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Diffusion of reacting epoxy and amine monomers in polysulfone: a diffusivity model

G. Rajagopalan[a], J.W. Gillespie Jr.[a,b,*], S.H. McKnight[c]

[a]Center for Composite Materials and Department of Materials Science and Engineering, University of Delaware, Newark, DE 19716, USA
[b]Department of Civil and Environmental Engineering, University of Delaware, Newark, DE 19716, USA
[c]Army Research Laboratory, Materials Directorate, Aberdeen Proving Grounds, Aberdeen, MD, USA

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Abstract

In this work, a diffusivity model based on free volume theory is presented for the simultaneous diffusion of diglycidyl ether of bisphenol A (DGEBA) epoxy and bis(*p*-aminocyclohexyl) methane (PACM 20) amine monomers into amorphous polysulfone (PSU). This model is expected to predict and explain the diffusion behavior of the epoxy and amine monomers into PSU during the initial time periods. The overall free volume of the polymer system is estimated using a Kelley–Bueche approximation for free volume in a binary mixture consisting of a non-reacting thermoplastic and the reacting thermoset. The fractional free volume of the thermoset is estimated by the DiBenedetto equation. The model is valid only for low epoxy–amine concentrations and degrees of cure. The diffusivity model developed here suggests that reaction reduces the species diffusivity with increasing cure from a loss of the overall fractional free volume for diffusion. Further, a model for increased epoxy diffusivity from amine-induced PSU swelling is presented and validated using data from previous studies on the single-component diffusion of epoxy into amine-swollen PSU. By combining the reaction and swelling terms with the Arrhenius epoxy diffusivity, the epoxy diffusivity expression during the simultaneous diffusion and reaction of epoxy and amine into PSU for small times, is determined. Parametric studies on the nature of diffusivity are performed to determine the influence of the various free volume parameters on thermoset diffusion, and these studies show that the thermoset diffusivity, in general, decreases with time from reaction.

Keywords: Epoxy–amine/polysulfone; Cure-dependent diffusivity model; Free volume theory

1. Introduction

The study of the transport of thermosets into thermoplastics is important from both a technological and scientific point of view. As thermosetting monomers concurrently diffuse and react into fully polymerized thermoplastics, an interphase is formed during processing. Within the interphase chain entanglements and a network structure are established. This network structure represents one mechanism for adhesion at dissimilar polymeric material interfaces. Previous work [1–3] has shown that the size of the interphase is largely controlled by the processing conditions of time and temperature and the diffusivity of the thermosetting monomers into the thermoplastic. Cure kinetics, and the available free volume within the system govern the thermoset diffusivity. This overall free volume is determined by the thermoplastic and the volume fraction and degree of cure of the diffusing thermoset.

As seen previously [4], there are few empirical studies on the diffusion of thermosetting monomers into thermoplastics and these studies have not produced a unified, comprehensive theoretical framework to understand the interdiffusion of reacting thermosets into thermoplastics. Further, the interphase plays a critical role in the load transfer across dissimilar material interfaces [1–3]. Thus, in order to design and produce controllable diffuse interphase regions the diffusion process must be evaluated and modeled. One main component essential for such a mathematical study is a model for the diffusivity of the thermoset into the thermoplastic. For the present study, a model is developed that incorporates swelling and reaction effects, identified in previous experimental studies performed using the Attenuated Total Reflectance-Fourier Transform Infrared Spectroscopy (ATR-FTIR) technique [1,2,4]. During the initial stages, small molecular amine was

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* Corresponding author. Center for Composite Materials, University of Delaware, Newark, DE 19716, USA. Tel.: +1-302-831-8702; fax: +1-302-831-8525.

E-mail address: gillepie@ccm.udel.edu (J.W. Gillespie Jr.).

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Nomenclature

A	Absorbance
B	Critical free volume size for diffusion
c_e, c_a	Epoxy, amine concentration
c_{e0}, c_{a0}	Initial epoxy, amine concentration
D	Diffusivity
$D_{e(a)}$	Amine concentration-dependent epoxy diffusivity
D_e, D_a	Epoxy, amine diffusivity
$D_{e(a)}^{cure}$	Cure and amine concentration-dependent epoxy diffusivity
D_a^{cure}	Cure-dependent amine diffusivity
d_p	Depth of penetration
E_x/E_m	Ratio of segmental mobilities of crosslinked to uncrosslinked monomer
f	Fractional free volume
f_g	Fractional free volume at the glass transition temperature
F_x/F_m	Ratio of lattice energies of crosslinked to uncrosslinked monomer
K_1, K_2, k_1, k_2	Reaction rate constants
l	Film thickness
M, M_w	Molecular weight
M_e	Entanglement molecular weight
R	Universal gas constant
R_r	Reaction rate
T	Temperature
t	Time
T_g	Glass transition temperature
T_{g0}	Glass transition temperature of uncrosslinked monomer
v_1	Difference in fractional free volume of thermoset and thermoplastic
α	Degree of cure
β	Thermal expansion coefficient
ε	Volume fraction of penetrant
γ	Swelling constant

found to diffuse into PSU an order of magnitude more rapidly and swell the PSU. The apparent diffusivity of the epoxy was further enhanced in the presence of amine-saturated PSU. At later stages, thermoset reaction produces crosslinking and increases the molecular weight of the diffusing monomers, thereby hindering transport and decreasing monomer diffusivity. Thus various stages are involved in the diffusion of reacting thermosets into thermoplastics viz. an initial interdiffusion of the monomers into the thermoplastic, followed by crosslinking and gelation of the thermoset, and finally reaction-induced phase separation [5,6]. All thermodynamic considerations of compatibility are expected to be valid only in the initial time periods where interdiffusion is dominant. Further, with phase separation and possibly network formation, the diffusion of the monomers largely occurs within the network, and diffusion into the thermoplastic ceases. Hence, in this paper, we present a theoretical approach to develop a reaction-dependent diffusivity model in the framework of the Fujita free volume theory for the diffusion of reacting thermosetting monomers into amorphous thermoplastics during the initial interdiffusion regime. Further, an elementary model for the increased epoxy diffusivity from amine-induced PSU swelling observed in a previous study [4] is also presented and validated. By combining the swelling and reaction contributions to diffusivity, the diffusivity model is obtained. This model is intended to explain and predict several features of the diffusing thermoset, the most significant being an increase in diffusivity from swelling and a subsequent decrease from reaction.

The diffusivity of a monomeric species is related to its chain length and weight in an inverse manner. Reaction between the epoxy and amine leads to the formation of crosslinks and branching, leading to an increase in molecular weight with time. Consequently, the diffusivity of this reaction product decreases with time until the molecular weight is so large as to prevent diffusion. The dependence of the self-diffusion coefficient of the thermoset D on molecular weight M prior to gelation may follow a form used in previous linear polymerization models [7]:

$$D = D_0 M^{-1} \qquad (M < M_e) \tag{1}$$

$$D = D_0 M_e M^{-2} \qquad (M > M_e) \tag{2}$$

Eq. (1) pertains to Rouse diffusion, while Eq. (2) handles

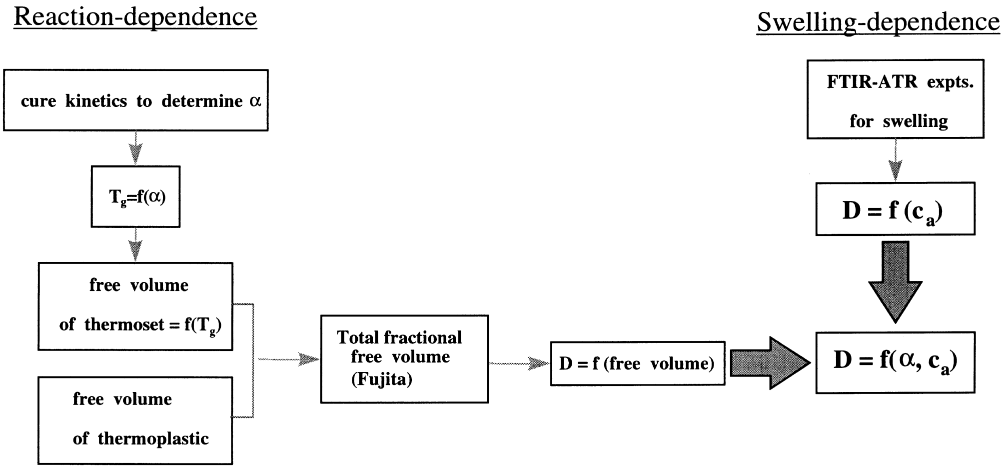

Fig. 1. Methodology for the determination of epoxy diffusivity expression. Corresponding amine diffusivity is reaction dependent only.

entangled situations. M_e is an entanglement molecular weight and is typically assumed to be 30,000 after de Gennes [7,8]. This approach may be inadequate for thermosetting systems. Indeed, recent work by Yu and von Meerwall [9] on the effect of molecular weight, branching, and free volume on the diffusivity in a DGEBA epoxy as a function of time during curing with diamino diphenyl sulfone (DDS) has revealed that the diffusivity of the polymer is found to be more strongly dependent on the molecular weight than predicted by the Rouse model, suggesting that branching in such epoxy systems has considerably more influence on the transport in these unentangled systems up to gelation. For the present work, the thermoset diffusivity is related to the degree of cure α through the free volume approach. Such an approach is simpler since the cure kinetics of various resins, including the present system, are well studied and characterized, and it affords the means to simple modeling. In general, the diffusivity in a curing epoxy–amine system decreases with increasing degree of cure α, which follows the same trend as the molecular weight of the resin system.

Free volume theories of diffusion in polymers are based on the classic work by Cohen and Turnbull [10,11], which postulated that molecular transport of momentum or mass in liquids occurs through a redistribution of the free volume in the system. Their end result for the diffusivity is written as follows:

$$D = D_0(T)\exp\left(B\left(1-\frac{1}{f}\right)\right) \tag{3}$$

where $D_0(T)$ is the Arrhenius diffusivity, B a constant which includes the critical size for motion, and f the fractional free volume. This concept has given rise to several diffusion theories [12,13]. Of specific interest to our work is the Fujita free volume theory. This theory has been used to study the mutual diffusion of gases and low-molecular weight liquids in polymers [14–17]. It is examined in greater detail in Section 2.5.

The free volume based diffusivity model, Eq. (3), has been used successfully to predict the changes in the thermoset diffusivity during cure in bulk epoxy–amine [18–20]. This approach uses the increasing glass transition temperature of the curing thermoset as a central parameter that reflects the changes in the thermoset free volume. As cure proceeds, the molecular weight increases through the formation of crosslinks. This tends to decrease the overall thermoset free volume [21]. This, consequently, leads to an increase in the glass transition temperature [22] and thermoset viscosity [23]. From knowledge of the cure kinetics of the epoxy–amine system, this quantity is related to the degree of cure through the DiBenedetto relation [22]. The present study extends this approach to the study of the interdiffusion of reacting thermosets into thermoplastics by using the Fujita free volume theory. This theory is applied here by approximating the initial behavior of the thermosetting monomers to that of low molecular weight solvents. Hence, the theory is valid only at low degrees of cure, and at the initial stages of diffusion. Previous experimental studies have shown that this is the actual time scale for interphase formation [1,2].

The organization of this paper is as follows: the methodology for reaction dependence of the monomer diffusivity is outlined and the corresponding model developed. Next, the swelling model is presented and validated. The diffusivity model is presented next, by combining the reaction and swelling dependencies of the epoxy diffusivity. Parametric studies on the normalized diffusivity are presented.

2. Determination of the mechanism-dependent diffusivity expression

The schematic of the methodology for diffusivity determination is as shown in Fig. 1, where the methodology for determining the swelling dependence of epoxy diffusivity is also shown. From the cure kinetics, the evolution of the

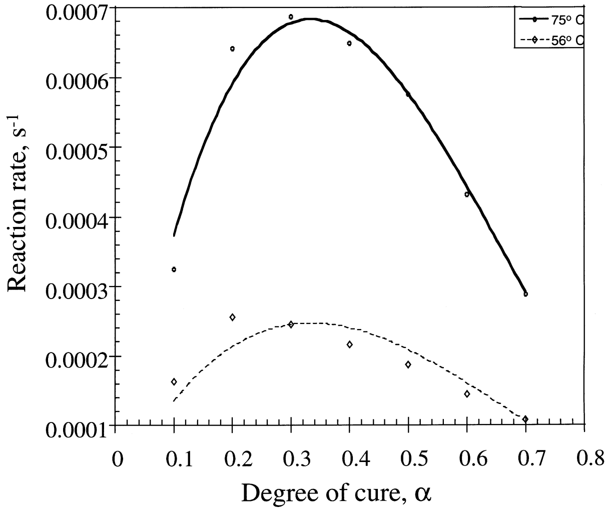

Fig. 2. Reaction rate vs. α at two temperatures for the DGEBA–PACM 20 system studied in this work. Fit of Eq. (7) to experimental data from Sanford [19].

glass transition temperature with cure is determined. Using the free volume relation for thermoplastic systems, and using the Kelley–Bueche expression [24], an average free volume expression is derived for the thermoset–thermoplastic system. Finally the diffusivity dependence on free volume is used to determine the effect of reaction on diffusivity during the diffusion of reacting thermosets into amorphous thermoplastics. By combining with the swelling model, the complete expressions for the epoxy and amine diffusivities are determined. The individual steps in the model development, starting from a description of the free volume model, are given below.

2.1. Free volume model

Diffusion processes largely occur through holes, or voids, present in the system. Their existence results from the irregularities of the molecular packing and defines free volume. In this approach, the glass transition temperature determines the temperature at which the features of a polymer change [25,26] from the rubbery state to a glassy state. This temperature is of importance since it determines the macromolecular features of the bulk polymer that control the diffusion process. Several authors have discussed the role of free volume and the glass transition temperature on diffusion processes in polymers [10–12,27,28]. As the temperature decreases, the molecular mobility slows down, and hence diffusion is characteristically slow below the glass transition temperature.

Williams et al. [29] showed that the fractional free volume displays a linear relationship with temperature, with a discontinuity at the glass transition temperature T_g. This change in slope is from a sudden onset of expansion of the free volume. Hence:

$$f = f_g + \beta(T - T_g) \tag{4}$$

where f_g is the fractional free volume at T_g, and β the thermal expansion coefficient of the free volume. β is typically $4.8 \times 10^{-4}\ \mathrm{K}^{-1}$ for temperatures greater than T_g; $4.8 \times 10^{-5}\ \mathrm{K}^{-1}$ for temperatures lesser than T_g. These parameters are assumed to remain constant. Further the values for f_g and β are constant and they are 0.025 and $4.82 \times 10^{-4}\ \mathrm{deg}^{-1}$, respectively [29].

In curing thermosets, the glass transition temperature evolves with the degree of cure [22]. Hence, the value of the coefficient of thermal expansion in Eq. (4) is valid for thermosets in the temperature range of T_g to $T_g + 100$°C. This situation occurs at the first stage of the curing reaction as T_g increases but is smaller than the external, imposed temperature.

It is clear from Eq. (4) and the above discussion that the fractional free volume of the thermoset changes with cure as the glass transition temperature evolves. In order to predict such changes, the explicit cure dependence of the thermoset glass transition temperature is essential. Hence knowledge of the thermoset cure kinetics is necessary. Section 2.2 reviews the curing kinetics for the epoxy–amine system studied in this work.

2.2. Cure kinetics of DGEBA (Epon 828)–PACM 20 epoxy–amine system

The cure model for this resin system was developed by Sanford [19,20]. The main results of the kinetic model that was developed are presented in this section. The rate of the curing reaction can be expressed as a function of time and temperature. The reaction between epoxies and amines is generally autocatalytic in nature, due to the formation of proton donors like the hydroxyl group. The form of the reaction rate equation used to describe this intrinsic kinetics is

$$R_r = -\frac{dc_e}{dt} = (K_1 + K_2(c_{e0} - c_e))c_e c_a \tag{5}$$

where R_r is the reaction rate, K_1 and K_2 are the reaction rate constants and have an Arrhenius temperature dependence, c_{e0} is the initial epoxide concentration, and c_e and c_a are the reactive epoxide and amine hydrogen concentrations. If α is defined as the extent of reaction of the epoxide and amine hydrogen groups, then:

$$1 - \alpha = \frac{c_e}{c_{e0}} = \frac{c_a}{c_{a0}} \tag{6}$$

where c_{a0} is the initial amine hydrogen concentration. Using this expression in Eq. (5), we get:

$$R_r = \frac{d\alpha}{dt} = (k_1 + k_2\alpha)(1 - \alpha)^2 \tag{7}$$

where

$$k_1 = K_1 c_{e0} c_{a0} \tag{8}$$

$$k_2 = K_2 c_{e0}^2 c_{a0} \tag{9}$$

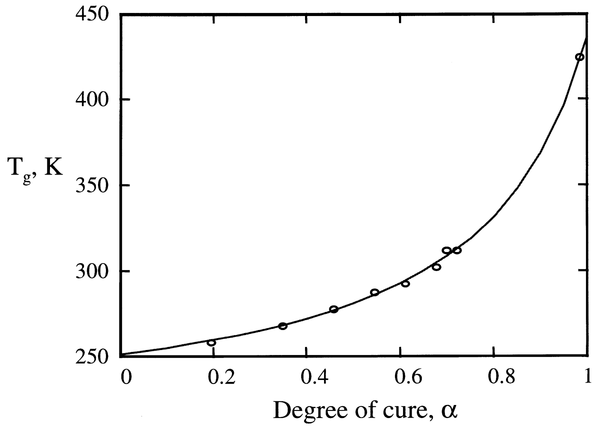

Fig. 3. T_g vs. α for the DGEBA–PACM 20 epoxy–amine system [30].

A plot of the reaction rate vs. the degree of cure for various temperatures will yield the values for these constants. Such a plot is shown in Fig. 2 for temperatures of 56 and 75°C. Curve fits at different temperatures gave the following values for k_1 and k_2:

$$k_1(\mathrm{s}^{-1}) = 0.0 \tag{10}$$

$$k_2(\mathrm{s}^{-1}) = 1.47 \times 10^5 \exp\left(-\frac{12,022}{\mathrm{R}T}\right) \tag{11}$$

where R is in cal mol^{-1} K^{-1}. The degree of cure α can now be defined using Eqs. (5) and (6) as:

$$\alpha = \frac{(k_1 + k_2(c_{e0} - c_e))c_e c_a t}{c_{e0}} \tag{12}$$

where t is the time of cure. Using the cure kinetics, the evolution of the glass transition temperature with the degree of cure α can be determined using the DiBenedetto relation. This is discussed in Section 2.3.

2.3. The DiBenedetto equation

The glass transition temperature is an important parameter in the study of diffusion of reacting thermosets into thermoplastics as it reflects the amount of free volume in the curing thermoset available for diffusion, and the average free volume available in the thermoset–thermoplastic polymer system. Hence, as seen in Eq. (4), T_g reflects the free volume in the polymer system. As T_g increases the mobility of the molecules decreases as the system gets increasingly rigid. The thermoset is said to vitrify when the glass transition reaches the temperature of cure of the system; however, reactions can proceed beyond this point. The DiBenedetto model [22] provides a reliable relation between T_g and extent of cure to predict the properties of the reacting thermoset during cure.

By expressing the ratio of the crosslinked to uncrosslinked T_gs as proportional to their corresponding ratios of lattice energy to mobility and, further, assuming that lattice energy and mobility vary linearly with extent of crosslinking, DiBenedetto derived the following equation:

$$\frac{T_g - T_{g0}}{T_{g0}} = \frac{\left(\frac{E_x}{E_m} - \frac{F_x}{F_m}\right)\alpha}{1 - \left(1 - \frac{F_x}{F_m}\right)\alpha} \tag{13}$$

where T_g is the glass transition temperature at a degree of cure α, T_{g0} the glass transition of the uncrosslinked monomer, E_x/E_m the ratio of the segmental mobilities of the crosslinked to uncrosslinked monomers, and F_x/F_m the corresponding ratio of lattice energies. Enns and Gilham [30] applied this expression to predict the glass transition in curing epoxies, including the system studied here. Eq. (13) has been successfully used to fit T_g vs. extent of cure data for various epoxy resin systems [30–33]. The DiBenedetto model is quite simple to use and it can be used to accurately predict T_g over the entire range of the reaction. Fig. 3 shows the fit of Eq. (13) to the glass transition temperature vs. α data for the epoxy–amine system studied here. The values of the curve fit constants are given in Table 1.

2.4. Diffusivity in curing thermoset systems

Using the cure kinetics and the dependence of T_g on α, the overall self-diffusivity of the uncrosslinked epoxy and amine moieties in a curing epoxy–amine system can be determined using the free volume approach [20]. By inserting the cure dependence of thermoset T_g (Eq. (13)), in Eq. (4) and using Eq. (3) to express the diffusivity, we get:

$$D = D_0 \exp\left(B\left(1 - \frac{1}{0.025 + \beta(T - T_g(\alpha))}\right)\right) \tag{14}$$

where $T_g(\alpha)$ is the cure-dependent glass transition temperature.

The model fits to calculated diffusivity data are shown in Fig. 4 for three temperatures [19]. B for the curing DGEBA (Epon 828)– PACM system studied here has been determined to be 1.1 [19]; indeed, for most liquid–polymer systems B is between 0.9 and 1.2 [25]. Normalized diffusivity decreases more drastically for higher temperatures in the curing epoxy–amine system. This model has also been used to make reliable predictions on the nature of diffusivity with α for other epoxy systems [34–36].

Expression (12) aids in understanding the manner in which the T_g of the curing thermoset controls diffusivity. Using the Fujita free volume theory, this expression can be extended to the determination of the diffusivity relation

Table 1
Ratio of lattice energies, segmental mobilities and uncrosslinked monomer glass transition temperature for the epoxy system studied, obtained from fit of Eq. (13) to T_g data from Enns and Gillham [30]

Epoxy–amine system	E_x/E_m	F_x/F_m	T_{g0}
DGEBA–PACM 20	0.337	0.194	254 K

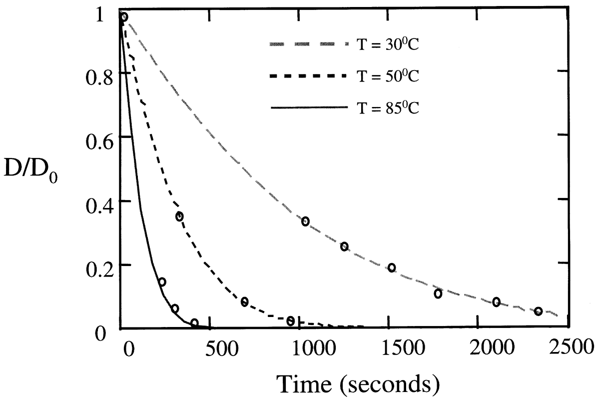

Fig. 4. Normalized experimental diffusivity vs. time showing fits of Eq. (14) [19].

for the interdiffusion of reacting thermosets into thermoplastics.

2.5. The Fujita free volume theory

Fujita [12] employed a modified form of the Doolittle expression and used the dependence of the molar friction coefficient of the penetrant on the average fractional free volume at a temperature T in the system, when the volume fraction of the penetrant is ε, to arrive at an expression relating the diffusivity of the penetrant in the polymer solid i.e. PSU in our study. His relation for the diffusivity is:

$$\ln\frac{D_T}{D_0} = B\left\{\left(\frac{1}{f(0,T)}\right) - \left(\frac{1}{f(\varepsilon,T)}\right)\right\} \tag{15}$$

where D_T is the diffusivity in the polymer–penetrant system, D_0 the diffusivity in the polymer at zero penetrant concentration, $f(\varepsilon = 0, T)$ the fractional free volume of the pure polymer as given in Eq. (4) and $f(\varepsilon, f)$ the fractional free volume with penetrant. In the regions of sufficiently low concentrations (unentangled regime) of penetrant it can be assumed that [12]:

$$f(\varepsilon, T) = f(0,T) + \varepsilon v_1 \tag{16}$$

where v_1 is the difference in the fractional free volumes of the thermoplastic and thermoset. v_1 may be a function of temperature, but to a first approximation, should be independent of concentration. The above expression is written as follows for the purpose of the present work:

$$f_{\mathrm{tp-ts}}(\alpha, \varepsilon, T) = f_{\mathrm{tp}}(\varepsilon = 0, T) + (f_{\mathrm{ts}}(\alpha, T) - f_{\mathrm{tp}}(\varepsilon = 0, T))\varepsilon \tag{17}$$

$$v_1 = f_{\mathrm{ts}}(\alpha, T) - f_{\mathrm{tp}}(\varepsilon = 0, T) \tag{18}$$

where “tp” and “ts” refer to the thermoplastic and thermoset, respectively, $f_{\mathrm{tp-ts}}(\alpha,\varepsilon,f)$ is the fractional free volume in the thermoplastic–thermoset system, and is a function of cure and thermoset volume fraction, $f_{\mathrm{ts}}(\alpha,f)$ is the cure-dependent fractional free volume of the thermoset, and can be defined as in Eq. (4) with a cure-dependent T_g, and ε is the total volume fraction of the penetrant (epoxy and amine) in the thermoplastic. Eq. (17) presents a simple linear interpolation of the thermoset and thermoplastic fractional free volumes to arrive at the average free volume in the polymer system, and is similar to the Kelley–Bueche expression [24] for polymer–solvent systems in the unentangled regime. This situation can be expected in the initial interdiffusion regime (for $\alpha < 0.3$ [4]) in the present thermoset–PSU system, where the degree of cure is low.

3. Diffusivity model derivation

The overall fractional free volume of the thermoplastic–thermoset system, Eq. (17), is affected by the cure and volume fraction of the diffusing epoxy–amine monomers. The diffusivity expression for a curing bulk epoxy–amine system was examined in Eq. (13) where the fractional free volume approach was used to describe the diffusivity in a curing epoxy–amine system. Specifically the fractional free volume of the thermoset changes with cure, as seen previously, while the corresponding relation for amorphous PSU is a constant, and is obtained by inserting the thermoplastic glass transition temperature (PSU $T_g = 191$°C) in Eq. (4).

Using Eq. (17) with the diffusivity relation, Eq. (15), gives:

$$\frac{D^{\mathrm{cure}}_{\mathrm{e(a)}}}{D_{\mathrm{e(a)}}(c_{\mathrm{a}}, T)} = \exp\left(\frac{B}{f(\alpha = 0, \varepsilon, T)} - \frac{B}{f(\alpha, \varepsilon, T)}\right) \tag{19}$$

for the epoxy, where $D^{\mathrm{cure}}_{\mathrm{e(a)}}$ is the cure- and amine concentration-dependent epoxy diffusivity, $D_{\mathrm{e(a)}}(c_{\mathrm{a}},T)$ is the amine concentration dependent epoxy diffusivity that provides the swelling dependence that is to be determined, and:

$$\frac{D^{\mathrm{cure}}_{\mathrm{a}}}{D_{\mathrm{a}}(T)} = \exp\left(\frac{B}{f(\alpha = 0, \varepsilon, T)} - \frac{B}{f(\alpha, \varepsilon, T)}\right) \tag{20}$$

where $D^{\mathrm{cure}}_{\mathrm{a}}$ is the cure-dependent amine diffusivity, $D_{\mathrm{a}}(f)$ the Arrhenius amine diffusivity in PSU [1,37]. The thermoset volume fraction, ε, in Eqs. (19) and (20) is the sum of the epoxy and amine concentrations in PSU i.e. $\varepsilon = c_{\mathrm{e}} + c_{\mathrm{a}}$. By using the T_g relation for the thermoset, and the associated constants for the epoxy–amine system given in Table 1, Eqs (19) and (20) can be written as:

$$\frac{D^{\mathrm{cure}}_{\mathrm{e}}}{D_{\mathrm{e(a)}}(c_{\mathrm{a}}, T)} = \exp\left(B\left(-\frac{s_1\alpha\varepsilon}{(f^0_{\mathrm{tp}}(1-\varepsilon)(1-s_2\alpha) + (f^0_{\mathrm{ts}} - (f^0_{\mathrm{ts}}s_2 + s_1)\alpha)\varepsilon)(f^0_{\mathrm{tp}}(1-\varepsilon) + f^0_{\mathrm{ts}}\varepsilon)}\right)\right) \tag{21}$$

Table 2
Diffusivity of end-capped epoxy into amorphous PSU film and amine–PSU film at 80°C. Numbers in parentheses are the regression coefficients [4]

Peak (cm^{-1})	Epoxy diffusivity into amorphous PSU film (m^2/s)	Epoxy diffusivity into amine–PSU film (m^2/s)	Amine diffusivity from amine–PSU film (m^2/s)
1609	6.5×10^{-15} (0.96)	2.3×10^{-14} (0.90)	–
1508	4.8×10^{-15} (0.99)	1.5×10^{-14} (0.97)	–
2918	–	–	5.7×10^{-14} (0.99)
Average diffusivity	6.0×10^{-15}	2.0×10^{-14}	

and,

$$\frac{D_\mathrm{a}^\mathrm{cure}}{D_\mathrm{a}(T)} = \exp\left(B\left(-\frac{s_1 \alpha \varepsilon}{(f_\mathrm{tp}^0(1-\varepsilon)(1-s_2\alpha) + (f_\mathrm{ts}^0 - (f_\mathrm{ts}^0 s_2 + s_1)\alpha)\varepsilon)(f_\mathrm{tp}^0(1-\varepsilon) + f_\mathrm{ts}^0 \varepsilon)}\right)\right) \tag{22}$$

where:

$$s_1 = \beta T_\mathrm{g0}\left(\frac{E_x}{E_m} - \frac{F_x}{F_m}\right) \tag{23}$$

$$s_2 = 1 - \frac{F_x}{F_m} \tag{24}$$

$$f_\mathrm{tp}^0 = f_\mathrm{tp}(0, T) \tag{25}$$

$$f_\mathrm{ts}^0 = f_\mathrm{ts}(\alpha = 0, T) \tag{26}$$

We have generated a model whose main results are given by Eqs. (21) and (22). This model is capable of explaining the change in the diffusivity of thermoset monomers into amorphous thermoplastics with reaction during the initial interdiffusion regime. Previous experiments [4] suggest that reaction and related thermodynamic effects tend to dominate over the interdiffusion process for a degree of cure α close to 0.3 and beyond. It is expected that the proposed model is valid only in the $\alpha < 0.3$ regime. Predictive capabilities of this model are expected to be limited by the range of validity of the various inherent empirical models for e.g. the Arrhenius diffusivity model and the autocatalytic model for reaction. Section 4 describes the model development for the increased epoxy diffusivity from amine-induced PSU swelling, $D_{\mathrm{e(a)}}(c_\mathrm{a}, f)$, using previously published experimental ATR-FTIR data [4].

4. Swelling dependence of epoxy diffusivity

In a previous study [2,4] an end-capped, non-reactive DGEBA epoxy was synthesized from the reactive DGEBA resin to enable a study of the effects of swelling on epoxy diffusivity without hindrances from reaction. Consequently, diffusion of this epoxy into an amine swollen PSU film saturated with the equilibrium concentration of amine (0.61 at 80°C [1,2,4]) was studied using the ATR-FTIR technique. The results on the baseline and increased epoxy diffusivity are given in Table 2 [4]. From these results, the end-capped epoxy diffusivity into a 61% by volume amine–PSU film was determined to be about three times as large as the baseline diffusivity into amorphous PSU. Further, it appeared that the amine was diffusing from the film to the epoxy bath in a manner opposite to that of the epoxy.

This dependence of epoxy diffusivity on the equilibrium amine concentration can be modeled using the empirical relation proposed by Kwei and Wang [38]. They studied the diffusion with swelling of organic vapors and liquids in glassy polymers. This expression holds if the polymer segments are free to move and mix with the penetrant molecules, and has been shown to be valid for many polymers. Expressing the ratio of the enhanced epoxy diffusivity in the presence of amine to its Arrhenius diffusivity through a simple exponential concentration dependence, we can write:

$$\frac{D_{\mathrm{e(a)}}(c_\mathrm{a}, T)}{D_\mathrm{e}(T)} = \exp(\gamma c_\mathrm{a}) \tag{27}$$

where γ is a constant, $D_{\mathrm{e(a)}}(c_\mathrm{a}, f)$ the enhanced epoxy diffusivity in the presence of amine in PSU, $D_\mathrm{e}(f)$ the Arrhenius epoxy diffusivity in PSU [1,37], and c_a the amine concentration. Eq. (27) is valid for our work provided the diffusion of amine to the bath does not significantly change the extent of PSU swelling in the timescale for end-capped epoxy diffusion into the film. This was verified through changes in density measured during the drying of 61 vol.% amine–PSU film samples at 80°C. These measurements reveal a reduction in the swollen PSU volume of about 10% in the timescale of interest. Hence Eq. (27) can be used in good confidence to predict the influence of the amine concentration on epoxy diffusivity. The parameter γ is calculated to be 2.1 for a 61% amine-saturated PSU film exhibiting a diffusivity ratio as 3.3 from Table 2.

Assuming that the factor γ is independent of temperature, an Arrhenius relation for diffusivity can be expressed, in m^2/s:

$$D_{\mathrm{e(a)}}(c_\mathrm{a}, T) = D_\mathrm{e}(T)\exp(2.1 c_\mathrm{a}) \tag{28}$$

where

$$D_\mathrm{e}(T) = 52.3 \times 10^{-4} \exp\left(-\frac{18{,}500}{\mathrm{R}T}\right) \tag{29}$$

is the Arrhenius epoxy diffusivity into PSU [1,37]. Eq. (28) is

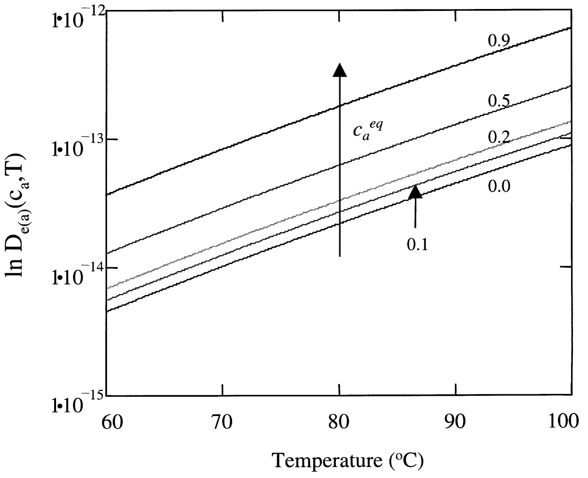

Fig. 5. Effect of equilibrium volume fraction of amine on observed epoxy diffusivity, using Eq. (33).

the desired explicit expression for the swelling dependence of the epoxy diffusivity on amine concentration, where extent of PSU swelling increases in direct proportion to amine concentration in PSU. A free volume-based approach was not considered here since a stoichiometric concentration of amine (volume fraction = 0.25) is used during combined epoxy–amine diffusion into PSU, which limits the maximum possible amine concentration in PSU to 0.25, and provides an upper limit for PSU swelling. Then, the corresponding effect on overall polymer free volume is expected to be on a smaller scale than reaction effects on free volume. Fig. 5 shows the effect of equilibrium amine volume fraction on the epoxy diffusivity. As the amount of amine increases, PSU swelling increases thereby increasing the epoxy diffusivity.

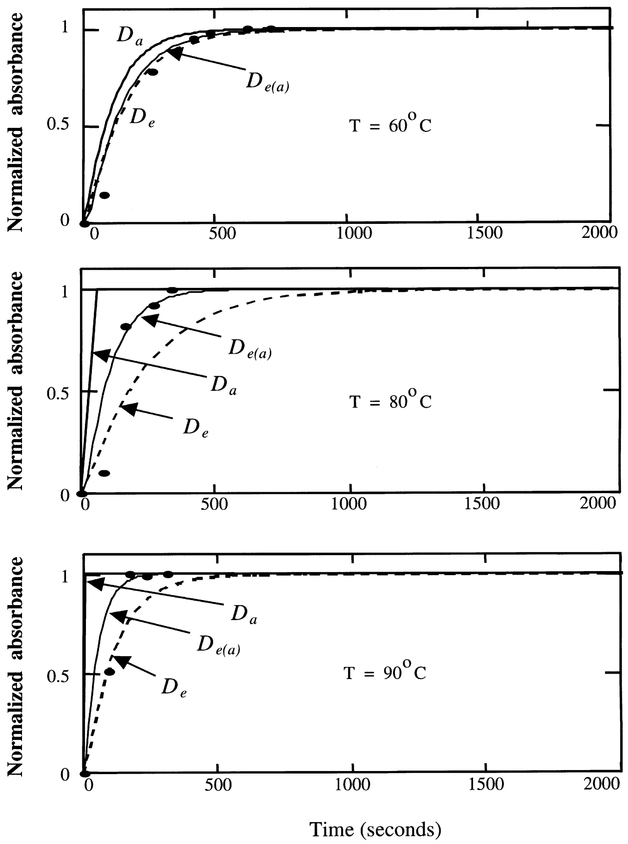

Fig. 6. Comparison of experimental 1036 cm^{-1} peak absorbance with predicted absorbance profile using the enhanced epoxy diffusivity Eq. (33) in Eq. (30) bound by the normalized absorbance predicted using epoxy and amine Arrhenius diffusivities for diffusion only.

Table 3
Predicted epoxy diffusivity using Eq. (33) vs. temperature during the simultaneous diffusion and reaction of epoxy and amine

T (°C)	D_a (m^2/s)	D_e (m^2/s)	Predicted $D_{e(a)}$ using Eq. (33) (m^2/s)	$D_{e(a)}$ using fit from Eq. (30) (m^2/s)
60	6.4×10^{-15}	4.5×10^{-15}	5.5×10^{-15}	6.0×10^{-15}
80	6.3×10^{-13}	2.2×10^{-14}	3.0×10^{-14}	2.6×10^{-14}
90	5.2×10^{-12}	4.5×10^{-14}	6.5×10^{-14}	5.5×10^{-14}

The swelling model proposed above can be validated with ATR-FTIR data obtained previously [4]. Fig. 6 shows the comparison of the 1036 cm^{-1} DGEBA peak absorbance data, during the diffusion-reaction experiments using the thin PSU films, with the absorbance–time profiles for the epoxy and amine at 60, 80, and 90°C predicted using the Arrhenius diffusivity expressions for epoxy and amine, respectively [1,2,4,37]. These absorbance profiles are obtained using the following expression:

$$\frac{A(t)-A_\infty}{A_0-A_\infty}=\frac{\sum_{n=0}^{\infty}F_n\exp\left(-\left(\frac{(2n+1)\pi}{2l}\right)^2Dt\right)}{\sum_{n=0}^{\infty}F_n}\tag{30}$$

where $A(t)$, A_0, and A_∞ are the absorbances at time t, $t=0$, and $t=\infty$, respectively, D is the diffusivity, and

$$F_n=\left[\frac{(-1)^n}{2n+1}\frac{l}{d_p}+\frac{\pi}{4}\exp\left(-2\frac{l}{d_p}\right)\right]\times\left[\frac{1}{((2n+1)\pi)^2+16\left(\frac{l}{d_p}\right)^2}\right]\tag{31}$$

The Arrhenius epoxy diffusivity expression is given in Eq. (29) while that for the amine is:

$$D_a(T)(\mathrm{m^2/s})=1.044\times10^{21}\exp\left(-\frac{54,000}{\mathrm{R}T}\right)\tag{32}$$

The effect of PSU swelling is evident as an increased epoxy diffusivity at the higher temperatures.

Eq. (28) can be used to interpret the data in Fig. 6 for the study of simultaneous diffusion of epoxy and amine. Since a stoichiometric quantity of epoxy to amine (0.75/0.25 vol.%)

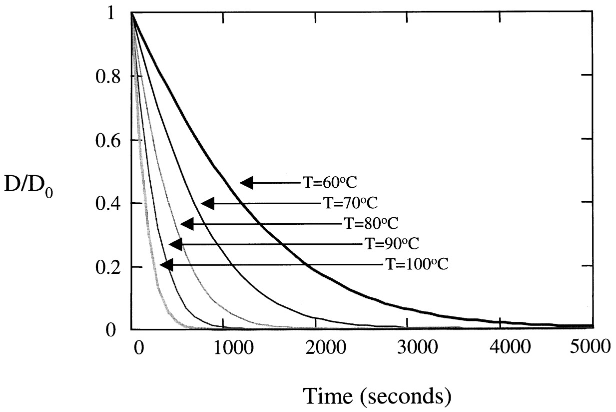

Fig. 7. Variation of normalized diffusivity as a function of time, for various temperatures. $B = 1.1$, volume fraction thermoset, $\varepsilon = 0.03$.

was used in this study, it is expected that the maximum possible normalized amine concentration in the bath and PSU is 0.25. Hence incorporating this value in Eq. (28) gives:

$$D_{e(a)}(c_a, T) = 52.3 \times 10^{-4} \exp(2.1 c_a^{norm}) \exp\left(-\frac{18,500}{RT}\right) \tag{33}$$

where c_a^{norm} is the stoichiometric amine concentration in the bath (0.25) and is also assumed to approximate that in the film. Using Eq. (33) with the absorbance equation [1,2,4] concentration profiles can be predicted at the three temperatures studied to calculate normalized absorbance values. This is also shown in Fig. 6. It is seen that these predictions are accurate and represent well the physical behavior of this system. The results are summarized in Table 3 where the Arrhenius diffusivities of the epoxy and amine are shown, along with predicted epoxy diffusivities using Eq. (33). Further the absorbance data was fit to Eq. (30) to determine the increased epoxy diffusivity, and these values are also presented in Table 3. It is seen that the predictions of the diffusivity model developed show good agreement with the diffusivities determined using the fits to data. It should be noted that Eq. (33) provides an upper bound on the observed increase in epoxy diffusivity since, in reality, the diffusivity decreases with time from reaction. Also the equilibrium amine concentration in the PSU film may not reach 0.25. Further, in Table 3, the diffusivity values obtained using fits of Eq. (30) to the non-reactive epoxy peak absorbance data are apparent diffusivity values, as diffusivity decreases with time during the diffusion-reaction experiment.

In this section, we have presented a cure-dependent diffusivity model for the diffusion of epoxy and amine into amorphous PSU using the Fujita free volume theory. Further, we have presented and validated a swelling model to explain the increased epoxy diffusivity observed during the simultaneous diffusion with reaction of epoxy and amine into amorphous PSU [2,4]. In combination with the cure dependence of the epoxy diffusivity derived in this work, the complete diffusivity model for the epoxy into amorphous PSU is obtained. The corresponding model for the amine displays the reaction dependence only. This diffusivity model can be validated by inserting in a transport model and predicting diffusion depths of the thermoset into the thermoplastic, termed interphase, with temperature and validating with experimentally measured interphase sizes [1–3].

The parametric studies on the effects of the various parameters on the epoxy diffusivity expression in Eq. (19) are described in Section 5.

5. Parametric study on diffusivity

In this section, parametric studies on the reaction and swelling-dependent diffusivity expressions are performed. These studies will assist in determining the nature in which time (t), temperature (f) and related parameters (c_a and ε) influence the overall rate of diffusivity change.

5.1. Effect of time t and temperature T

The effect of time on normalized diffusivity is also evident from Fig. 7 for the various temperatures. It is seen that diffusivity tends to decrease with increasing time. For the thermoset, the degree of cure α is a function of time (Eq. (12)), and increases with time. Consequently, the glass transition temperature of the curing thermoset increases with time (Eq. (13)), hence decreasing the fractional free volume (Eq. (4)) and, consequently, the diffusivity.

The temperature affects the amount of fractional free volume in the system, as seen from Eq. (4). Using Eq. (21) without the swelling dependence, a parametric analysis of the variation of normalized diffusivity with temperature is given in Fig. 7 for an arbitrary ε, where D_0 is the Arrhenius diffusivity. Normalized diffusivity decreases more rapidly at higher temperatures than at lower ones. The reason for this is as follows: as the temperature increases, thermoset cure is accelerated and the rate of crosslink formation is higher. This causes a more rapid decrease of the free volume with increasing temperature and hence the observed trend in normalized diffusivity with time for changing temperatures.

5.2. Effect of amine concentration c_a

The effect of the amine concentration on overall epoxy diffusivity from swelling (Eq. 28) seems fairly obvious—increasing c_a increases the diffusivity, and was described in Fig. 5. However, during the combined diffusion with reaction of a stoichiometric amount of epoxy and amine into PSU, the extent of swelling and, thereby, the increase in epoxy diffusivity, is limited by the stoichiometric concentration of the amine (0.25 vol.%).

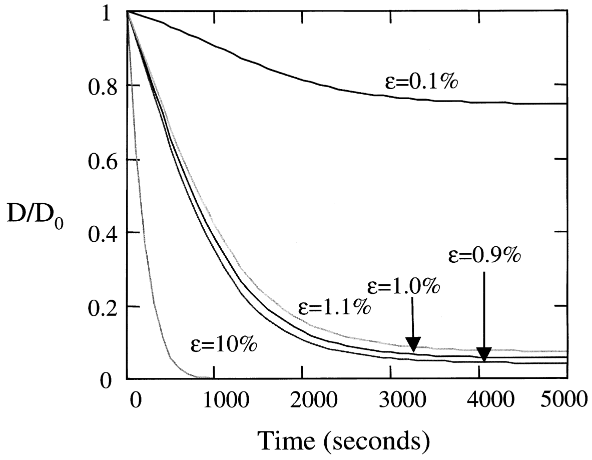

Fig. 8. Variation of normalized diffusivity as a function of time for varying volume fraction thermoset, ε. $T = 80°\mathrm{C}$, $B = 1.1$.

5.3. *Effect of thermoset volume fraction* ε

As mentioned before, ε is the total volume fraction of the epoxy and amine in the thermoplastic i.e. it is the sum of the concentrations of the epoxy and amine in the thermoplastic at any given time. These results are presented in Fig. 8. It is seen that very low percentages of thermoset can change normalized diffusivity significantly. For this epoxy–amine–PSU system, it is seen that normalized diffusivity can vary drastically from 1% of thermoset in the thermoplastic. This can be explained by considering the Fujita expression for the average fractional free volume in the thermoset–thermoplastic system, particularly the effects of ε on normalized diffusivity. The overall free volume is a constant, equaling that in the thermoplastic when ε is zero. Correspondingly, the normalized diffusivity is a constant with time. When ε is 1, the situation approaches that of a curing thermoset. The decrease in normalized diffusivity is most rapid with time for this case. Therefore, the larger the departure from the pure thermoplastic case, more rapid the decrease in normalized diffusivity and in the limit $\varepsilon \longrightarrow 1$ it approaches that for a curing thermoset. In reality, the situation is dynamic i.e. ε changes with time as diffusion occurs. Since normalized diffusivity decreases with increasing ε, this study shows that a trade-off is reached at a certain time, and this will depend on the temperature of the system.

An interesting observation here is that while the epoxy diffusivity increases with amine concentration c_a during swelling (Fig. 5), it decreases with increasing volume fraction of epoxy and amine, $\varepsilon(c_a + c_e)$, from reaction. This can be explained as follows: at small times, the degree of cure α is low, and diffusion is dominant [1,2,4]. Hence c_a increases with time, and leads to swelling which increases observed epoxy diffusivity [2,4]. However, with time, reaction begins to dominate over diffusion, and the corresponding effect on thermoset diffusivity becomes significant, leading to the decrease with time [2,4].

From the parametric study, it is seen that all four parameters (t, T, c_a, and ε) influence the interdiffusion of thermoset monomers into amorphous thermoplastics strongly. While epoxy diffusivity increases with increasing amine concentration from PSU swelling, an increase in the other parameters leads to a rapid decrease in the normalized diffusivity with time. Temperature affects diffusivity in an Arrhenius manner, and through the thermoset reaction rate, which influences diffusivity. c_a and ε affect the overall fractional free volume in the system.

In general, it is seen that the diffusivity is a complex function of many variables. These include the glass transition temperatures of the components, the process-related properties of the thermoset cure, the amount of thermoset in the thermoplastic, and the critical free volume size available for a diffusive jump.

6. Conclusions

The present study presents a preliminary diffusivity model for multi-component diffusion accompanied by reactive and swelling processes. This diffusivity model was presented for the case of DGEBA epoxy–PACM 20 amine monomer diffusion into amorphous PSU, where the mechanisms of swelling and reaction are present. The model is valid only during the initial time scales of interdiffusion of the monomers into PSU. The reaction component of the model was developed using certain assumptions to the Fujita theory for diffusion in binary solvent–polymer systems. By considering the initial solution behavior of the thermosetting monomers to approximate that of a low molecular weight solvent, this theory was extended to the study of diffusion in thermoset–thermoplastic systems. The model developed here is valid for low degrees of cure α and low thermoset volume fractions. It accounts for the decrease in thermoset diffusivity with increasing reaction, through a loss in the overall fractional free volume of the material system. The range of applicability of the various empirical sub-models used limits the predictive capabilities of the model. An engineering use for such a model is in processing, where for maximum bond strength between dissimilar materials, the diffusion depth (interphase size) should be a maximum.

Previous work presented experimental ATR-FTIR data on the diffusion of the current epoxy and amine system into amorphous PSU [4] showing how swelling and reaction affect the diffusion process. The diffusivity model developed in this work provides valuable insight into how swelling and reaction affect monomer diffusivity. In order to gain further theoretical understanding of this intricate process, future work should focus on the formulation and development of mass transport models for the diffusion with reaction of epoxy and amine into amorphous PSU, incorporating the diffusivity model developed here. Such models will help understand the experimental ATR-FTIR data, and also provide invaluable insight into the nature of interphase formation in such material systems.

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