Investigation of Influence Factors in Electron Beam Curing of Epoxy Resins Using a Calorimetry Technique

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Received 17 November 2006; accepted 3 August 2008
DOI 10.1002/app.29170
Published online 19 November 2008 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Because of the complexity of the electron beam (EB) curing process, current understanding of EB curing of polymer resins and composites is limited. This article describes an investigation of different factors affecting EB curing of epoxy resin such as dose rate, time interval between irradiation doses, moisture, and photoinitiator concentration using a calorimetry technique. Results show that higher dose rate resulted in a higher and faster temperature increment in the uncured resin samples, and thus a higher degree of cure. In the multiple-step EB irradiation, a shorter time interval between irradiation doses resulted in higher temperature in the resin samples and therefore higher degree of cure. Results indicate that moisture could delay crosslinking reaction in the early stages of the cure reaction, but accelerates it later in the curing process. Given a reasonable percentage of photoinitiator, experiments confirmed that samples with higher photoinitiator concentration reach higher degree of cure under same EB irradiation conditions. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 111: 2318–2327, 2009

Key words: EB curing; epoxy; calorimetry

INTRODUCTION

Electron beam (EB) curing of composites is a technology that offers significant potential in manufacturing of cost-effective composite structures. During EB curing process, high-energy electrons are used to initiate cure reactions of polymer resins. In comparison with conventional composites curing processes, EB curing has many advantages such as reduced cycle time, long resin shelf life, and low temperature curing.[1] Although significant progress has been made in improving properties of EB-cured composite materials in recent years,[2,3] due to the complexity of process, the basic mechanisms of EB curing and the influence of processing conditions on material properties are still largely unknown, presenting a significant barrier to progress.[4] To improve the properties of EB-cured composites and to produce high quality parts, efforts have to be made to control and optimize the curing process. Therefore, it is important to investigate the factors that could influence the EB curing of resins and composites.

It has been confirmed by many researchers that various factors such as total dose, dose rate, temperature, photoinitiator concentration, and moisture can influence EB curing of resin and composites. First of all, the investigation of the influence of EB irradiation dose has been a subject of many research studies. Research has shown that the total EB irradiation dose can influence the degree of cure,[5–7] glass transition temperature,[6,8–10] mechanical properties,[7,11,12] and fiber/matrix interfacial properties.[11,13] However, a more important factor in EB curing is the dose rate. Dose rate can influence the temperature rise in the part, processing time, and total dose required for full cure of composite part. It is understandable that even with same irradiation dose, if the dose rate were different, the properties of the cured part could be totally different. Also, in EB curing, an appropriate dose rate (kGy/s) has to be selected to avoid overheating the part to be cured. Currently, less information is available about influence of dose rate (kGy/s) on the EB curing process, and on the properties of EB-cured resin and composites. Although the influence of dose/pass has been reported,[11,14–16] dose/pass is not equivalent to dose rate since the rate of dose application in a given pass can vary

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Contract grant sponsors: Canadian Department of National Defence, New Initiatives Fund of the NRC Institute for Aerospace Research.

Journal of Applied Polymer Science, Vol. 111, 2318–2327 (2009)

tremendously, considering different length of time in different passes. Another factor that has to be considered in EB curing process is the photoinitiator concentration. Sui et al.[7] reported that the gel fraction, glass transition temperature, and high temperature (rubbery) modulus of EB-cured epoxy resin increased with increasing photoinitiator concentration, when the samples were irradiated under low EB doses. Moreover, moisture and temperature influence on EB curing of epoxy resin has been also reported.[14,17]

Several techniques such as DSC, FTIR, DMA have been used to study the cure of EB-cured epoxy systems. However, these techniques are in practice limited to investigating curing after EB irradiation has ceased, makes it difficult to correlate the degree of cure of the part with important process parameters such as dose, dose rate, and temperature. To solve this problem, efforts have been made to develop techniques to monitor EB curing process in recent years. A dielectric sensing system,[18] and a real time *in situ* spectroscopic characterization technique,[17] for example, has been developed to monitor EB curing of resins and composites. As an alternative technique, a calorimetry technique has been developed at the NRC (National Research Council Canada) to study the EB curing of polymer resins.[19,20]

In this study, the NRC-developed calorimetry technique was employed to investigate EB curing of epoxy resins. Relationships between resin cure rate and irradiation parameters such as dose rate and time interval between irradiation passes were studied. Furthermore, influence of moisture and concentration of photoinitiator on cure behavior of epoxy resin was investigated. It was found in the study that temperature plays a very important role in the EB curing of epoxy resin, which will be discussed in another paper.

EXPERIMENTAL

The calorimeter used in the EB curing experiments is shown in Figure 1. It consists of eight removable cylindrical blocks of low-density insulating foam that were mounted on a wooden base via small pins. Within each of the foam blocks was embedded a syringe, filled with either fully precured or completely uncured resin specimens. The precured specimens were used as "references" to calculate EB dose rate, while the uncured specimens were used for cure rate and degree of cure measurements. Each of the syringes had embedded in it a small thermocouple, which was placed as close as possible to the geometric center of the syringe. The materials and dimensions of the calorimeter were chosen to simulate a one-dimensional (radial) heat transfer case (in the region of the thermocouple) that could be readily modeled in the data reduction.

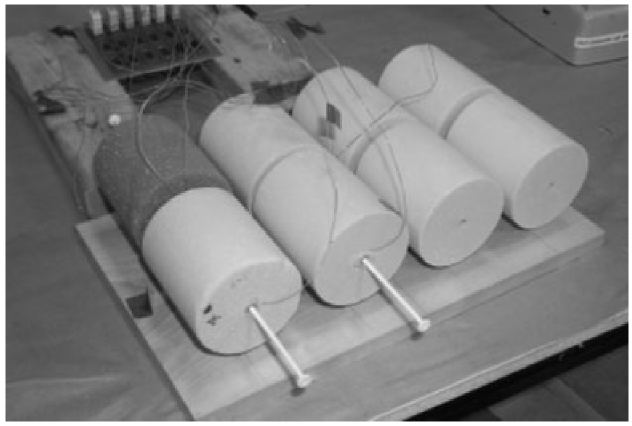

Figure 1 EB calorimeter.

Experiments were carried out to monitor the EB curing of epoxy resin using the calorimeter. After resin samples were embedded in the foam, the calorimeter was placed under the accelerator and irradiated by EB. The EB irradiation of the samples was conducted at Acsion Industries in Pinawa (MB), Canada, using a linear accelerator (10 MeV, 3.8 kW), and at the Laboratory for Research on EB Curing of Composites at the University of Dayton Research Institute (UDRI), OH, using a linear accelerator (3 MeV, 500 W). Temperature change in precured and uncured epoxy samples under EB irradiation were monitored by the calorimeter. K-type thermocouples were used to measure the temperature in the samples. Temperature change in the samples was recorded at a set time step (in most cases less than one second). Temperature data acquisition lasted until the rate of temperature change became very small.

Dose rate effect

Two trials were conducted to investigate influence of dose rate on EB curing of epoxy at UDRI. The resin used was Tactix 1-2-3 (an epoxy resin based on diglycidyl ether of bisphenol A, namely, DGEBA) initiated with 3 phr CD 1012 (a diaryliodonium hexafluoroantimonate salt). In the experiment, the uncured and precured samples were irradiated at two different dose rates. The scheduled total EB dose in the two trials was the same, 8 kGy, with this dose delivered over two different periods of time, 0.5 and 2 min, respectively. Both trials were conducted at ambient temperature.

Effect of time interval between irradiation passes

Two trials were conducted at UDRI to determine the effect of the time interval between irradiation passes.

The resin used in the tests was Tactix 1-2-3 initiated with CD 1012 (3 phr). In the experiment, the uncured and precured samples were subjected to multiple-pass EB irradiation. All the conditions (dose, dose rate, temperature, etc.) in the two trials were set to the same, except the time interval between irradiation passes. Same parameters for the two trials include: Total dose, 8 kGy; irradiation pass, 4; and dose per pass, 2. The time interval between irradiation passes in the two trials are 1 and 5 min, respectively. Both trials were carried out starting at room temperature.

Influence of photoinitiator concentration

To investigate the influence of photoinitiator concentration on the EB curing process, two trials were conducted at UDRI. The resin system used in the two trials was uncured "dry" Tactix 1-2-3 resin initiated by different levels of CD 1012. Photoinitiator concentration in the two trials is 0.5 and 1 phr, respectively. Other parameters in the two trials are the same: Total dose, 12 kGy; irradiation pass, 6; dose per pass, 2; time between pass, 3 min. The tests were conducted at ambient temperature.

Influence of moisture

To investigate the influence of moisture on EB curing of epoxy, a series of EB cure trials were carried out at Acsion Industries. The resin systems used in the tests were uncured "wet" and "dry" EPON 825 (DGEBA) resin initiated with 3 phr DPI-1 (a diaryliodonium salt). The "wet" samples contained 1 wt % of water. Specimens were irradiated in a single pass at doses of 5, 6, and 8 kGy. The tests were conducted at room temperature.

CALORIMETER ANALYTICAL MODEL

To understand the data reduction in the EB calorimetry technique, the detailed analysis model is described in this section. Resin temperatures measured by the embedded thermocouples during EB irradiation were acquired by a computer-based data acquisition system. A one-dimensional numerical finite difference model then used this data to calculate the resin cure rate and the EB dose and dose rate. Some important assumptions employed by this model include:

- Heat flow in resin, syringe, and foam is one-dimensional (radial direction only)
- No contact resistance between resin and syringe, or between syringe and foam

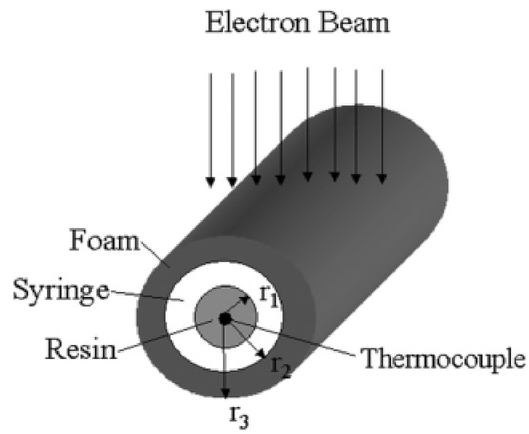

Figure 2 Idealized simulation unit.

- A convective boundary condition exists at the foam surface
- Temperature in the resin is uniform and the same as that measured by the thermocouple embedded in the resin
- Absorbed EB dose is uniform throughout the calorimeter and the same as that calculated from the reference specimens

The idealized simulation unit is shown in Figure 2. To conduct the analysis, nodes were first placed in the syringe and foam. For an N-node network, the nodal arrangement is shown in Figure 3 (temperature at node 0 was assumed to be the same as the measured epoxy temperature, so only the temperature distribution from node 1 to node N is calculated). The distance between two nodes can be calculated as follow:

At $0 < i \leq N_s$

$$\Delta r_2 = \frac{r_2 - r_1}{N_s} \tag{1}$$

At $N_s < i \leq N$

$$\Delta r_3 = \frac{r_3 - r_2}{N_f} \tag{2}$$

where r_1 is the radius of the resin (inside radius of syringe), r_2 the outside radius of the syringe, r_3 the outside radius of the foam; i is the number of the node; N_s and N_f are the number of nodes selected in the syringe and foam, respectively.

The volume of the nodes can be obtained from the following equations:

At $i = 0$:

$$\Delta V_i = \pi \Delta r_2 r_1 L \tag{3}$$

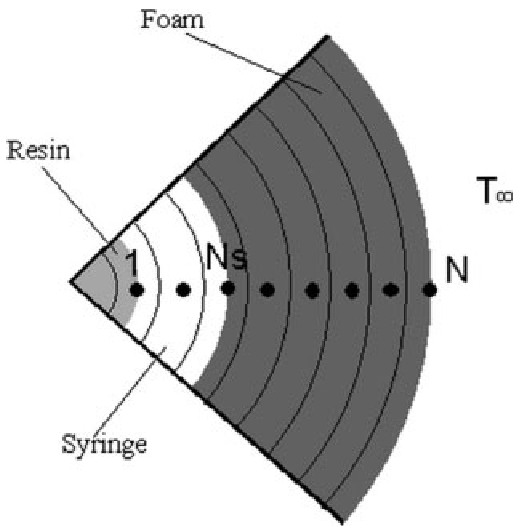

Figure 3 Nodal arrangements.

At $0 < i < N_s$:

$$\Delta V_i = 2\pi\Delta r_2(r_1 + i\Delta r_2)L \quad (4)$$

At $i = N_s$:

$$\Delta V_i = \pi\Delta r_2(r_1 + i\Delta r_2)L + \pi\Delta r_3(r_1 + i\Delta r_2) \quad (5)$$

At $N_s < i < N$:

$$\Delta V_i = 2\pi\Delta r_3(r_2 + (i - N_s)\Delta r_3)L \quad (6)$$

At $i = N$:

$$\Delta V_i = \pi\Delta r_3(r_2 + (i - N_s)\Delta r_3)L \quad (7)$$

where L is the length of the syringe, since the calculation was carried out per unit length, L was set equal to 1.0.

The thermal resistance of each node can be expressed as follows:

At $0 < i < N_s$:

$$R_+ = \frac{\Delta r_2}{2\pi k_s(r_1 + i\Delta r_2 + \Delta r_2/2)} \quad (8)$$

$$R_- = \frac{\Delta r_2}{2\pi k_s(r_1 + i\Delta r_2 - \Delta r_2/2)} \quad (9)$$

At $i = N_s$:

$$R_+ = \frac{\Delta r_3}{2\pi k_f(r_1 + i\Delta r_2 + \Delta r_3/2)} \quad (10)$$

$$R_- = \frac{\Delta r_2}{2\pi k_s(r_1 + i\Delta r_2 - \Delta r_2/2)} \quad (11)$$

At $N_s < i < N$:

$$R_+ = \frac{\Delta r_3}{2\pi k_f(r_2 + (i - N_s)\Delta r_3 + \Delta r_3/2)} \quad (12)$$

$$R_- = \frac{\Delta r_3}{2\pi k_f(r_2 + (i - N_s)\Delta r_3 - \Delta r_3/2)} \quad (13)$$

At $i = N$:

$$R_+ = \frac{1}{2\pi r_3 h} \quad (14)$$

$$R_- = \frac{\Delta r_3}{2\pi k_f(r_2 + (i - N_s)\Delta r_3 - \Delta r_3/2)} \quad (15)$$

where R_+ is the node thermal resistance in the positive direction, R_- is the node thermal resistance in the negative direction, k_s is the thermal conductivity of the syringe, and k_f is the thermal conductivity of the foam; The convective coefficient, h, used in all model predictions was 10 W/m^2 °C. Because the surface temperature of the foam was relatively close to the ambient temperature, it was found that h had little influence on the results of the analysis.

The basic equation used by the analytical model was that for one-dimensional radial heat transfer, i.e.:[21]

$$\frac{k}{r}\frac{\partial}{\partial r}\left(r\frac{\partial T}{\partial r}\right) + \dot{Q} = \rho c_p \frac{\partial T}{\partial t} \quad (16)$$

where c_p is the specific heat capacity, r is the radius; k is the thermal conductivity, and $\dot{Q}$ is the internal heat generation.

This equation was solved using a one-dimensional finite difference analysis. The first step in the analysis was discretization of the calorimeter area into elements and nodes, which was done as shown in Figure 3. As illustrated, the temperature at node 1 was a model input and set equal to the measured resin temperature. Hence, temperature distribution was calculated only within the syringe and foam.

Discretizing eq. (16), the energy balance in the volume associated with node i for time step k can be expressed as:[22]

$$\dot{Q}_i + \sum_m \frac{T_m^{k+1} - T_i^{k+1}}{R_{im}} = \rho_i c_{pi} \Delta V_i \frac{T_i^{k+1} - T_i^k}{\Delta t} \quad (17)$$

where T_m^k represents the temperature of the nodes adjoining node i and R_{im} is the thermal resistance between node i and the adjoining nodes.

Collecting terms and rearranging, eq. (17) can be written as:

$$[A]\{T\}^{k+1} = \{B\} \quad (18)$$

where $[A]$ and $\{B\}$ are coefficient matrices, and $\{T\}^{k+1}$ is the matrix of calorimeter nodal temperatures at time step $k + 1$, with

$$[A] = \begin{bmatrix} \frac{1}{R_{10}} + \frac{1}{R_{12}} + \frac{C_1}{\Delta t} & -\frac{1}{R_{12}} & 0 & 0 & 0 & \cdots & 0 \\ -\frac{1}{R_{12}} & \frac{1}{R_{12}} + \frac{1}{R_{23}} + \frac{C_2}{\Delta t} & -\frac{1}{R_{23}} & 0 & 0 & \cdots & 0 \\ 0 & -\frac{1}{R_{23}} & \frac{1}{R_{23}} + \frac{1}{R_{34}} + \frac{C_3}{\Delta t} & -\frac{1}{R_{34}} & 0 & \cdots & 0 \\ 0 & 0 & -\frac{1}{R_{34}} & \frac{1}{R_{34}} + \frac{1}{R_{45}} + \frac{C_4}{\Delta t} & -\frac{1}{R_{45}} & \cdots & 0 \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdots & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdots & \cdot \\ 0 & 0 & 0 & 0 & 0 & -\frac{1}{R_{N,N-1}} & \frac{1}{R_{N,N-1}} + \frac{1}{R_{N+}} + \frac{C_N}{\Delta t} \end{bmatrix}$$

$$\{T\}^{k+1} = \begin{bmatrix} T_1^{k+1} \\ T_2^{k+1} \\ T_3^{k+1} \\ T_4^{k+1} \\ \cdot \\ \cdot \\ T_N^{k+1} \end{bmatrix}$$

$$\{B\} = \begin{bmatrix} \frac{T_{\text{resin}}^k}{R_{01}} + \frac{C_1}{\Delta t} T_1^k + q_1 \\ \frac{C_2}{\Delta t} T_2^k + q_2 \\ \frac{C_3}{\Delta t} T_3^k + q_3 \\ \frac{C_4}{\Delta t} T_4^k + q_4 \\ \cdot \\ \cdot \\ \frac{C_N}{\Delta t} T_N^k + \frac{T_\infty}{R_{N+}} + q_N \end{bmatrix}$$

Solution of eq. (18) for syringe and foam nodal temperatures during irradiation (using, for example, Gauss-Jordan elimination) required knowledge of calorimeter material properties, boundary, and initial conditions as well as the rate of heat generation in each model element, $\dot{Q}_i$. In this case, it was the calculation of the heat generation rate that was most complex.

As discussed in Ref. 23 for EB cured composites and resins, there were typically two major contributors to internal heat generation during irradiation: the energy imparted by the impinging electrons, $\dot{Q}_e$, and the exothermic energy given off by the resin curing reaction, $\dot{Q}_R$. The energy generated by the impinging electrons can be calculated using:

$$\dot{Q}_e = \rho \dot{D}_R \tag{19}$$

where $\dot{D}_R$ is the EB dose rate (in units of Gy/s).

For neat resin, the exothermic energy generation rate can be determined from:

$$\dot{Q}_R = \frac{d\alpha}{dt} \rho_r \Delta H_R \tag{20}$$

where α is the resin degree of cure, and ΔH_R is the total heat of reaction, i.e., the total energy given off by the resin during a "complete" reaction.

In the EB process model described in Ref. 24 dose rate was provided as a model input, and the heat generation rate was calculated from a cure kinetics model. This information was then used to calculate temperature distribution in a component as it varied over time. In this case, the problem was nearly the inverse: given a known resin temperature with time, calculate its heat generation rate and, from this, its rate of cure.

The algorithm used to calculate the EB dose rate applied to each specimen and the rate of cure in each initially uncured specimen was comprised of two parts. In part I, the measured temperatures of each of the precured reference specimens were used to calculate the dose rate (at the reference specimen locations) throughout the irradiation process. In part II, the calculated dose rates and the measured temperatures of the initially uncured specimens were used to determine their rates of cure.

There are two main parts to the simulation:

1. Part I—Calculation of EB Dose Rate from Reference Specimens

Step 1: Estimate dose rate during each time step k. This is done using the approximation that the change in temperature of the precured resin specimens is solely due to energy absorbed from the EB, with no energy loss to the syringe or foam (and no energy generated from the curing reaction, since the specimen is already cured), thus:

$$\dot{D}_R^k = \frac{dT_r^k}{dt} c_{pr} \tag{21}$$

Step 2: Assuming that absorbed EB dose is uniform throughout the calorimeter, use eq. (19) to calculate the heat generated by the EB in the syringe and foam elements illustrated in Figure 3.

Step 3: Using the calculated heat generation rates, solve eq. (17) for calorimeter nodal temperatures during irradiation, using as a resin temperature boundary condition the measured temperature, (T_1), of the reference specimen.

Step 4: Calculate the total electron energy absorbed by the calorimeter using:

$$\dot{Q}_e^k = \dot{D}_R^k \left\{ \rho_r V_r + \sum_N \rho_i \Delta V_i \right\} \tag{22}$$

where the subscript "r" represents the resin and subscript "i" represents the syringe and foam elements of the calorimeter as in Figure 3.

Step 5: Calculate the heat lost by convection from the foam surface to the surrounding air, using:

$$Q_{\text{conv}}^k = h\left(T_N^k - T_\infty\right) \tag{23}$$

where T_N^k is the temperature of the foam surface, T_∞ is the temperature of ambient air, and h is the convective coefficient.

Step 6: Using calculated temperatures, calculate the change in total calorimeter internal energy, ΔE_{int}, at each time step using:

$$\Delta E_{\text{int}}^k = \rho_r c_{pr} V_r \Delta T_r^k + \sum_N c_{pi} \rho_i \Delta V_i \Delta T_i^k \tag{24}$$

where the subscript "r" represents the resin and subscript "i" represents the syringe and foam elements.

Step 7: Calculate the "imbalance" in total calorimeter energy by subtracting from the change in internal energy, the energy input from the EB and the energy loss by convection.

$$\dot{Q}_{\text{Error}}^k = \Delta E_{\text{int}}^k + Q_{\text{conv}}^k - \dot{Q}_e^k \tag{25}$$

Since there is no exothermic heat generated by the reference specimens, this imbalance represents the error in the estimated EB dose rate.

Step 8: Compare the calculated energy imbalance with a predefined "tolerance" value. If the value is greater than the tolerance, recalculate the dose rate at each step using:

$$\dot{D}_R^k = \frac{dT_r^k}{dt} c_{pr} + \frac{\dot{Q}_{\text{Error}}^k}{m_T} \tag{26}$$

where $m_T = m_r + m_s + m_f$, is the sum mass of the resin, syringe, and foam in the calorimeter, and return to Step 2.

If the calculated energy imbalance is within tolerance, continue on to Part II.

2. Part II—Calculation of Resin Cure Rate

Part II of the algorithm uses as an input the calculated EB dose rate from the reference specimen in Part I to calculate the cure rate of an initially uncured resin specimen. It should be noted that to do this properly, the two specimens must be exposed to the same dose rate at the same time.

Steps 1–5 of Part II of the algorithm are nearly identical to Steps 2–6 of Part I, with the exception that the temperature used as the boundary condition (T_1) in Part I, Step 3 is the measured temperature of the initially uncured specimen.

Step 6: Calculate the exothermic energy generation of the curing specimen. This is done using the same equation as in Part I, Step 7, with the exception that in this case the energy imbalance is not due to an error, but to the specimen heat generation, i.e.,

$$\dot{Q}_R^k = \Delta E_{\text{int}}^k + Q_{\text{conv}}^k - \dot{Q}_e^k \tag{27}$$

Step 7: Calculate the resin cure rate using eq. (20) and integrate with time to calculate degree of cure.

The software for the analytical model was written in Microsoft Visual Basic. The output of the simulation is automatically saved in Comma Delimited format (i.e., *.csv) and can be graphically analyzed using Microsoft Excel. A user-friendly interface has been developed for the redesigned calorimeter software. Calibration trials have demonstrated the accuracy of the model prediction.[19]

RESULTS AND DISCUSSION

In the EB curing experiments, temperature changes in the precured and uncured resin samples were measured by the embedded thermocouples. The measured temperature profile in the precured samples was assumed to be induced only by the absorption of electron energy, while the temperature profile in the uncured epoxy samples also included the heat generated in the resin crosslinking reaction. Therefore, temperature changes measured in the precured samples during irradiation were used to calculate EB dose and dose rate, and temperature changes in the uncured resin samples were used to determine the cure rate and degree of cure. Using the calorimeter analysis model mentioned above, the influence of different factors on EB curing of epoxy resins was analyzed and discussed in following sections.

Dose rate effect

Before discussion of dose rate effect on EB curing of epoxy resins, it is necessary to give a brief description of the concept of dose rate. Generally, dose rate can be defined as the rate of dose delivered during a specified time period. This means the value of dose rate strongly depends on the selection of the "time period." For example, for the pulsed linear accelerator, which is often used for EB curing, a pulsed EB is emitted from the electron gun. Thus, if the "time period" is selected relative to a single electron pulse, which occurs in a very short time period, then the

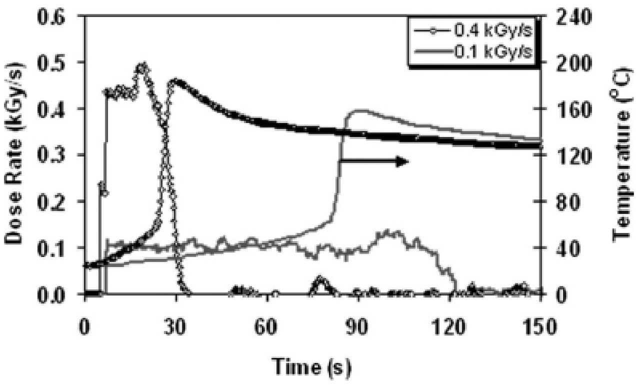

Figure 4 Measured dose rate and temperature rise in the uncured resin samples.

dose rate will be relatively high (e.g., 6 MGy/s for Acsion's 10 MeV linear accelerator). This dose rate is often called the "instantaneous dose rate." The instantaneous dose rate is proportional to the quantity of electrons in a single electron pulse. If the time period is selected to span multiple electron pulses, then the dose rate is often called the "average dose rate" (kGy/s). The average dose rate is the instantaneous dose rate, integrated over multiple pulse periods, divided by the total time for the multiple pulses. In this article, it should be noted that "dose rate" used is the "average dose rate."

Dose rate is an important parameter for EB curing of resins and composites. First of all, higher dose rate results in faster temperature rise in the parts and can therefore influence the processing time of EB curing. Furthermore, dose rate has an influence on the total dose required for full curing of resins and composites. In the current work, two trials were conducted to investigate the dose rate effect. Figure 4 shows the dose rate applied to the samples, which was obtained by the calorimetry measurement. It can be seen in Figure 4 that the average dose rate in the first trial was about 0.4 kGy/s with about 30 s of irradiation, while in the second trial was about 0.1 kGy/s with about 120 s of irradiation. It can be calculated that the actual total doses in these two trials were about 12 kGy, which was 50% higher than what was scheduled irradiation dose (8 kGy). The reason was that the scheduled dose was measured at the base of the calorimeter, while the samples inside of the calorimeter received a higher dose rate due to the position of the calorimeter (elevated closer to the scan horn). The temperature profiles of the samples are also shown in Figure 4. The results indicate that higher dose rate resulted in a faster and higher temperature rise in the uncured resin samples. Figure 5 shows that the cure reaction started earlier under high dose rate irradiation, confirming that dose rate is a parameter relating to the processing time of EB curing. The degrees of cure of the resin samples were 0.87 and 0.84 in the both trials. The sample that was irradiated under higher dose rate reached a higher degree of cure (but not that different in this case).

Influence of time interval between irradiation passes

In this experiment, resin samples were irradiated by the EB with two different time intervals between irradiation passes: 1 and 5 min. All other conditions were kept the same in the experiment. Figure 6 shows the dose versus time obtained by the calorimetry measurement, which shows that the actual EB dose received by the samples was about 11 kGy. The difference of the time interval between the irradiation passes can also be clearly observed in Figure 6. The four passes of irradiations were already completed in the first trial by the time the second irradiation pass had just started in the second trial. It is also shown in Figure 6 that time interval between irradiation doses can influence the temperature rise in the uncured resin samples: The peak temperature

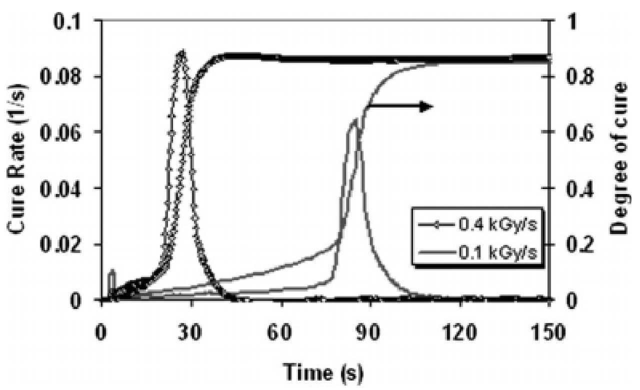

Figure 5 Dose rate effect on cure rate and degree of cure.

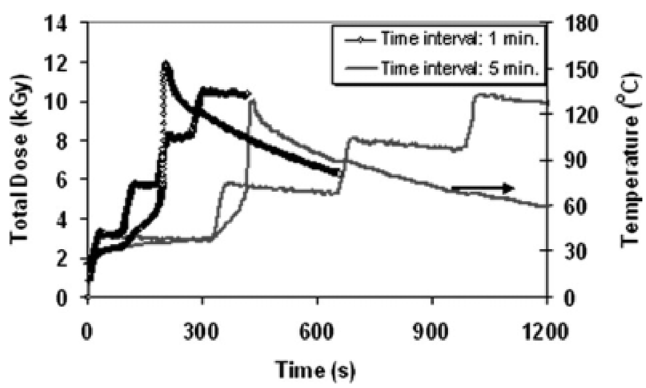

Figure 6 Irradiation doses with different time intervals and corresponding temperature rise in the samples.

reached was 152.5°C when the time interval was 1 min, while the peak temperature was 134.7°C when the time interval was 5 min. Figure 7 shows that time interval between irradiation passes can influence the cure rate and degree of cure. The shorter the time interval was the earlier the cure reaction started. The degrees of cure of the resin samples in the two trials were 0.83 and 0.76 when the time interval was 1 and 5 min, respectively. Therefore, it can be concluded that in a multiple-pass EB curing process, the shorter the time interval between the irradiation passes is, the higher the temperature rises in part and therefore the higher degree of cure.

In fact, the influence of time interval between irradiation passes can be attributed to the dose rate effect. As mentioned in the introduction, "dose/pass" is a term that is often used in EB curing of composites, However, it is not very appropriate to use "dose/pass" to describe EB curing without considering the duration of the "pass," as well as time interval between irradiation passes. For example, Figure 6 shows that the dose/pass in the two trials is the same: 2 kGy/pass, due to the different time intervals between irradiation passes in the two trials, however, the final degrees of cure in the two samples are different. Therefore, the "average dose rate" could be a more practical parameter to describe EB curing under single pass or multiple-pass EB irradiation. The average dose rate (kGy/s) in a single pass of irradiation equals the dose increment during a single pass divided by the pass duration, while the average dose rate (kGy/s) in the multipass irradiation dose rate (kGy/s) equals the total dose during multiple passes divided by the total time for the passes, including the time interval between passes. Using this definition, the average dose rates in these two trials were calculated as 0.027 and 0.0078 kGy/s, respectively. It should be noted that the influence of average dose rate on EB curing is likely to be a

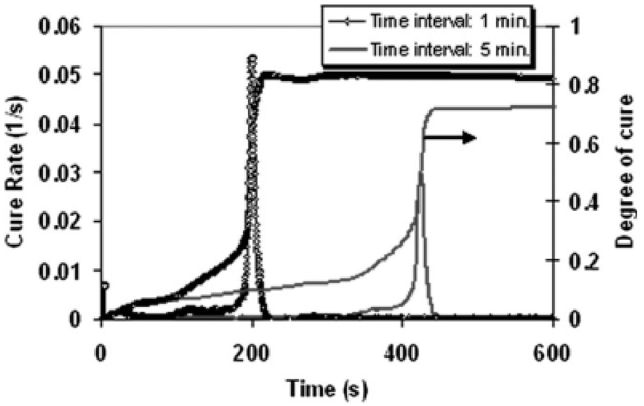

Figure 7 Influence of time interval between irradiation passes on cure rate and degree of cure.

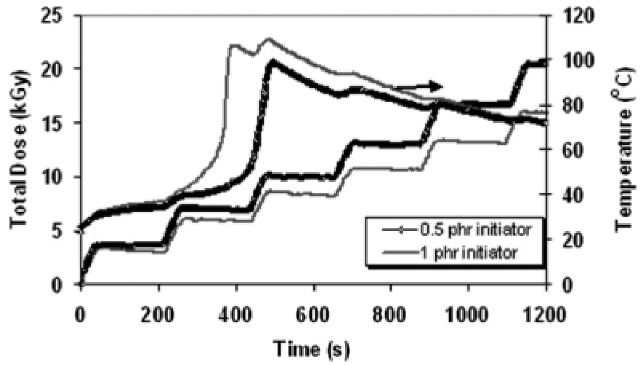

Figure 8 Irradiation doses received by samples with different photoinitiator concentrations and temperature profiles.

temperature-related phenomenon, which will be discussed in another paper.

Influence of photoinitiator concentration

Photoinitiator concentration is a factor that has to be considered in the EB curing process. One reason is that photoinitiator concentration has an important effect on overall material cost since most photoinitiators are expensive. Also, photoinitiator concentration can influence the curing process and final properties of the EB cured part. There is usually an optimal photoinitiator concentration in EB curing of resin and composites. One possible definition for an optimal photoinitiator concentration for EB curing of resin and composites is the lowest photoinitiator concentration that can allow the resin to achieve a desired degree of cure under a given EB dose.

As described in section 2.3, two trials were conducted at UDRI to investigate the influence of photoinitiator concentration on the EB curing of epoxy resin. The resin used in the experiments was "dry" Tactix 1-2-3 initiated with CD 1012. The photoinitiator concentration in the two tests was 0.5 and 1 phr, respectively. Figure 8 shows the EB doses received by the samples in each irradiation step and temperature profiles of the samples. It can be seen in Figure 8 that the actual total dose received by the samples with 0.5 phr photoinitiator was higher than the sample with 1 phr photoinitiator. However, the temperature increase in the sample with 0.5 phr photoinitiator during EB irradiation were lower than in sample with 1 phr photoinitiator, indicating that photoinitiator concentration can influence the amount of the exothermal of the cure reaction. It can be observed from Figure 9 that the cure reaction started earlier in the samples with higher percentages of photoinitiator concentration. The final degree of cure (average of four samples) was 0.67

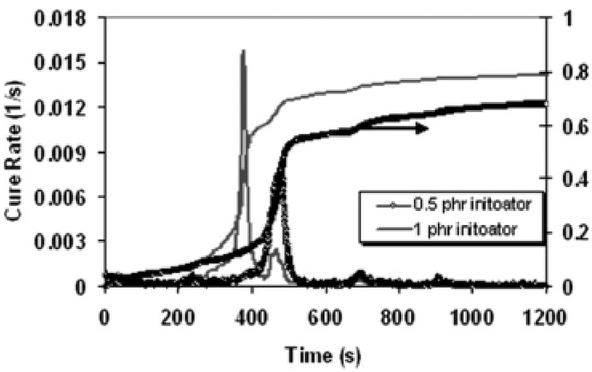

Figure 9 Influence of photoinitiator concentration on cure rate and degree of cure.

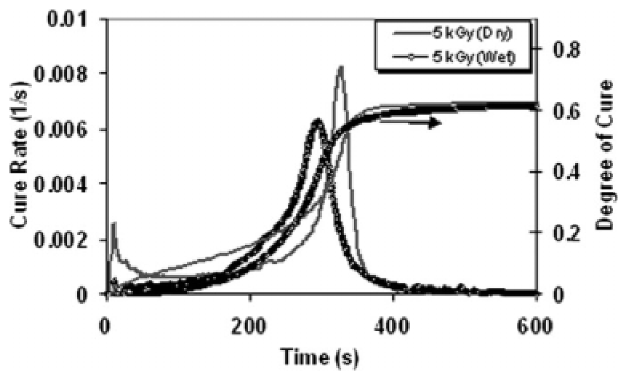

Figure 11 Calculated cure rate and degree of cure (5 kGy).

when the photoinitiator percentage was 0.5 phr, and 0.80 when the photoinitiator concentration was 1 phr, indicating that higher photoinitiator concentrations result in higher degree of cure under the same EB irradiation conditions. However, there could be a critical value of the photoinitiator concentration, above which the degree of cure does not increase anymore with increasing photoinitiator concentration, although this was not investigated in this study.

Influence of moisture

To investigate the influence of moisture on EB curing of epoxy resin, "wet" and "dry" samples were irradiated under single pass EB at 5, 6, and 8 kGy. The EB dose and dose rate imparted on the samples were measured by the calorimeter and shown in Figure 10.

The calculated degree of cure and cure rate versus time for the three runs are shown in Figures 11–13. It can be seen in these pictures that there is not a significant influence of moisture on the final degree of cure in the "wet" and "dry" samples. However, clear differences exist in the cure rates—there are two peaks in the cure rate versus time plots of all the "dry" samples, while a single peak appears in the plots of all the "wet" samples, indicating that moisture initially suppresses the cure reaction. However, it is later observed that the main cure reactions (the main peaks in the cure rate plots) of all the "wet" samples start earlier in time than in the "dry" samples, indicating that moisture eventually accelerates the cure reaction.

SUMMARY

EB curing is an attractive technique that offers the potential to cure polymer resins and composites efficiently. However, current understanding of the processes of EB curing of polymer resins and composites is limited due to both the complexity of the cure process and the lack of available cure monitoring techniques.

This article describes the investigation of different factors affecting EB curing of epoxy resin, such as, dose rate, time interval between irradiations, moisture, and photoinitiator concentration using a calorimetry technique developed at the NRC. This

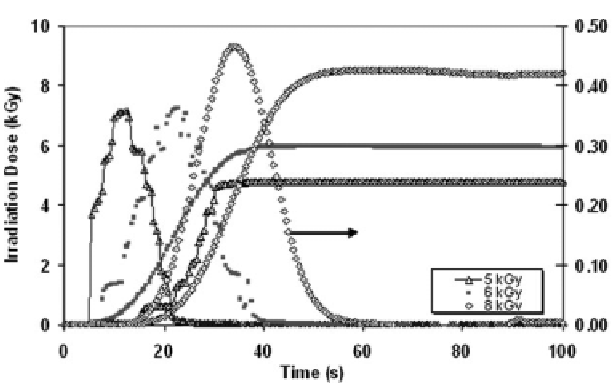

Figure 10 Calculated dose and dose rate versus time.

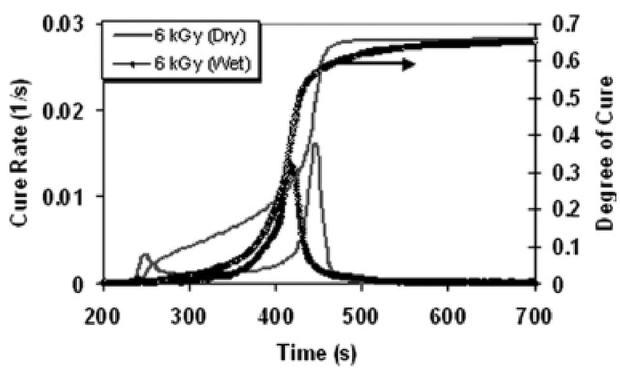

Figure 12 Calculated cure rate and degree of cure (6 kGy).

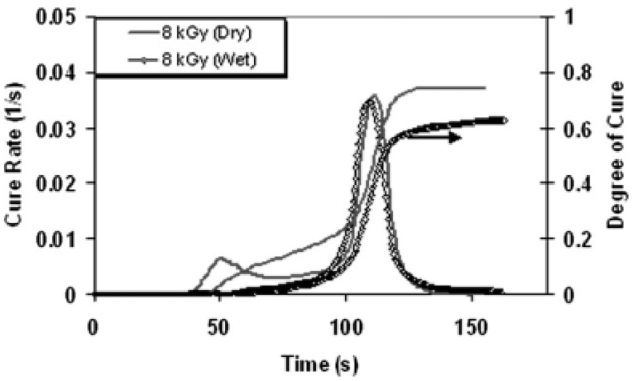

Figure 13 Calculated cure rate and degree of cure (8 kGy).

technique uses measurement of the temperatures of precured (reference) and uncured resin specimens to calculate dose rate and cure rate with time. Temperature changes in precured and uncured resin specimens were recorded during the EB irradiation. A one-dimensional finite difference model was developed to calculate the EB irradiation energy and the exothermic energy evolved by the resin cure reaction. Results showed that higher dose rate resulted in a higher and faster temperature increment in the uncured resin samples and thus, a higher degree of cure. In the multiple-step EB irradiation, a shorter time interval between irradiations resulted in higher temperature in the resin samples and therefore higher degree of cure. The influence of time interval between irradiation passes can be attributed to the dose rate effect. Experimental results showed that the "average dose rate (kGy/s)" could be a more practical parameter to describe EB curing under single pass or multiple-pass EB irradiation than "dose/pass." Results indicated that moisture could delay crosslinking reaction in the initiation stage of the cure reaction, but accelerate it when resin temperature reaches a certain value. Given a reasonable percentage of photoinitiator, there is evidence that samples with higher photoinitiator concentration reach higher degree of cure under same EB irradiation conditions.

Further research on the effect of processing temperature on the cure kinetics and properties of EB-cured polymer resins will be conducted in the future.

The authors thank Dr. C. Li at NRC for her help with the experiments. The support of Acsion Industries Ltd., MB, Canada, and Laboratory for Research on EB Curing of Composites at the University of Dayton Research Institute (UDRI), OH, USA, for conducting the EB irradiation trials is also gratefully acknowledged.

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