

# Mass Transfer Effects in Degradation of Bismaleimide Matrix Composite

IRENE SALIN and JAMES C. SEFERIS\*

Polymeric Composites Laboratory, Department of Chemical Engineering, University of Washington, Seattle, Washington 98195

## SYNOPSIS

The role of mass transfer effects in degradation of carbon fiber reinforced bismaleimides was examined utilizing the concepts of Thiele modulus and effectiveness factor. Unidirectional samples were aged at 250, 260, and 270°C. The weight loss rates from the three types of composite surfaces (resin covered surface, 0° surface, and 90° surface) were obtained from the weight loss data of different sample geometries. As observed previously, the weight loss rate from the resin covered surface showed a typical behavior for a reaction that becomes increasingly diffusion limited. The effective reaction and diffusion coefficients were obtained based on the initial and final weight loss rates, and activation energies for reaction and diffusion were also determined. The activation energy for diffusion was an order of magnitude higher than customary, indicating that phenomena other than diffusion (increase in effective surface area due to cracking) also contributed to the weight loss rate. Overall, this work illustrated the applicability of an unreacted core type model to composite degradation and the importance of accounting for the anisotropy as well as mass transfer effects in composite degradation. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

Anisotropic degradation of polymer matrix composites has been investigated and reported in the literature. Particular focus has been given to bismaleimide<sup>1-3</sup> and PMR-15,<sup>4-6</sup> both high temperature composite systems. In both of these systems, weight loss was found to depend on the fiber orientation with respect to the exposed surfaces. Optical microscopy revealed a degraded layer on the sample surfaces. Consequently, a shrinking core type model was developed and extended to account for the anisotropic weight loss.<sup>1,2</sup> This methodology was derived based on kinetic and mass transfer considerations and predicted the weight loss of unidirectional samples as a function of sample size and fiber angle with respect to exposed surfaces. It was also expanded to explain differences in the degradation of neat resin and composite and was shown to be applicable to general laminate lay-ups.<sup>7</sup>

The model equations were originally derived based on the shrinking core model, assuming either diffusion or reaction to be the rate controlling step. This work addressed the mass transfer effects in composite degradation.

## BACKGROUND

According to the anisotropic degradation model, the total weight loss,  $Q_c$ , is

$$Q_c = \sum A_i q_{c,i} \quad (1)$$

with

$$q_{c,i} = D_{E,i} t^n \quad (2)$$

where  $i$  refers to the composite surface,  $A$  is the surface area ( $\text{cm}^2$ ),  $q_c$  is the weight loss per unit surface area ( $\text{g}/\text{cm}^2$ ),  $t$  is time in hours,  $n$  is a characteristic time exponent, and  $D_E$  is an effective diffusion coefficient ( $\text{g}/\text{cm}^2 \text{h}^n$ ). This model was derived for a 1-dimensional slab geometry and then extended to

\* To whom correspondence should be addressed.

3 dimensions by assuming that degradation proceeds independently on different surfaces. If degradation is purely diffusion controlled, the weight loss per unit surface area  $q_c$  can be written as

$$q_c = D't^{0.5} \quad (3)$$

with

$$D' = [8(\rho_o - \rho_d)C_{As}D/\beta]^{0.5} \quad (4)$$

where  $D'$  is the effective diffusion coefficient described in eq. (2),  $\rho_o$  and  $\rho_d$  ( $\text{g}/\text{cm}^3$ ) are the densities of the undegraded and degraded material,  $D$  is the oxygen diffusion coefficient in the diffusion layer ( $\text{cm}^2/\text{h}$ ),  $C_{As}$  is the surface concentration of oxygen, and  $\beta$  is a conversion factor that relates the amount of weight lost in grams to the amount of oxygen reacted in moles.<sup>1,2</sup>

If the weight loss rate is limited by the reaction kinetics, then

$$q_c = K't \quad (5)$$

with

$$K' = 2k_s C_{As}/\beta \quad (6)$$

where  $k_s$  is a first-order rate coefficient for the surface reaction of oxygen with the polymer.<sup>1,2</sup>

Previous work investigated the applicability of this methodology to the anisotropic weight loss of a bismaleimide (BMI) composite.<sup>1-3,7</sup> The weight loss of different sample geometries was measured, and the values of weight loss fluxes were extracted from the data. The model parameters  $n_i$  and  $D_{E,i}$  [eqs. (1), (2)] were determined from plots of  $\log(q_{c,i})$  vs.  $\ln(\text{time})$ . The time exponents for the resin covered surface were approximately 0.5 for the different temperatures, whereas the time exponents for the cut surfaces ( $0^\circ$  and  $90^\circ$  surfaces) were greater than unity. This was explained by an increase in the effective surface area due to cracking.

The overall degradation of the BMI was modeled as diffusion controlled. In reality, reactions are often not controlled by a single reaction step. Reaction and diffusion rates can be of a same order of magnitude, or the controlling step may change as reaction proceeds. A switchover from reaction control to diffusion control is often observed in solid-state reactions.<sup>8,9</sup> The reaction starts as reaction controlled and becomes increasingly diffusion limited upon formation of the ash layer. Derivation of the rate expressions for various particle geometries can be found in standard chemical engineering texts.<sup>10,11</sup>

Borrowing from traditional catalysis, Thiele modulus and effectiveness factor can be used to estimate the relative magnitudes of reaction and diffusion. Effectiveness factor,  $\eta$ , is defined as the ratio of the rate with diffusion resistance to the rate in surface conditions, that is, in the absence of any mass transfer effects. The effectiveness factor can be written for a first-order reaction in a 1-dimensional slab geometry ( $L$  = slab half-thickness) as<sup>11</sup>

$$\eta = \frac{\tan h\phi}{\phi} \quad (7)$$

where

$$\phi^2 = \frac{\tau_D}{\tau_K} = L \frac{k_s}{2D} \quad (8)$$

Here  $\phi$  is the Thiele modulus and  $\tau_D$  and  $\tau_K$  are the times required to achieve complete conversion if diffusion or reaction alone controls the rate. When  $\phi \rightarrow 0$ ,  $\eta \rightarrow 1$ , which signifies no appreciable diffusion resistance. For strong diffusion resistance,  $\phi \rightarrow \infty$  and  $\eta \rightarrow 0$ . If the rate is initially controlled by the reaction and diffusion can be neglected, then the initial data can be used to determine  $K'$  according to eq. (5). Similarly, the data in the diffusion controlled regime can be used to determine  $D'$  from eq. (3).

## EXPERIMENTAL

A 26-ply carbon fiber reinforced BMI composite was used in this work.<sup>1-3,12</sup> Samples were cut from a unidirectional laminate that had been cured according to the manufacturer's recommendations.<sup>12</sup> Two sets of samples were made. Samples denoted by A were approximately  $4 \times 2$  cm whereas samples denoted by B were  $4 \times 0.5$  cm. Two different fiber orientations were used. In samples denoted by 1, the fibers were oriented along the longest sample dimension (4 cm); samples denoted by 2 had fibers oriented across the shorter sample dimension. The sample set consisted of samples A-1, A-2, B-1, and B-2. A set of samples were aged in a tube furnace at 250, 260, and  $270^\circ\text{C}$  in air.

## RESULTS AND DISCUSSION

The weight loss data of the unidirectional samples at different temperatures were analyzed to obtain the weight loss values for different surfaces at different temperatures. The weight loss data of all

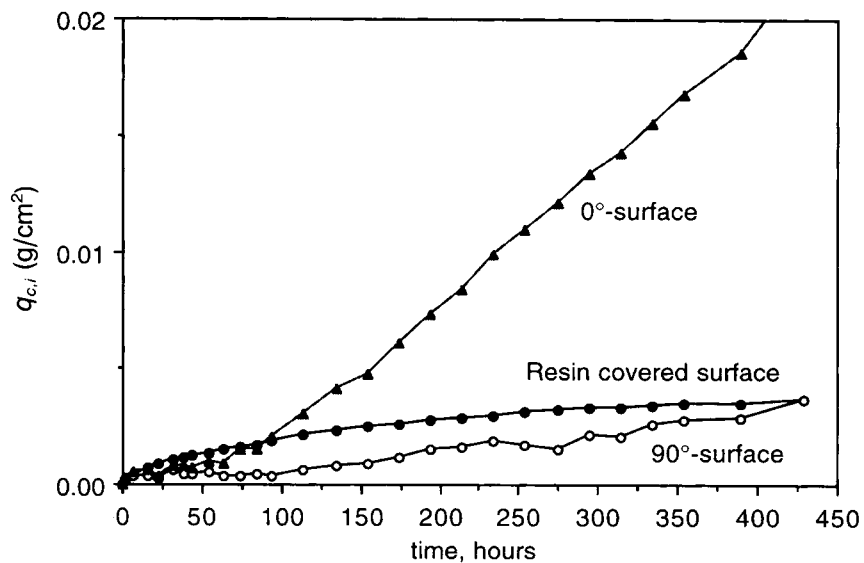


Figure 1 BMI weight loss at 250°C.

samples (A-1, A-2, B-1, and B-2) at each temperature were used to obtain  $q_{c,i}$ . A least squares fitting<sup>13</sup> was carried out because the procedure involved weight loss data from four samples and three unknown weight loss per unit surface area terms. The generated  $q_{c,i}$ 's for 250°C are presented as a function of time in Figure 1. Similar results were obtained at 260 and 270°C.

The weight loss in the resin covered surface showed a typical behavior for a reaction that becomes increasingly diffusion limited. The relative

changes in the reaction rate for this surface were examined by utilizing the concepts of effectiveness factor and Thiele modulus. Figure 2 shows the weight loss rate, the flux for the resin covered surface, as a function of time at 250, 260, and 270°C. The reaction rate first dropped rapidly and then approached a relatively constant slope. The effectiveness factors can be calculated from the rate data assuming that the rate was initially controlled by the reaction and became increasingly diffusion limited. The initial reaction controlled weight loss rates

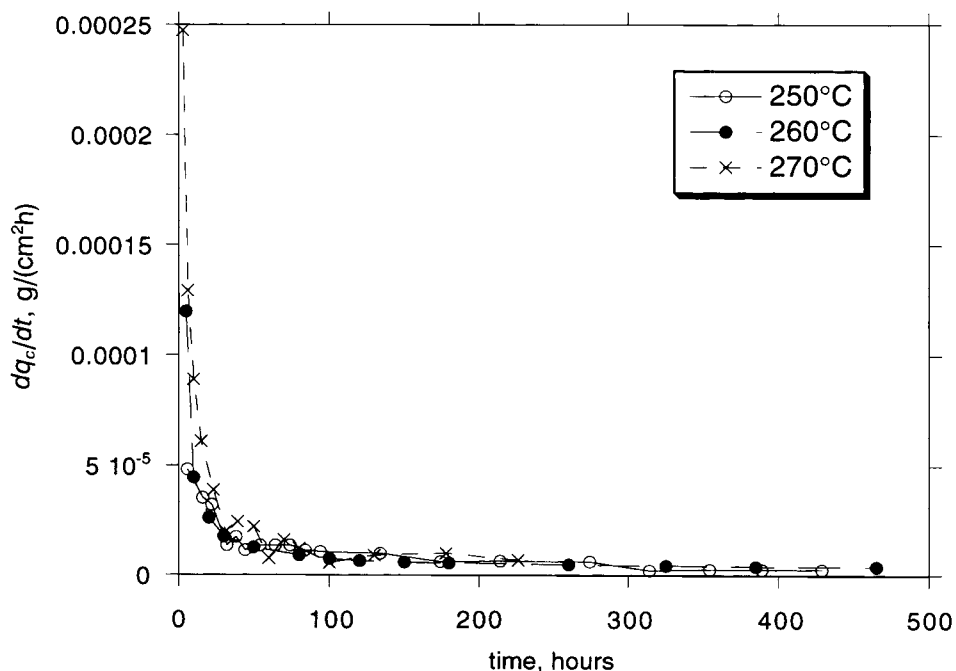


Figure 2 Weight loss rates for the resin covered surfaces at 250, 260, and 270°C.

were determined as the first data points in Figure 2, and the effectiveness factors were then determined by dividing the rate data in Figure 2 by these values. The effectiveness factor is a function of Thiele modulus as shown in eq. (7). Consequently, the Thiele moduli were also determined from the effectiveness factors. Figure 3 shows the logarithm of the effectiveness factor as a function of the logarithm of the Thiele modulus at 250°C, which is a typical way of presenting this kind of data. The data at other temperatures were analyzed similarly.

Values of the parameters  $K'$  and  $D'$  can be obtained from the initial and final rates of weight loss. The initial slope of the weight loss rate curves shown in Figure 2 would be equal to  $K'$ . Similarly, if the weight loss per unit surface area,  $q_c$ , is plotted as a function of the square root of time, then the slope would be equal to  $D'$  [eq. (3)]. The values of these quantities were determined at all temperatures and are summarized in Table I.

The coefficients determined from the initial and final weight loss rates from the resin covered surface (Table I) are related to the reaction and diffusion coefficients. Consequently, the apparent activation energies for the reaction and diffusion can be determined (Fig. 4). The activation energies and logarithms of the preexponential factors obtained were 196 kJ/mol and 14.98 h<sup>-1</sup> and 94 kJ/mol and 5.35 h<sup>-1</sup> for reaction and diffusion, respectively. The reaction activation energy was in the range of values obtained for this material,<sup>7,12</sup> but the activation en-

**Table I** Parameters  $K'$  and  $D'$  Determined from Initial and Final Portions of Flux for Resin Covered Surface

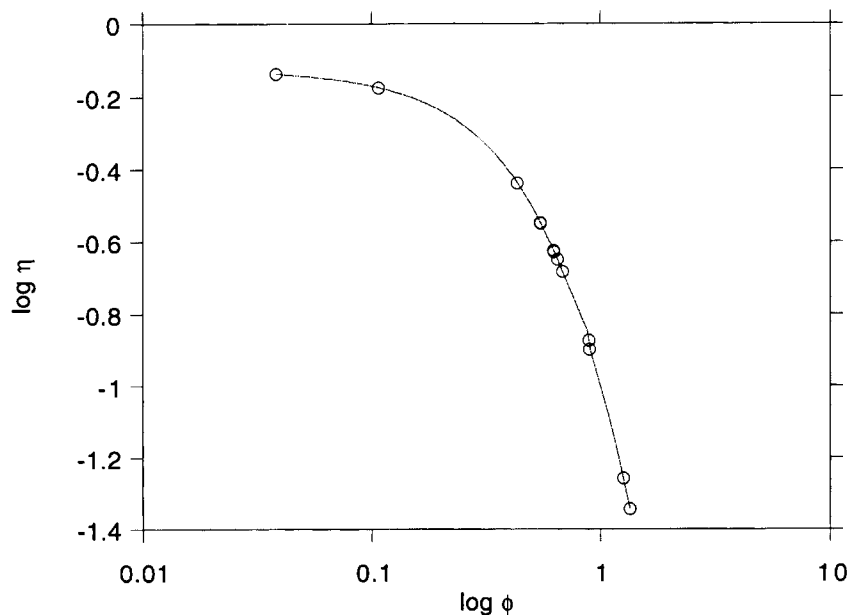
Coefficient <sup>a</sup>	250°C	260°C	270°C
$K'$	0.0000483	0.000120	0.000247
$D'$	0.0000885	0.000147	0.000196

<sup>a</sup> Units for  $K'$  are g/(cm<sup>2</sup> h). Units for  $D'$  are g/(cm<sup>2</sup> h<sup>0.5</sup>).

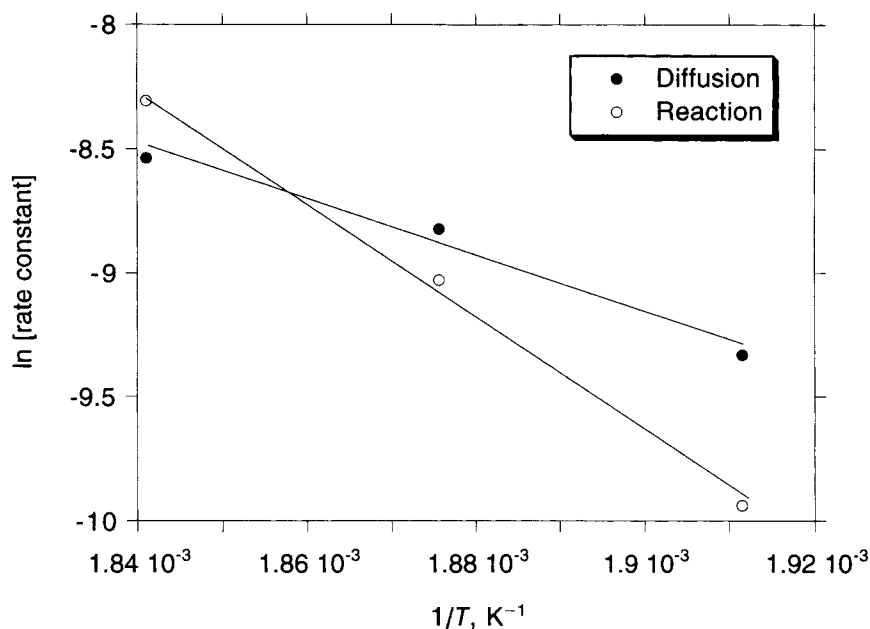
ergy attributed for diffusion was an order of magnitude higher than that for true molecular diffusion. This may have been due to cracking and porosity development in the composite that caused the observed weight loss rate to differ from the true diffusion limited rate. The porosity and crack development may increase at the higher experimental temperatures, giving inflated rate constants for these situations that could in turn lead to artificially high overall activation energies. However, this work established that the mass transfer limitations become dominating very quickly in the beginning of the degradation.

## CONCLUSIONS

The role of mass transfer effects in the degradation of carbon fiber reinforced BMI was examined utilizing the concepts of Thiele modulus and effective-



**Figure 3** Effectiveness factor ( $\eta$ ) as a function of Thiele modulus ( $\phi$ ) for the resin covered surface at 250°C.



**Figure 4** Determination of activation energies for reaction and diffusion. Rate constants were determined from the initial (reaction controlled) and final (diffusion controlled) weight loss rates for the resin covered surface.

ness factor. The weight losses from the three types of composite surfaces (resin covered surface, 0° surface, and 90° surface) were obtained from the weight loss data of different sample geometries. As observed previously, the weight loss rate from the resin covered surface showed a typical behavior for a reaction that becomes increasingly diffusion limited. The effective reaction and diffusion coefficients were obtained based on the initial and final weight loss rates, respectively. The activation energies for reaction and diffusion were also determined. The activation energy for diffusion was an order of magnitude higher than customary, indicating that phenomena other than diffusion (increase in effective surface area) also contributed to the weight loss rate. The weight loss rates from the surfaces where fibers were exposed to air accelerated at all temperatures. This was attributed to cracking. Overall, this work illustrated the applicability of an unreacted core type model to composite degradation and the importance of accounting for the anisotropy as well as mass transfer effects in composite degradation.

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