Prediction of Cure Overheating in Thick Adhesive Bondlines for Wind Energy Applications

Alessandro G. Cassano, Scott E. Stapleton, Christopher J. Hansen, and Marianna Maiaru
University of Massachusetts Lowell, MA, 01854, USA

Abstract: Bondline failure is a key failure mode in wind turbine blades. One of the dominant sources of failure can be the degradation of the adhesive due to the cure overheating. Substantial variation in bondline thickness can result in different thermal histories for the adhesive layer due to the exothermic curing of common adhesives. Predictive guidance on the impact of this variability in adhesive cure temperature cycle is extremely limited. A finite element model capable of tracing the thermal and conversion histories in the adhesive has been developed to address this problem. To be successful in predicting the effects of the exothermic reaction on temperature within the adhesive in cure cycle simulations, the standard heat transfer equation has been coupled with a cure kinetics model in Abaqus/CAE implementing user subroutines. The model is shown to successfully capture the thermal and conversion histories for different cure temperature cycles, including the thickness effects of the adhesive on the exothermic reaction. The accuracy of the model strongly depends on the fidelity of the cure kinetics law implemented to the actual conversion in the adhesive for prescribed cure cycles. This study can provide an efficient approach to optimize the cure cycles of thick bondline, reducing the cure time and maintaining the integrity of adhesives bonds.

Keywords: Cure kinetics, Heat Transfer, Adhesives, Thick bondlines

1. Introduction

Thick adhesive bondlines (>10 mm) are commonly used in wind turbine blade manufacturing. The curing of thermosets like epoxies in thick composite laminates has been extensively studied (Kim, 1997). The overheating due to the exothermic reaction affects the mechanical performance of composite laminates and can result in a drop of the interlaminar shear strength (Esposito, 2016), (Lahuerta, 2017). However, the effects of cure overheating in thick bondlines is not well understood and predictive tools, which enable the optimization of cure cycles, are missing. The heat generated by the exothermic reaction can lead to degradation in the center of thick adhesives where the peak temperature is reached, reducing the quality of the bondline, which can cause premature cracks and failure. Variations in bondline thickness may result also in different thermal histories within the adhesive and development of gradients in the conversion during the cure cycles (Antonucci, 2002; Sorrentino, 2015).

Several studies have been conducted on the simulation of thick composites curing (Park, 2003). To take in account the thickness influence on the exothermic reaction in the curing process of
thermosets, the heat transfer equations have been coupled with cure kinetics models. The first models considered one or two-dimensional problems solved by finite difference method (Bogetti, 1991). Later, finite element packages were developed to address three-dimensional problems by several authors (Park, 2001), (Hoon Oh, 2002). Nowadays commercial finite elements software enable the coupling of cure kinetics law with the heat transfer equation by adding user subroutines to the model (Rabearison, 2009; Shevtsov, 2012; Anandan, 2017).

In the current study, a computational model, which enables the prediction of the thermal and conversion histories in thick adhesive bondlines is developed. The heat transfer problem is coupled with an analytical cure kinetics law in Abaqus. In the first part, the governing equations of the problem are presented. The cure kinetics model is characterized by isothermal DSC experiments and implemented in the model using user subroutines. The FE model and problem assumptions are discussed and two numerical examples are shown to demonstrate the effectiveness of predictive models in cure cycle design. The adhesive system used in the model is a commercial epoxy-based resin in combination with a slow curing agent by Hexion. A standard cure cycle is compared with a two-step cure cycle and the results from the simulation are presented. Finally, the potential of enhancing cure cycles for thick adhesive bondline is discussed.

2. Materials and methods

The curing process of a thick adhesive bondline was simulated using the commercial FE software Abaqus (Abaqus Users Manual, 2016). A geometry, which is a simplified representation of the trailing edge of a wind turbine blades was modelled in Abaqus/CAE to simulate the effects of bondline variation in the cure process. The facesheets are glass fiber-reinforced composite panels (GFRP) and the bonding material is an adhesive with bondline variation from 0.2 mm to 40 mm (Figure 1).

![Figure 1. a) Wind turbine blade sketch (GFRP laminates in grey and adhesive bondlines in green) and b) trailing edge simplified geometry.](image)

The adhesive system used in this study is a commercial epoxy-based resin paste (EPIKOTE™ Resin MGS BPR 135G3) and a slow curing agent (EPIKURE™ Curing Agent MGS BPH 137G). The matrix system used for the laminates is also a commercial resin by Hexion EPIKOTE™ Resin MGS® RIMR135 and EPIKURE™ Curing Agent MGS. Both the EPIKOTE™ and EPIKURE™ systems are from Hexion Inc. The thermal properties of the materials used in the cure model, listed
in Table 1, are taken from literature on similar epoxy systems (Kalogiannakis, 2004; Bailleul, 1196; Sweeting, 2004; Sundqvist, 1977).

Table 1. Thermal properties of the trailing edge materials.

<table>
<thead>
<tr>
<th></th>
<th>Specific heat $C_p$ (J/Kg °C)</th>
<th>Conductivity $\lambda$ (W/m °C)</th>
<th>Density $\rho$ (Kg/m$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass fiber composites (GFRP)</td>
<td>805</td>
<td>0.47</td>
<td>1870</td>
</tr>
<tr>
<td>Cured adhesive</td>
<td>1100</td>
<td>0.43</td>
<td>1270</td>
</tr>
<tr>
<td>Uncured adhesive</td>
<td>1640</td>
<td>0.21</td>
<td>1200</td>
</tr>
</tbody>
</table>

As is the standard approach in industrial manufacturing, in the model the GFRP is assumed to be fully cured; the only reactive part is the adhesive. To characterize the heat generated by the exothermic reaction, a cure kinetics model was developed for the adhesive system and coupled with the heat transfer equation.

3. Governing equations

The general governing equation of the heat transfer problem is:

$$\rho C_p \frac{dT}{dt} = -\text{div}\{\lambda T\left[-\text{grad}T\right]\} + q$$  \hspace{1cm} (1)

where $\rho$ is the density, $C_p$ the specific heat, $\lambda$ the thermal conductivity and $q$ the heat source. Due to the exothermic nature of this process, an additional term that describes the heat flux generated from the chemical reactions involved is needed:

$$\rho C_p \frac{dT}{dt} = -\text{div}\{\lambda T\left[-\text{grad}T\right]\} + q + \rho \Delta H \frac{d\alpha}{dt}.$$  \hspace{1cm} (2)

The additional term is a function of $\Delta H$, which is the total enthalpy and the rate of curing $d\alpha/dt$. A kinetic curing law has to be coupled with the former heat transfer equation, to solve the coupled system for the unknown fields of temperature, $T$ and cure, $\alpha$:

$$\frac{d\alpha}{dt} = K(T)f(\alpha)$$  \hspace{1cm} (3)

Equation 3 expresses the general formula for a cure kinetics law, and can be split in two functions: $K(T)$, which depends on the temperature in an Arrhenius form, and $f(\alpha)$, which depends on the degree of curing and can vary based on the hypothesis about the $n$-th and $m$-th order of the reactions (Halley, 1996):

$$K_i = A_i \exp\left(-\frac{E_i}{RT}\right)$$  \hspace{1cm} (4)

$$f(\alpha) = (1 - \alpha)^n \alpha^m$$  \hspace{1cm} (5)
where $A_i$ is the pre-exponential factor, $E_i$ is the activation energy of the reaction and $m$, $n$ are called exponential factors and describe the order of the reaction. The kinetic law implemented in this study is the Kamal and Sourour autocatalytical model (Sourour, 1976), defined as:

$$\frac{d\alpha}{dt} = (K_1 + K_2 \alpha^m)(1 - \alpha)^n.$$  \hspace{1cm} (6)

In order to determine these parameters, a differential scanning calorimetry (DSC) analysis was conducted on the adhesive system. Regarding the adhesive, because the thermal properties of the adhesive evolves during the curing cycle (Kalogiannakis, 2004), they have been defined as a linear combination of the uncured and cured values depending on $\alpha$:

$C_p(\alpha) = \alpha C_p(1) + (1 - \alpha)C_p(0)$ \hspace{1cm} (7)

$\lambda(\alpha) = \alpha \lambda(1) + (1 - \alpha)\lambda(0)$ \hspace{1cm} (8)

and

$\rho(\alpha) = \alpha \rho(1) + (1 - \alpha)\rho(0)$. \hspace{1cm} (9)

4. **Cure kinetics characterization**

The cure kinetics characterization was done by isothermal DSC performed at three different temperatures. A non-isothermal DSC at a constant rate of 10 °C/min in the range of temperatures 0°C to 250°C was run to calculate the total enthalpy of the reaction.

The parameters of the selected cure kinetics model were calculated by non-linear curve fitting of Equation 6 on the experimental results shown in Figure 1.2 and are summarized in Table 2.

**Table 2. Cure kinetics parameters.**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pre-exponential factor ($K_1$)</td>
<td>1088564</td>
</tr>
<tr>
<td>Activation energy ($K_1$)</td>
<td>61530</td>
</tr>
<tr>
<td>Pre-exponential factor ($K_2$)</td>
<td>2792.52</td>
</tr>
<tr>
<td>Activation energy ($K_2$)</td>
<td>43159</td>
</tr>
<tr>
<td>$m$th order reaction</td>
<td>0.85</td>
</tr>
<tr>
<td>$n$th order reaction</td>
<td>1.81</td>
</tr>
<tr>
<td>Total enthalpy ($\Delta H$)</td>
<td>280000</td>
</tr>
</tbody>
</table>

5. **FE model**

A 2-D model, representative of a section of the trailing edge (TE), was modelled in Abaqus/CAE. The curing temperature was applied as a boundary condition at the top and bottom of the facesheet and the edges were assumed insulated (no heat exchanged with the environment). The adhesive and the facesheets are considered perfectly bonded at the interface. The initial temperature in the adhesive and GFRP was set as an initial condition to 22°C. The geometry was modelled as one part and different material properties were assigned by partition of the part. The partition ensures a
perfectly bonded interface. Figure 3 shows the partition between the adhesive and GFRP and the mesh adopted in the model.

![Figure 3](image_url)

**Figure 3.** a) TE model boundary conditions (continuous lines temperature boundary conditions, dotted lines insulated edges) b) TE geometry partition and mesh with 4-nodes linear quadrilateral elements.

The element type was the standard 4-nodes linear heat transfer quadrilateral (DC2D4) elements with approximate size of 0.1 mm. The analysis was performed using Abaqus/Standard solver for nonlinear transient heat transfer problems. The solution requires an iterative scheme with variable time increments and maximum allowable temperature change per increment set to 0.25°C.

In order to couple the general heat transfer equation with the cure kinetic law, two subroutines were implemented. The first subroutine is USDFLD, where the kinetics law is defined and the degree of curing is approximated in the time domain as

\[ \alpha^{n+1} = \alpha^n + \left(\frac{d\alpha}{dt}\right)^{n+1} \Delta t \]  \hspace{1cm} (10)

where \( \alpha^{n+1} \) is the degree of curing at the actual time step and \( \alpha^n \) represents the degree of curing from the previous time step. The variable \( \alpha \) has to be initialized and a value of 0.0001 was set as the initial degree of curing. The second subroutine is HETVAL, which takes into account the heat generated from the exothermic reaction and outputs the additional term stored in Equation 2. The FE software solves the coupled equations and outputs the temperature and degree of curing, allowing one to trace the thermal and curing histories of the adhesive.

6. Results and discussion

To assess the importance of guidelines on the design of curing cycles for thick adhesive, two different cure cycles were compared. The first curing cycle was a one-step cycle, the temperature ramp up to 80°C with a constant rate of 0.5 °C/min and then held at 80°C for 12 hours. This cure cycle was suggested by the supplier (Hexion Inc.) in the technical datasheet for bondline thicknesses up to 30 mm. The second cycle was a two-step curing cycle, with an intermediate step at 30°C for 3 hours, before ramping at 80°C at 0.5 °C/min. The aim of the intermediate step is to release most of the energy from the exothermic reaction at lower temperature to reduce the peak.
temperature in the adhesive below a fixed threshold temperature of 170°C. The two curing cycles are shown in Figure 4.

**Figure 4. Input curing cycle profiles (temperature boundary T(t) conditions).**

Figure 5 shows a contour plot at the time step where the peak temperature in the adhesive was achieved with the one-step cure cycle. Due to the thickness variation of the adhesive a high gradient in the temperature is observed along the bondline length. The peak temperature was reached in the area where the adhesive is thicker. In Figure 5, five points are highlighted. They refer to nodes in the middle of the bondline, where the thickness is approximately 0.2 mm (Node 114), 10 mm (Node 1946), 20 mm (Node 2774), 30 mm (Node 2855) and 40 mm (Node 1002).

**Figure 5. Trailing edge temperature contour plot for the one-step cure cycle at time 72 min.**
Figure 6 shows the thermal histories in five points in the adhesive for the two curing cycles. The peak temperature in the adhesive is achieved in both cases at Node 114, where the thickness is 40 mm. The peak temperature for the one-step cure cycle is 203°C; with the two-step cure cycle, it was possible to control the peak temperature without exceeding the threshold temperature of 170°C. It is worthwhile to note that in the adhesive regions with thickness up to 20 mm the effect of the exothermic reaction is limited and the temperature in the adhesive mostly follows the cure cycle while the thicker regions are largely affected by the exothermic reaction. The different behavior of the adhesive depending on the thickness leads to the development of high gradients of temperature within the bondline, which also influences the degree of curing $\alpha$.

![Temperature vs. Time plots for different points along the centerline of the trailing edge](image)

**Figure 6.** Temperature vs. time plots for different points along the centerline of the trailing edge a) one-step cure cycle and b) two-step cure cycle.

The development of $\alpha$ vs. time is presented in Figure 7 for both cure cycles. A full degree of curing is reached by the end of both cure cycles. However, while the one-step cure cycle shows small gradients for $\alpha$ through the bondline, the two-step cure cycles leads to different conversion histories. In fact, the intermediate step at 30°C is able to keep the peak temperature in the thicker region of the adhesive below the threshold of 170°C. On the other hand, it affects the development of $\alpha$ in the thinner parts where the exothermic reaction is smaller.
This comparative study on two different cure cycles shows the importance of guidelines and a predictive model on the design of curing cycles for thick adhesives. The first goal in cure cycle design is to avoid peak temperature that can lead to degradation in the adhesive. Secondly, a full degree of conversion at the end of the cure cycle has to be achieved in order to ensure acceptable mechanical properties.

7. Conclusions and future work

In this study, a predictive model is presented to aid the design of cure cycles for thick adhesives with high bondline variation. The heat transfer equation is coupled with an analytical cure kinetics model in the commercial software Abaqus by user subroutines. The cure kinetics parameters were derived by nonlinear fitting of isothermal DSC experiments. The presented model has shown the capabilities to drive the cure cycle design, being able to trace the thermal and conversion histories within the bondline, by taking into account the influence of the thickness on the exothermic reaction. The standard cure cycle was compared with a two-step cure cycle to assess the effectiveness of this predictive tool. Full degree of conversion in the adhesive was achieved at the end of both cure cycles. The proposed cure cycle enables the control of the temperature below the fixed threshold of 170°C. However, a higher gradient in the degree of curing history for the latter cure cycle is observed.

This study demonstrate the potential of predictive tools in the design of cure cycles. But it is necessary to confirm the results from the simulations with experimental results. If the temperatures in the bondline can be monitored with thermocouples during the cure cycle and compared against the results from simulations, the challenge could be validating the predicted results for the final degree of curing. In fact, poorly fitted cure kinetics models can affect the prediction of the thermal and conversion histories. Fidelity of these predictive models to the real conversion of thick bondline with large variations can enable the shortening of curing cycles maintaining the
efficiency of adhesives bonds. Future work will include the validation of the model with experiments.

A further development of the model will be the coupling with mechanical properties to study the effects of temperature and conversion gradients on the evolution of residual stresses within the bondline, in which little research has been conducted.

8. Acknowledgements

This material is based upon work supported by the National Science Foundation (NSF) under Grant Number IIP-1362022 (Collaborative Research: I/UCRC for Wind Energy, Science, Technology and Research). Any opinions, findings and conclusions or recommendations expressed in this material are those of the authors and do not necessarily reflect the views of the National Science Foundation. The authors would like to thank the WindSTAR IAB for funding of this project as well as our technical mentors Paul Ubrich at Hexion and Nicholas Althoff, Chris Savio and Amir Riahi at GE for their advice and support.

9. References

9. Hexion Inc., EPIKOTE Resin MGS BPR 135G- Series and EPIKURE Curing Agent MGS BPH 134G-137GF