness measured with a micrometer. Figure 2 summarizes the thickness changes as a function of time at the three temperatures. Each point represents the average of three measurements on each of the three parts. The mass gains of the parts are shown in Fig. 3. To see if the experimental procedure, namely, immersion and interruption of absorption affected the results, the water uptake of a single part was measured continuously at 59°C and 96% RH using a sensitive microbalance. No significant effects were seen.

Finally, water desorption from the parts was briefly examined. To measure the rate of thickness decrease, an initially saturated part at 70°C was allowed to desorb into a dry nitrogen atmosphere (also 70°C). The thickness change was monitored continuously in a thermomechanical analyzer. The equilibrated 59°C part was desorbed into a vacuum in the microbalance with its mass decrease measured. The results of these experiments are shown in Fig. 4.
DIFFUSION EQUATION

The diffusion equation can be solved numerically for the detent geometry. However, for simplicity and ease of computation, the part was modeled as a hollow right circular cylinder having inner and outer radii of a and b, respectively, and height, h. Assuming Fickian diffusion and a constant diffusion coefficient, diffusion is governed by the equation

\[
\frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial C}{\partial r} \right) + \frac{\partial^2 C}{\partial z^2} = \frac{1}{D} \frac{\partial C}{\partial t}, \quad C = C(r, z, t)
\]  \hspace{1cm} (1)

subject to the conditions

\[
\begin{align*}
C(a, z, t) &= C(b, z, t) = C_0 \\
C(r, 0, t) &= C(r, h, t) = C_0 \\
C(r, z, 0) &= 0; \quad a < r < b, \quad 0 < z < h,
\end{align*}
\]

where D is the diffusion constant, C(r, z, t) is the concentration at time t and \( C_0 \) is the saturation concentration. Owing to the nature of the initial and boundary conditions, the solution to Eq. (1) can be expressed as a product of two one dimensional solutions: \(^2,3\)

\[
\frac{C}{C_0} = 1 - 4 \sum_{m=0}^{\infty} \sum_{n=1}^{\infty} \frac{1}{(2m+1)} \sin\left[\frac{(2m+1)\pi z}{l}\right] \frac{J_0(\alpha_n) U_0(r\alpha_n)}{J_0(\alpha_n) + U_0(r\alpha_n)} \times \frac{\alpha_n^2 + \frac{(2m+1)^2 \pi^2}{l^2}}{x h^2} e^{-D t}
\]  \hspace{1cm} (3)
where
\[ U_0(\alpha_n) = J_0(\alpha_n) Y_0(b\alpha_n) - J_0(b\alpha_n) Y_0(\alpha_n), \]

\( J_0(x) \) and \( Y_0(x) \) are Bessel functions and the \( \alpha_n \) are the positive roots of
\[ U_0(a\alpha_n) = 0. \]

The amount of water taken up after time \( t \), \( M_t \), is obtained by integrating \( C \) over the cylinder volume
\[
\frac{M_t}{M_\infty} = 1 - \frac{16}{\pi(b^2-a^2)} \sum_{m=0}^{\infty} \sum_{n=1}^{\infty} \frac{1}{\alpha_n(2m+1)^2} e^{-Dt\left[\frac{a^2}{h^2} + \frac{(2m+1)^2\pi^2}{h^2}\right]} x \]

\[ x \frac{J_0(a\alpha_n)}{J_0(a\alpha_n) + J_0(b\alpha_n)} \left\{ \left[ bJ_1(b\alpha_n) - aJ_1(a\alpha_n) \right] Y_0(b\alpha_n) \right. \]

\[ - \left. \left[ bY_1(b\alpha_n) - aY_1(a\alpha_n) \right] J_0(b\alpha_n) \right\}. \tag{4} \]

The fractional regain, defined as \( \frac{M_t}{M_\infty} \), is the quantity derived directly from the water sorption experiments.

**RESULTS**

From the 50°C and 71°C data it is found that Nylatron has absorbed approximately 4% moisture at equilibrium. This is about the amount that would be estimated for nylon 6,6 containing 40% impermeable glass filler. The saturation moisture content is
essentially independent of temperature as is found in nylon 6,6\textsuperscript{4} and polymers in general.\textsuperscript{5} In addition, as shown in Fig. 5, a linear relationship was found between the water uptake and the thickness change for these parts. After a slow initial increase, the thickness increases by about 0.6% for each 1% rise in water content. The nonzero intercept in Fig. 5 is consistent with a threshold concentration below which swelling does not occur.\textsuperscript{6}

The water absorption of the detents was analyzed in terms of diffusion constants according to Eq. (4). The parts were modeled as hollow cylinders having inner and outer radii of 0.14 and 0.30 in. respectively, and a height of 0.125 in. D was then varied in Eq. (4) until the predicted regain curves suitably matched experiment. Figures 6-9 compare theory and experiment for the four temperatures examined. The excellent agreement indicates that the model geometry adequately describes the part. D, however, is somewhat sensitive to the cylinder dimensions chosen. To examine this effect, the 59\degree C data were analyzed in terms of several cylinders having the extremes of the detent dimensions with the derived D's showing variations of up to 20%. This figure is typical of variations in D generally found in the literature, thus, the material constants for Nylatron are reasonably well determined. As a final check on the diffusion picture, the two desorbing parts (see Fig. 4) indicate that the process is reversible and that the rate of desorption is consistent with the D's found above.
Although the final mass uptake and thickness change of a detent is independent of temperature at constant humidity, the rate of approach to equilibrium is a strong function of temperature. This strong dependence of D on temperature, as exhibited in Figs. 6-9, indicates that the diffusion is a thermally activated process. Figure 10 shows an Arrhenius plot in which the diffusion constants are found to obey the equation

\[ D = 4.23 \exp(-6740/T) \]  

Both the constants, D (in cm²/s), and the activation energy (13.4 kcal/mole) are consistent with literature values for nylon.  

The theory of diffusion presented above along with the empirical relationship between moisture content and swelling permit the dimensional changes of the parts to be predicted, as a function of time, for a variety of environmental conditions. The diffusion constants merely scale the time axis of the fractional regain (FR) curves. That is, the product of D and time is a constant for a given FR. Figure 11 shows the relationship between the FR and the D-time product. Once D is computed at a given temperature from Eq. (5), the time, t, to a given FR is easily determined. The mass gain at t is obtained by multiplying the FR by the equilibrium moisture content, \( M_\infty \). The corresponding thickness change of a part is obtained from the mass gain with the aid of Fig. 5. While no work was done at humidities lower than 96% RH, the rate of approach to
equilibrium (as measured by the FR) should be independent of RH. The RH simply determines $C_o$ in Eq. (3). Figure 12 gives $C_o$ for nylon 6,6 ("Zytel" 101). $^4$ $C_o$ for Nylatron can be approximated by dividing the corresponding "Zytel" 101 figure by 2, reflecting the large fraction of impermeable filler in the Nylatron.

**SUMMARY**

The dimensional stability and moisture absorption characteristics of Nylatron GS-51-13 detent wheels were investigated as a function of temperature. The swelling of the parts was found to be linearly related to the amount of water uptake. The diffusion equation was solved for a simplified model of the detent geometry and used to determine the diffusion constants for Nylatron. The diffusion constants displayed Arrhenius behavior, adequately represented the data and were consistent with published values for nylon. As a result of this work, a model was developed to predict dimensional changes in the parts under a variety of environmental conditions.

**ACKNOWLEDGEMENTS**

I thank L. Orear (5814) for performing the microbalance experiments and J. A. Sayre (5813) for many valuable discussions.
REFERENCES


1. Diagram of a Nylatron detent where all numbers have units of inches. The detent was modeled as a hollow right circular cylinder having inner and outer radii of 0.14 and 0.30 in, respectively, and height of 0.125 in.

2. Thickness increases of the detents after being immersed in water at three different temperatures. The thickest portion of the detent (0.173 in. in Fig. 1) was monitored.

3. Mass uptake, as a function of time, for detents immersed in water at three different temperatures.

4. Thickness decrease in a 71°C detent and mass decrease in a 59°C detent when subjected to desorption. The curves have the same general shape and the rates of desorption are consistent with the diffusion picture presented in the test.

5. Linear relationship between the thickness increase and mass uptake of a detent. This relationship in conjunction with the theory of diffusion, can be used to predict dimensional changes in the parts as a function of environmental conditions.

6. Predicted fractional regain curve at 21°C and 100% RH, with D = 4.8 x 10^-10 cm^2/s. Circles represent measured values.

7. Calculated fractional regain curve at 50°C and 100% RH, with D = 3.1 x 10^-9 cm^2/s. Circles represent measured values.

8. Calculated fractional regain curve at 59°C and 96% RH, with D = 5.7 x 10^-9 cm^2/s. Circles represent measured values.

9. Calculated fractional regain curves at 71°C and 100% RH, with D = 1.4 x 10^-8 cm^2/s. Circles represent measured values.

10. Arrhenius plot of the diffusion coefficients as a function of temperature. The activation energy is 13.4 kcal/mole.

11. Fractional regain as a function of the product of the diffusion constant and time. Once the diffusion constant is calculated from Eq. 5, the time to a given fractional regain is easily determined.

12. Equilibrium concentration of water in a nylon 6,6 ("Zytel" 101) as a function of relative humidity. Nylatron values are approximately a factor of 2 smaller due to its large fraction of impermeable filler.
FIGURE 2

0 = 71C
+ = 50C
X = 21C
FIGURE 3
$0 = \text{DECREASE IN THICKNESS (MILS)}$

$+ = \text{4\textsuperscript{th} FRACTIONAL MASS DECREASE}$
FIGURE 5

THICKNESS CHANGE (MILS) vs. % WATER

$0 = 71{\text{C}}$
$+ = 50{\text{C}}$
$X = 21{\text{C}}$
FIGURE 6

FRACTIONAL REGAIN

0 100 200 300 400 500

TIME IN HOURS

0.2 0.4 0.6 0.8 1.0

FRACTIONAL REGAIN

0 100 200 300 400 500

TIME IN HOURS

TEMP=21°C
RH=100%
D=4.8E-10

FIGURE 6
FIGURE 7

TEMP=50°C
RH=100%
D=3.1E-9
FIGURE 8

TEMP=59C
RH=96%
D=5.7E-9
FIGURE 9

TEMP=71°C
RH=100%
D=1.4E-8
FIGURE 10

\( -\log D \) vs. \( (1/T) \times 1000 \) K

The figure shows a linear relationship between \(-\log D\) and \((1/T) \times 1000\) K, with data points plotted and a fitted line.

FIGURE 10
FIGURE 11
MOISTURE CONTENT AS A FUNCTION OF RELATIVE HUMIDITY

FIGURE 12
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<th>Name</th>
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<tbody>
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<td>C. R. Blaine</td>
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<td>N. M. Nelson</td>
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<td>2540</td>
<td>K. Gillespie</td>
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<td>2544</td>
<td>J. P. Ford</td>
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<td>L. D. Miller</td>
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<td>R. G. Kepler</td>
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<td>L. A. Harrah</td>
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<td>R. A. Assink</td>
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<td>R. J. Martinez</td>
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<td>K. E. Mead</td>
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<td>J. G. Curro</td>
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<td>D. D. Drummond</td>
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<td>M. R. Keenan (5)</td>
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<td>5813</td>
<td>J. A. Sayre</td>
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<td>F. P. Gerstle</td>
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<td>5814</td>
<td>L. Orear</td>
</tr>
<tr>
<td>5833</td>
<td>R. E. Fisher</td>
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<tr>
<td>8315</td>
<td>D. H. Doughty</td>
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<tr>
<td>3141</td>
<td>L. H. Erickson (5)</td>
</tr>
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<td>3151</td>
<td>W. L. Garner (3)</td>
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