Moisture Absorption Modeling Using Design of Experiments

Virginia Yong,[1] **H. Thomas Hahn**[1,2]

[1]*Materials Science and Engineering Department, University of California, Los Angeles, CA 90095*
[2]*Mechanical and Aerospace Engineering Department, University of California, Los Angeles, CA 90095*

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ABSTRACT: The effect of temperature and humidity on equilibrium moisture content of laminates was studied by response surface design. Two glass fabric-reinforced laminated composite materials with different epoxy matrix resins, laminates A and B, were studied. Laminates A and B used are cyanate ester and polyphenylene oxide modified epoxy based laminate, respectively. The results show that the response surface profiles of moisture absorption for the two laminate materials are similar though their amounts of moisture absorption are different. The temperature-humidity interaction effect and the quadratic effect of temperature are significant for laminate A. However, only the linear effects of temperature and humidity are significant for laminate B. Predictive models relating the important factors to the equilibrium moisture content were proposed in the article. The models developed can be used to predict and assess the reliability of the laminates for moisture related failures. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 1539–1543, 2007

Key words: design of experiments; laminate; modeling; moisture absorption

INTRODUCTION

Laminate manufacturing is a process consisting of encapsulating a ply (or several plies) of fabric within a polymeric resin. The fabric-resin combination provides dielectric as well as mechanical and thermomechanical properties. However, since the resins used in laminates are hydrophilic, the assembly can be susceptible to performance degradation and failure mechanisms driven by environmental moisture.[1] Resin manufacturers have attempted to improve the hygrothermal properties of resins by blending them with other thermosetting and thermoplastic components of higher glass transition temperatures and lower water absorption. Recent matrix formulations have combined epoxy resins with cyanate ester (CE) and polyphenylene oxide (PPO).[2,3]

The most common models for characterizing the hygrothermal effects in polymers are Fickian model[4] and Langmuir equation.[5] Unfortunately, the laws of Fickian and Langmuir are frequently inadequate for modeling the moisture absorption in polymers or polymer composites.[6,7]

Statistically based design of experiments (DOE) help to increase the speed of the development cycle time, improve reliability, reduce process variability, and increase overall product quality. At the nanoscale, the effects of design parameters on product characteristics cannot usually be known purely from phenomenological models and therefore, nanomanufacturing systems often require extensive data collection and analysis. As a result, statistically based DOE are playing an important and increasing role in nanomanufacturing.[8,9]

In this article, a modeling methodology based on statistically designed experiments was used to examine the dependence of equilibrium moisture content on temperature and relative humidity. Two laminate materials A and B, received from two manufacturers, were studied. Laminate A is a CE-modified epoxy resin. Laminate B is a PPO-modified epoxy resin. Both laminates are reinforced with electrical grade (E-glass) glass fabric.

EXPERIMENTAL

The laminates, with a thickness of 2.3 mm, were cut to dimensions of 80 mm by 10 mm coupons using a water-cooled diamond wheel. The hygrothermal environments for the tests were generated by an environmental chamber. Gravimetric analysis was conducted with a scale that has a resolution of $0.0001 \times g$ to assess moisture content, which was expressed as a percentage of the laminate's initial dry mass per eq. (1).

$$\text{Moisture content } (\%) = \frac{M_{\text{measured}} - M_{\text{dry}}}{M_{\text{dry}}} \times 100\% \qquad (1)$$

where M_{measured} is the measured mass at equilibrium moisture content (g), and M_{dry} is the dry mass (g).

Correspondence to: V. Yong (hyong@ucla.edu).

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TABLE I
Design Matrix of Moisture Absorption Experiments

Setting	Coded values Temperature (°C)	 Humidity (%RH)	Uncoded values Temperature (°C)	 Humidity (%RH)
1	−1	−1	39	39
2	−1	+1	39	81
3	+1	−1	81	39
4	+1	+1	81	81
5	−1.414	0	30	60
6	+1.414	0	90	60
7	0	−1.414	60	30
8	0	+1.414	60	90
9	0	0	60	60

The dry mass was obtained by baking the laminates at 115°C prior to each test. The measured mass at equilibrium moisture content was obtained by placing the laminate in isothermal environments at a constant relative humidity. The laminate mass was measured every 12 h. The dry mass and ''equilibrium'' saturated level of moisture content were attained when there was no observable change in the laminate mass, per the 0.0001 × *g* resolution.

SAS, produced by the SAS Institute, is an integrated statistical package that provides a complete, comprehensive, and integrated platform for statistical data analysis. In this study, SAS was used as the statistical software for the design of experiments (DOE). Response surface methodology (RSM) using the central composite design[8,10] was employed to develop the model of moisture content as a function of temperature and relative humidity. The four factorial points (n_f) were set with −1 and +1 level at 39 and 81, respectively. A blocking factor was used to examine any difference between the moisture content for different production lots of the same laminate material. An orthogonal design with six center points (n_c) at 60 (0 level) was used to estimate the mean square error

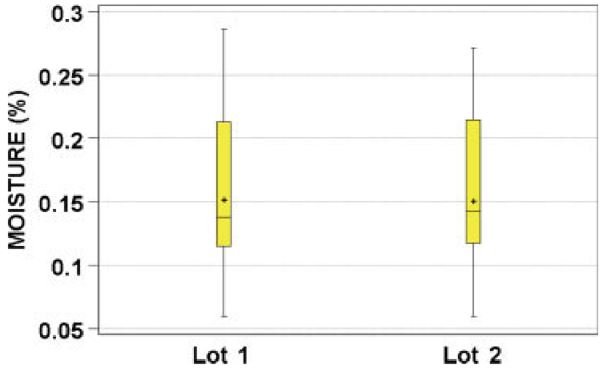
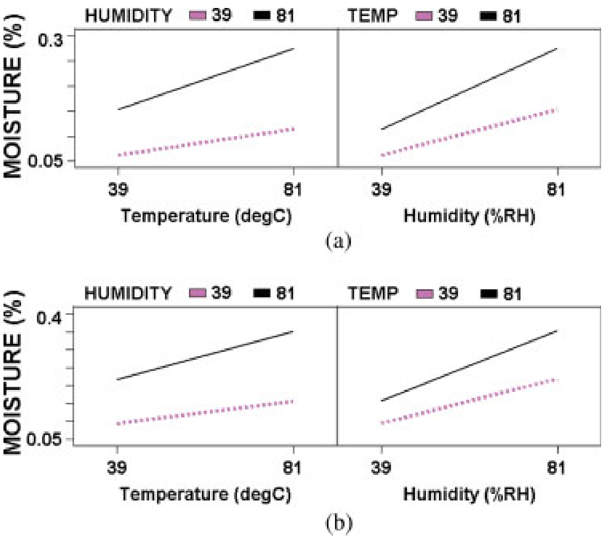


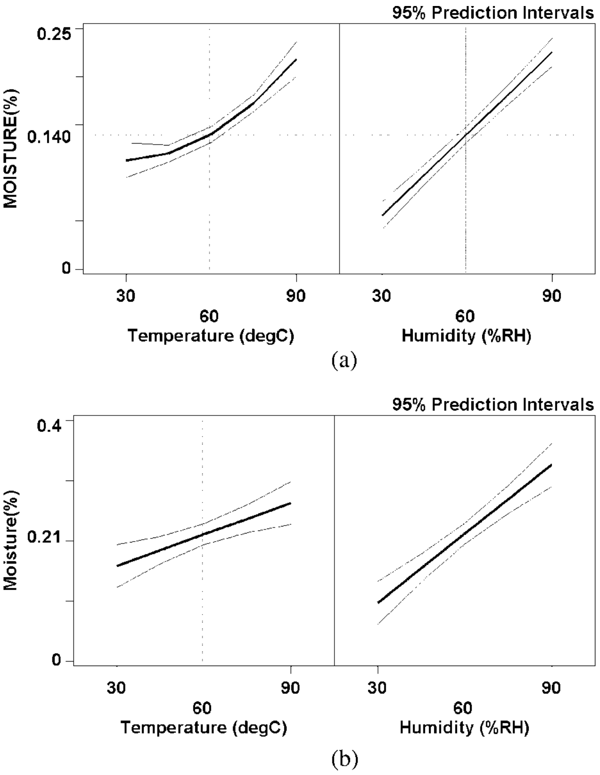
Figure 1 Box plot showing that there is no difference in moisture content for different production lots of the same laminate material. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]



(a)

(b)

Figure 2 Interaction plots for (a) laminate A, cyanate ester modified epoxy resin, and (b) laminate B, polyphenylene oxide modified epoxy resin, showing that both temperature and humidity increase the moisture absorption, and temperature–humidity interaction appears slightly significant. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]



(a)

(b)

Figure 3 Prediction profile plots for (a) laminate A, cyanate ester modified epoxy resin, and (b) laminate B, polyphenylene oxide modified epoxy resin, showing that humidity has a larger effect than temperature in moisture absorption. The nonlinear effect of temperature appears to be significant for laminate A.

TABLE II
Fit details of moisture absorption experiments

(a) Laminate A - cyanate ester modified epoxy resin

Master Model

Term	Estimate	Std Err	MS	F	Pr > F
Temp	0.03794	0.00367	0.01143	107.11	0.0001
Humidity	0.06048	0.00367	0.02904	272.13	0.0001
Temp * Temp	0.01336	0.00395	0.00122	11.43	0.0117
Temp * Humidity	0.01715	0.00517	0.00118	11.02	0.0128
Humidity * Humidity	0.00263	0.00395	0.00005	0.44	0.5277

Predictive Model

Term	Estimate	Std Err	MS	F	Pr > F
Temp	0.03794	0.00354	0.01143	115.14	0.0001
Humidity	0.06040	0.00353	0.02899	292.10	0.0001
Temp * Temp	0.01304	0.00378	0.00118	11.88	0.0087
Temp * Humidity	0.01715	0.00498	0.00118	11.85	0.0088

(b) Laminate B - polyphenylene oxide modified epoxy resin

Master Model

Term	Estimate	Std Err	MS	F	Pr > F
Temp	0.03754	0.01081	0.01119	12.07	0.0104
Humidity	0.08122	0.01081	0.05236	56.48	0.0001
Temp * Temp	−0.00018	0.01165	0.00000	0.00	0.9882
Temp * Humidity	0.01780	0.01522	0.00127	1.37	0.2806
Humidity * Humidity	−0.00635	0.01165	0.00028	0.30	0.6026

Predictive Model

Term	Estimate	Std Err	MS	F	Pr > F
Temp	0.03752	0.01005	0.01119	13.92	0.0039
Humidity	0.08142	0.01005	0.05268	65.57	0.0001

(MS_E) and the sum of the square of curvature effect ($SS_{curvature}$). Four (2×2) axial points (n_a) with -1.414 level set at 30 and $+1.414$ level set at 90 were augmented to the factorial points to make the design rotatable. Two replicates were used for each treatment combination to increase the number of degrees of freedom for the mean square error estimation. The design matrix is shown in Table I.

RESULTS AND DISCUSSION

A box plot displays the minimum, the maximum, the lower, and upper quartiles (the 25th percentile and the 75th percentiles, respectively), and the median (the 50th percentile) of the measured parameter. The box plot shows that there is no significant difference in moisture content for different production lots of the same laminate material, as illustrated by the close values in median and variability of moisture content for different lots, lots 1 and 2 (Fig. 1).

The interaction effect plots indicate that both temperature and humidity increase the moisture absorption significantly as shown by the higher moisture content from level -1 to $+1$ (Fig. 2). The temperature–humidity interaction effect appears slightly significant as indicated by the nonparallelism of the $-$ and $+$ lines. A larger moisture content variation was also observed with an increase in temperature and humidity as shown by the wider 95% confidence intervals from level -1 to $+1$. Although both laminate materials exhibit a similar interaction plot, laminate B (PPO modified epoxy resin) was found to absorb a larger amount of moisture than laminate A (CE modified epoxy resin) at the same conditions.

The prediction profile plots show that the humidity has a larger effect than temperature in moisture absorption, as illustrated by a larger increase in moisture content from level -1.414 to $+1.414$ for humidity when compared with temperature (Fig. 3). The effect of humidity over the tested range appears to be linear. However, the nonlinear effect of temperature appears to be significant for laminate A (CE modified epoxy resin) [Fig. 3(a)].

Table II shows the fit details for equilibrium moisture content.[10,11] For laminate A (CE modified epoxy resin), the quadratic effect of humidity was found to be insignificant. Therefore, the sum of square of the

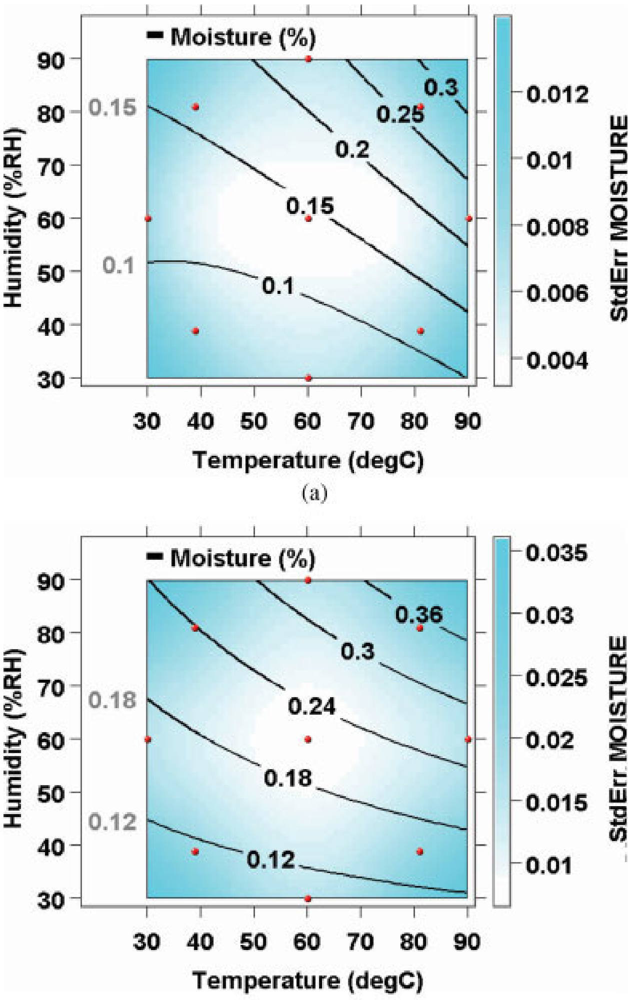


Figure 4 Contour plots showing the moisture profile of (a) laminate A, cyanate ester modified epoxy resin, and (b) laminate B, polyphenylene oxide modified epoxy resin. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

quadratic effect of humidity was pooled to obtain the pooled mean square error for the predictive model. The linear effects of temperature and humidity are highly significant at 0.01%. Both the temperature–humidity interaction effect and the quadratic effect of temperature were also found to be significant at 1%. For laminate B (PPO modified epoxy resin), both the linear effects of temperature and humidity are significant, at 0.5% and 0.01%, respectively. The temperature–humidity interaction term and the quadratic terms were found to be insignificant.

On the basis of the percentage contribution of the sum of square effect of each term in the master model, the linear effect of humidity was found to be the dominating factor in contributing to the moisture absorption. The linear effect of temperature is also a main factor, contributing to about one-quarter of the source of moisture absorption. Although the temperature–humidity interaction effect and the quadratic effect of temperature are significant for laminate A (CE modified epoxy resin), their effects only contribute about 5% of the source of moisture content.

The important terms to the response were identified, according to the F statistic in Table II. A second-order predictive model relating the important factors to the equilibrium moisture content was developed [eq. (2)].

$$M = \beta_0 + \beta_1 T + \beta_2 H + \beta_{11} T^2 + \beta_{22} H^2 + \beta_{12} TH \text{ for } 30 \le T \le 90 \text{ and } 30 \le H \le 90 \quad (2)$$

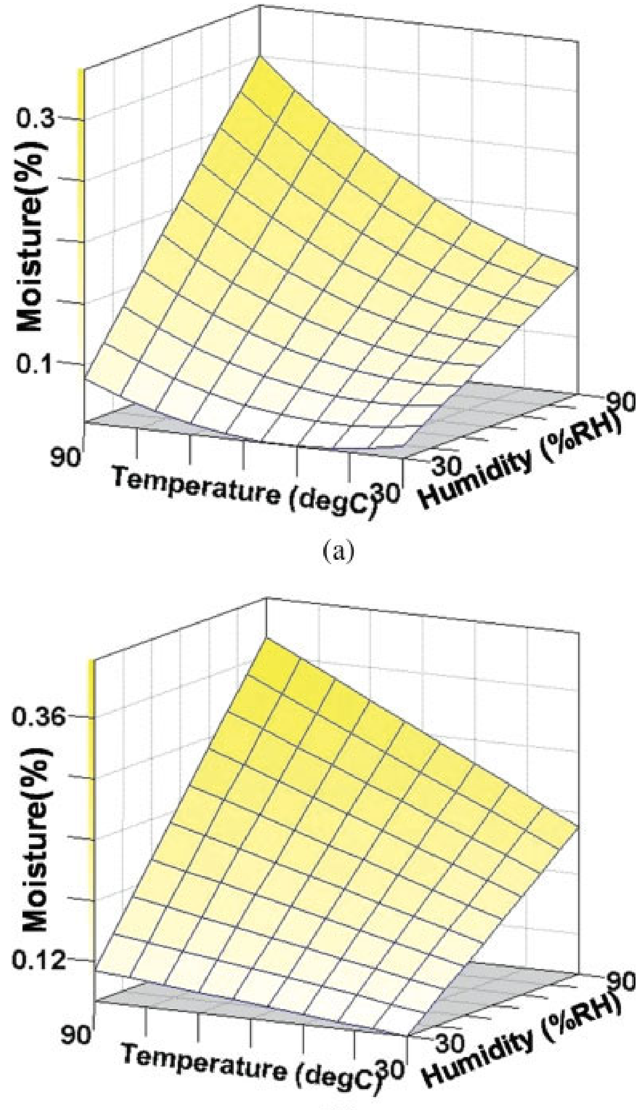


Figure 5 Surface plots for (a) laminate A, cyanate ester modified epoxy resin, and (b) laminate B, polyphenylene oxide modified epoxy resin, showing that the effect of temperature increases with humidity. The effect of humidity on moisture absorption also increases with temperature. A curvature effect of temperature was observed for laminate A. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

where M is moisture content (%), T is temperature (°C), and H is relative humidity (%RH). For laminate A (CE modified epoxy resin), $\beta_0 = 0.11$; $\beta_1 = -4.1 \times 10^{-3}$; $\beta_2 = 5.4 \times 10^{-4}$; $\beta_{11} = 3.0 \times 10^{-5}$; $\beta_{22} = 0$ (unimportant); and $\beta_{12} = 3.9 \times 10^{-5}$. The root mean square error (RMSE) is 0.0099; and the adjusted R-square is 0.97. For laminate B (PPO modified epoxy resin), $\beta_0 = -0.13$; $\beta_1 = 1.8 \times 10^{-3}$; $\beta_2 = 3.9 \times 10^{-3}$; and $\beta_{11} = \beta_{22} = \beta_{12} = 0$ (unimportant). The RMSE is 0.028, and the adjusted R-square is 0.87.

The adjusted R-square measures the proportion of variability in the data accounted for by the regression model. The model for laminate A (CE modified epoxy resin) has the adjusted R-square value of 0.97, which indicates that about 97% of the variability in equilibrium moisture content is explained by the model. The model for laminate B (PPO modified epoxy resin) is a simpler model. However, it also has a smaller adjusted R-square value of 0.87.

Figure 4 shows the contour plots of equilibrium moisture content. The nine dots on the contour plot correspond to the nine design points of the design matrix specified in Table I. Although the amount of moisture absorption is different for these two laminate materials, their moisture profiles were found to be similar.

The surface plots show that the effect of temperature on moisture absorption increases with humidity (Fig. 5). The effect of humidity on moisture absorption was also found to increase with temperature. For laminate A (CE modified epoxy resin), a curvature effect of temperature was observed. At a low humidity level of 30% RH, an increase in temperature, from 30 to about 50°C, reduces the moisture content. A further increase of temperature beyond 50°C causes an increase in moisture absorption.

CONCLUSIONS

The dependence of equilibrium moisture content on temperature and humidity was studied using statistical DOE. Two glass fabric-reinforced laminated composite materials with different epoxy matrix resins, laminate A (CE modified epoxy resin) and laminate B (PPO modified epoxy resin), were studied. The results show that both temperature and humidity increase the moisture content. The response surface profiles of moisture content are similar for the two laminate materials although their amounts of moisture absorption are different. Laminate B (PPO modified epoxy resin) was found to absorb a larger amount of moisture than laminate A (CE modified epoxy resin). The observed good resistance to moisture absorption of CE modified epoxy resin might be attributed to the formation of a higher crosslink density resin network when compared with that of the epoxy/PPO matrix.[3,12,13] For laminate A, both the temperature–humidity interaction effect and the quadratic effect of temperature are significant at 1%. For laminate B, only the linear effects of temperature and humidity were found to be significant.

The predictive model of laminate A (CE modified epoxy resin), which contains the interaction and quadratic terms has an adjusted R-square value of 0.97, which indicates that about 97% of the variability in equilibrium moisture content is explained by the model. The predictive model of laminate B (PPO modified epoxy resin) is simpler due to the absence of second-degree terms, however, it also has a smaller adjusted R-square value of 0.87.

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