Statistical Design in Isothermal Aging of Polyimide Resins

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SYNOPSIS
Recent developments in research on polyimides for high temperature applications have led
to the synthesis of many new polymers. Among the criteria that determines their thermal
oxidative stability, isothermal aging is one of the most important. Isothermal aging studies
require that many experimental factors are controlled to provide accurate results. In this
article we describe a statistical plan that compares the isothermal stability of several po-
lyimide resins, while minimizing the variations inherent in high-temperature aging studies.

INTRODUCTION
The NASA Lewis Research Center HITEMP pro-
gram in polymer matrix composites (PMC) focuses
on the development of high-temperature polymers
for advanced aircraft engine fan and compressor ap-
plications. One of this program’s main goals is to
produce polymers that can withstand engine oper-
ating temperatures up to 425°C (800°F). Therefore,
an important feature of these polymers is their ther-
mal oxidative stability at high temperatures.
Several polymer matrix resins have been devel-
oped at NASA Lewis to meet these goals. PMR-II-
50 and VCAP-75 are two matrix resins that were
investigated in engine component development pro-
grams.1,2 Additional resins developed at Lewis for
high-temperature applications are N-CYCAP, 12F-
VCAP, 3F, and MARVimides. DuPont Company
and TRW, Inc. have also developed resins for high-
temperature applications. These resins are Avimid-
N®, and AFR700B.

We report the findings of a study that we designed
and analyzed with formal statistical methodologies.
Specifically, the study was designed to compare, in
a valid quantifiable manner, the respective weight
losses among a selected set of five different resins
after 400 h of exposure to high temperature (371°C).
The resins included in our investigation were
Avimid-N, AFR700B, PMR-II-50, VCAP-75, and N-
CYCAP (Fig. 1).
Implementation of a statistically designed study
allowed us to address the following two questions.
Can we determine weight loss differences between
these polymers? If so, how accurate are the estimated
differences? The design for this study accounted for
a location effect within the oven, and a molding
powder or disk effect within a polymer. Two molding
powders were available for PMR-II-50, VCAP-75,
and N-CYCAP. One disk was produced from each of
these powders. We obtained two disks from each
resin developed by DuPont and TRW (2 Avimid-N
disks and 2 AFR700B disks, respectively). Although
the disks of Avimid-N came from a single batch of
molding powder as did the disks of AFR700B, the
molding powder–molding powder variability within
a polymer was treated in the same way as the disk–
disk variability within a polymer.

EXPERIMENTAL

Instrumentation
All infrared spectra were recorded with a Nicolet
model 510P Fourier Transform Spectrometer in KBr
pellets. All thermal analyses were recorded on a PL
Thermal Sciences Thermal Analysis System. Ther-
mogravimetric analyses were done with a Perkin-
Elmer TGS-2 on postcured neat resin samples under
air using a scan rate of 10°C/min. Thermomechan-
Figure 1 Polyimides aged at 371°C.

Figure 1 Polyimides aged at 371°C.
ISOTHERMAL AGING OF PI RESINS

N-CYCAP

To a finely dispersed mixture of HFDA (4.06 g, 9.15 mmol) and glacial acetic acid (50 mL) was added p-PDA (0.88 g, 8.15 mmol) and 4-amino [2.2] paracyclophane (0.37 g, 1.6 mmol). The reaction mixture was refluxed. Initially, the reaction mixture separated into two phases. However, after 30 min the mixture became a clear amber solution. The homogeneous solution persisted for approximately 15 min before forming a precipitate. Refluxing was continued for an additional 12–16 h. Acetic anhydride (6 mL) was added to the slurry and stirred for an additional 2–3 h while refluxing. The reaction was cooled to room temperature and poured into a beaker containing ice water (150 mL) and stirred for 30 min. The mixture was filtered, and the molding powder was washed with cold water (3 × 150 mL) and air dried. The prepolymer was then vacuum dried at 100°C overnight. Typical yields ranged from 95 to 100%.

Processing Polymide Molding Powders and Aging of Neat Resins

A cylindrical 2.54-cm hardened-steel mold equipped with a thermocouple was sprayed with a high-temperature release agent (monocoat E63FF) and dried at room temperature for 20 min. Sheets of Kapton (0.5-mm thick) were sprayed with release agent and cut to fit in the mold. The Kapton was placed in the mold on the top and bottom of the molding powder. The mold was charged with approximately 1.3 g of prepolymer and placed in a preheated (380°C) press. When the temperature of the mold reached approximately 230°C, 6.9 MPa was applied. The temperature was increased from 230 to 370°C over 7 min and held at 370°C. After 2 h, the mold was cooled to 200°C, then the pressure was released, and finally, the resin disk was removed. No sample weight loss was observed during the molding process. All resins were postcured at 371°C in air for 16 h. Samples were predried at 135°C in air for 1 h and then placed in a desiccator. Once the postcured resins were cooled to 25°C, they were weighed and then placed in the air oven. The samples were aged for 400 h at 371°C. All of the resins remained in the oven for the 400-h period, that is, weight losses were not recorded at periodic intervals. After aging, the samples were placed in a desiccator and cooled to 25°C. The final weight loss values were calculated as follows: the weight of resins after postcuring minus the weight of resin after 400 h aging equals the weight of resin remaining.

RESULTS AND DISCUSSION

Each disk from each polymer was split into eight equally sized samples. We partitioned the tray into four locations to provide a valid comparison of percent weight losses among the resins that experienced similar aging conditions. Each location was 3 slots by 7 slots, that is, 21 slots. For a given polymer–disk combination, two samples were randomly assigned to each of the four rectangular locations. This procedure produced 20 samples per location (5 polymers × 2 disks /polymers × 2 samples /disks). The resulting 20 samples in a given location were randomly allocated to the 21 slots (Fig. 2). In our analysis, the percent weight losses were consistently different, for a given resin pair, from location to location (Table I).

Least squares was used to fit the following model:

\[ y_{ijkl} = \mu + R_i + L_j + RL_{ij} + B_{k(i)} + LB_{jk(i)} + \epsilon_{ijkl} \]  

where \( y_{ijkl} \) is weight loss; \( \mu \) is overall constant; \( R_i \) is fixed polymer effect; \( L_j \) is fixed location effect; \( B_{k(i)} \) is random molding powder within polymer effect; \( RL_{ij} \) is fixed resin by location interaction effect; \( LB_{jk(i)} \) is random location by molding powder interaction effect within polymer; \( \epsilon_{ijkl} \) is random error.
were treated as normal random variables with zero means and variances $\sigma^2_{ij}$, $\sigma^2_{il}$, and $\sigma^2_{lb}$.

The normal probability plot (used to evaluate our normal theory assumption) and residual plot (used to evaluate the constant variance assumption for every $y_{ijkl}$) both detected violations of the corresponding assumptions (Fig. 3). Hence, a natural logarithm transformation was applied to the $y_{ijkl}$'s, and least squares was used to fit the model given by eq. (2). The resulting normal probability plot showed a negligible departure from the assumed normal theory, and the residual vs. the predicted plot revealed a constant variance (Fig. 4). Thus, our analyses are applicable on the natural log scale (ln).

Table II contains development of the expected mean squares (MS) for the model

$$\ln(y_{ijkl}) = \mu + R_i + L_j + RL_{ij} + B_{k(i)} + LB_{j(k(i))} + \epsilon_{l(ijk)}.$$  

Table II is derived from the rules Neter et al.\textsuperscript{4} described, and indicates how to form test statistics applicable to the questions motivating this article. Table III presents an analysis of variance (ANOVA) obtained using the least squares methodology. We see that the ANOVA given in Table III contains estimates of the corresponding expected MS given in Table II. Thus, to test the null hypothesis $[H_0: \text{Each of the 10 polymer differences are the same for each location (} RL_{ij} = 0 \text{ for every } ij\text{.)}]$ against the alternate hypothesis $[H_A: \text{There exists at least one difference among polymers that is not the same from location to location (} RL_{ij} \neq 0 \text{ for at least one } ij \text{ combination.)}]$, the appropriate test statistic $(F)$ is indicated by Table II to be

$$F_{12,15} = \frac{\text{MS location } \times \text{ polymer}}{\text{MS location } \times \text{ powder (polymer)}}.$$  

For example,

Table I  

<table>
<thead>
<tr>
<th>Location</th>
<th>Avimid-N</th>
<th>AFR700B</th>
<th>VCAP-75</th>
<th>N-CYCAP</th>
<th>PMR-II-50</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9.7</td>
<td>26.7</td>
<td>26.2</td>
<td>25.2</td>
<td>28.8</td>
</tr>
<tr>
<td>2</td>
<td>9.8</td>
<td>23.6</td>
<td>23.1</td>
<td>24.7</td>
<td>25.2</td>
</tr>
<tr>
<td>3</td>
<td>8.9</td>
<td>21.9</td>
<td>22.7</td>
<td>22.2</td>
<td>24.3</td>
</tr>
<tr>
<td>4</td>
<td>10.7</td>
<td>23.5</td>
<td>24.5</td>
<td>26.3</td>
<td>30.8</td>
</tr>
<tr>
<td>Average (1-4)</td>
<td>9.8</td>
<td>23.9</td>
<td>24.2</td>
<td>24.6</td>
<td>27.2</td>
</tr>
</tbody>
</table>

Means averaged across locations. Aging performed in a Blue M, Model CW160E-MP with a temperature capability up to 704°C. Environment for 371°C testing: 1 atm air.
For a level of significance $\alpha = 0.05$, we require $F_{(12,15,\alpha=0.05)} = 2.48$. Because $F_{(12,15,\text{calc})} < 2.48$, we do not have strong evidence to conclude that there exists at least one difference among polymers that is not the same from location to location ($H_A$). Instead, we conclude that there is no interaction of location with polymer type ($H_0$). In fact, the $p$ value (observed significance level) > 0.10.

Because polymer differences are consistent from location to location, it is valid to average the polymer log percent weight losses across locations before comparing them to one another. Therefore, to test this null hypothesis ($H_0$: All polymers are the same with respect to average log percent weight loss.) against an alternate hypothesis ($H_A$: At least one polymer is different from one or more polymers with respect to average log percent weight loss.), we use Table II to identify the appropriate statistic as

$$F_{12,15,\text{calc}} = \frac{0.00919039}{0.00521} = 1.7639.$$  \hspace{1cm} (4)

For example,

$$F_{4,5,\text{calc}} = \frac{2.842411}{0.00924} = 307.6202.$$  \hspace{1cm} (6)

For a level of significance $\alpha = 0.05$, we require $F_{(4,5,\alpha=0.05)} = 5.19$. Because $F_{(4,5,\text{calc})} > 5.19$, we have strong evidence to conclude that there exists at least one difference among the true average log percent weight losses for the respective polymers ($H_A$). The $p$ value < 0.01.

Fisher’s protected least significant difference (LSD)\(^6\) and Tukey’s honest significant difference (HSD)\(^4\) are the two multiple comparison methods we applied to evaluate the differences in percent weight loss from polymer to polymer (on the In scale) (Table IV). A 0.05 significance level was chosen for each method. Differences in the mean of the logs among the five polymers are displayed with material footnoted Table IV. Fisher’s protected LSD grouped the polymers as indicated by footnote a. With the more conservative Tukey’s HSD, we observed the grouping illustrated with footnote b.
Resins are grouped together when there is no significant difference in the weight loss among them on the natural log scale according to the method used. We conclude that there is a 5% chance that we have made at least one mistake in the seven significant differences detected using the LSD method, and in the four significant differences using the HSD method (footnotes a and b in Table IV).

The only difference in Tukey's HSD and Fisher's protected LSD is that PMR-II-50 is judged to be in the same group as AFR700B, VCAP-75, and N-CYC-CAP with Tukey's HSD (footnote b, Table IV), whereas the LSD method identified that an important difference existed between PMR-II-50 and the other polymers (footnote a, Table IV). Another graphic representation of Fisher's protected LSD and Tukey's HSD methods can be seen in Figures 5 and 6, respectively. The conclusions drawn from Figures 5 and 6 are mathematically equivalent to those drawn from Table IV(b). This corresponds to

![Graphs showing residual and normal probability plots](image)

**Figure 4** (a) Residual and (b) normal probability plots using the transformed data.

<table>
<thead>
<tr>
<th>Table II</th>
<th>Expected Mean Squares for Stated Model [Eq. (2)]</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Source</strong></td>
<td><strong>Degrees of Freedom</strong></td>
</tr>
<tr>
<td>Corrected total</td>
<td>79</td>
</tr>
<tr>
<td>Polymer</td>
<td>4</td>
</tr>
<tr>
<td>Location</td>
<td>3</td>
</tr>
<tr>
<td>Location \times polymer</td>
<td>12</td>
</tr>
<tr>
<td>Powder (polymer)</td>
<td>5</td>
</tr>
<tr>
<td>Location \times powder (polymer)</td>
<td>15</td>
</tr>
<tr>
<td>Error</td>
<td>40</td>
</tr>
</tbody>
</table>
Table III  Analysis of Variance for Fitted Model Using ln(y)

<table>
<thead>
<tr>
<th>Source</th>
<th>Degrees of Freedom</th>
<th>Sum of Squares</th>
<th>Mean Squares</th>
</tr>
</thead>
<tbody>
<tr>
<td>Corrected total</td>
<td>79</td>
<td>12.096</td>
<td></td>
</tr>
<tr>
<td>Polymer</td>
<td>4</td>
<td>11.369</td>
<td>2.8424</td>
</tr>
<tr>
<td>Location</td>
<td>3</td>
<td>0.29665</td>
<td>0.09888</td>
</tr>
<tr>
<td>Location × polymer</td>
<td>12</td>
<td>0.11028</td>
<td>0.00919</td>
</tr>
<tr>
<td>Powder (polymer)</td>
<td>15</td>
<td>0.04623</td>
<td>0.00924</td>
</tr>
<tr>
<td>Location × powder (polymer)</td>
<td>1</td>
<td>0.07816</td>
<td>0.00521</td>
</tr>
<tr>
<td>Error</td>
<td>40</td>
<td>0.19519</td>
<td>0.00488</td>
</tr>
</tbody>
</table>

The underscoring in Table IV(a). If the bounds do not overlap in Figures 5 and 6, significant differences exist above and beyond that due to randomness among the means of the natural log percent weight loss for each of the resins.

Tukey's HSD method is more conservative because its interpretation implies that not only is there at most a 5\% chance that we have made at least one mistake in the four identified differences, but that we have a 95\% chance or confidence that all the 10 intervals for the differences in means of the log percent weight losses actually include the true differences. This cannot be said using Fisher's protected LSD. The raw mean of percent weight loss for each of the polymers averaged across locations and for each location are shown in Table I.

The 10 HSD 95\% intervals mentioned in the previous paragraph take on the form

\[ \bar{D} \pm T \cdot s(\bar{D}). \]  

\( \bar{D} \) is the estimated difference in the average log percent weight loss, after averaging across locations, for a given pair of polymers. The estimated standard deviation of \( \bar{D} \) is

\[ s(\bar{D}) = \left[ \frac{1}{T} \text{MS powder (polymer)} \right]^{1/2}. \]  

The constant \( T \) is available from statistical tables. (See Neter et al.⁴ for details of Tukey's HSD multiple comparison methods.) Table V contains the 10 intervals constructed using Tukey's HSD 95\% confidence interval methodology.

Now, one might ask about the interpretation of our results in terms of the raw data (percent weight loss). We gain insight into this question by back-transforming with the exponential transformation. Because our normal probability plot revealed logs of the percent weight losses to be normally distributed, we are dealing with the lognormal distribution; that is, ln(y,\( y_w \)) is normally distributed. Denoting \( \delta \) as the true mean of a lognormally distributed random variable, \( \delta \) is also the median of the lognormally distributed random variable because of symmetry.

Table IV  Comparison of Fisher's Protected LSD Test and Tukey's Honest Significant Difference Test

<table>
<thead>
<tr>
<th>Resin</th>
<th>Avimid-N</th>
<th>AFR700B</th>
<th>VCAP-75</th>
<th>N-CYCAP</th>
<th>PMR-II-50</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean of ln</td>
<td>2.278</td>
<td>3.172</td>
<td>3.185</td>
<td>3.198</td>
<td>3.301</td>
</tr>
<tr>
<td>(b) Differences of Means&lt;sup&gt;⁵&lt;/sup&gt;</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Avimid-N</td>
<td>0.893&lt;sup&gt;ab&lt;/sup&gt;</td>
<td>0.906&lt;sup&gt;ab&lt;/sup&gt;</td>
<td>0.920&lt;sup&gt;ab&lt;/sup&gt;</td>
<td>1.022&lt;sup&gt;ab&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>AFR700B</td>
<td>0.013&lt;sup&gt;ab&lt;/sup&gt;</td>
<td>0.096&lt;sup&gt;ab&lt;/sup&gt;</td>
<td>0.026</td>
<td>0.129</td>
<td></td>
</tr>
<tr>
<td>VCAP-75</td>
<td>0.014</td>
<td>0.013</td>
<td>0.116&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.103&lt;sup&gt;a&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>N-CYCAP</td>
<td>0.013</td>
<td>0.014</td>
<td>0.116&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.103&lt;sup&gt;a&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>PMR-II-50</td>
<td>0.013</td>
<td>0.014</td>
<td>0.116&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.103&lt;sup&gt;a&lt;/sup&gt;</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup> Break in underscoring indicates an important statistical difference has been determined using Fisher's protected LSD: LSD<sub>0.05</sub> = 0.087.
<sup>b</sup> Break in underscoring indicates an important statistical difference has been determined using Tukey's HSD: HSD<sub>0.05</sub> = 0.188.
<sup>c</sup> After transformation.
Furthermore, the ln transformation is monotonic, that implies that if the median of the original variable \(y\) is, for example, \(m\), the median of the transformed variable (ln \(y\)) is ln \(m\). Hence, \(\delta = \ln(m)\). Back-transforming with the exponential function gives \(\exp(\delta) = m\), the median of the untransformed (or original) variable. To continue, if we let \(\delta_i = \ln(m_i)\), where \(\delta_i\) is the mean of the \(i^{th}\) lognormally distributed population and \(m_i\) is the median of the respective untransformed population, we have

\[
\delta_i - \delta_j = \ln(m_i) - \ln(m_j), \quad i \neq j. \tag{9}
\]

Thus, using the exponential transformation, we obtain

\[
\exp(\delta_i - \delta_j) = \exp[\ln(m_i) - \ln(m_j)]
\]

or

\[
\exp(\delta_i - \delta_j) = m_i/m_j. \tag{10}
\]

Now, \(m_i/m_j\) is the ratio of medians from respective populations in terms of the untransformed data. Turning to Table V, we use the exponential transformation of the end points from each of the respective intervals. The resulting confidence intervals estimate the ratio of the corresponding polymer median percent weight losses (with the same group or family confidence level equal to 95%). These intervals are given in Table VI.

There is one final yet important note regarding our findings. Deming and, more recently, Hahn and Meeker have detailed the important distinction between an enumerative and an analytic study. Our study is considered analytic. Hence, our results require the critical assumption that molding powders...
made in the future vary in the same manner as those selected for this study and that the procedure for making disks varies in the same manner in the future as for this study. This complies with the requirement noted by Hahn and Meeker\textsuperscript{10} that “analytic studies require the critical added assumption that the process about which one wishes to make inferences is statistically identical to that from which the sample was selected.”

**SUMMARY AND CONCLUSIONS**

A method was developed to reliably determine if differences exist in the thermal oxidative stability of resins. In addition to quantifying these differences by percent weight loss, the design of the experiment enabled us to correctly adjust for temperature gradients in the oven and the variability that exists within a resin type (i.e., molding powder–molding powder, disk–disk, and within a given disk). Finally, although two methods were used to determine differences in thermal oxidative stability, the only resin that was noticeably different (lowest weight loss) in both analyses was Avimid-N. We believe that this difference can be attributed to two factors. (1) Although all of the other polyimides in this study, which were addition-curing polyimides, have end caps, Avimid-N does not. These end caps have aliphatic carbons that can oxidize and contribute toward thermal oxidative weight loss. (2) Of the five polymers studied, Avimid-N was the only polymer not processed in our laboratories and we have no basis for comparing the processing conditions because those for Avimid-N are proprietary. However, it is well known that processing conditions contribute to the thermal oxidative stability of polymers.\textsuperscript{11}

The authors wish to thank Professor H. T. David, Department of Statistics at Iowa State University, and Professor David Weeks, Department of Statistics at Oklahoma State University for their advice on the statistical modeling. In addition, we express our gratitude to Marla Schuerman for her assistance in molding the resins and Dan Scheiman for the thermal analysis studies performed on these resins. Samples of AFR700B were purchased from Dr. Joseph Reardon at HYCOMP in Cleveland, OH. Avimid-N was supplied by Dr. Murty S. Tanikella at DuPont Advanced Composites.

**REFERENCES**


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