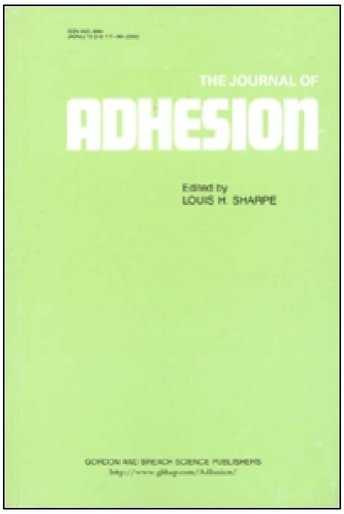

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In-Situ Evaluation of the Diffusion of Epoxy and Amine in Thermoplastic Polymers

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The current study investigates the diffusion of a bisphenol A type epoxy resin and a diamine curing agent into polysulfone (PSU) using a Fourier Transform Infrared Spectroscopy-Attenuated Total Reflectance (FTIR-ATR) technique. The diffusion of epoxy or amine through the film was monitored in real time by measuring the changing intensity of selected characteristic absorbance bands in each of the polymers. The diffusion coefficients for the epoxy and amine were determined independently using the appropriate solution to the diffusion equation and the experimental data. Diffusivities were evaluated at several temperatures, and an Arrhenius relationship was observed. Results show that the diffusivity of amine is an order of magnitude greater than the diffusivity of epoxy at each temperature tested. Furthermore, the epoxy diffusion appears to be Fickian, while the diffusion of amine appears to be non-Fickian.

Keywords: Diffusion; epoxy; amine; polysulfone infrared spectroscopy

INTRODUCTION

Thermoplastic-matrix composites offer several advantages over thermoset-matrix composites such as higher interlaminar toughness, infinite

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shelf life, and rapid manufacturing. However, difficulties in joining thermoplastic composites may potentially hinder the widespread use of these materials in structural applications. Joining thermoplastic composite components with structural adhesives often requires elaborate surface treatment of the thermoplastic composite adherends. These surface treatments have several limitations in production environments including finite shelf life, cost, and possible restrictions on part size and shape. Other methods of enhancing bond performance are available. It has been shown that adhesion between thermoplastic composites and epoxy-based adhesives is improved in instances where polymer interdiffusion across the interface is suspected [1]. This technique has been successfully employed on thermoplastic composite components used in the Composite Armored Vehicle Advanced Technology Demonstrator (CAV-ATD). The success has been attributed to interfacial diffusion of the pre-polymers into the thermoplastic material during processing. Upon final cure, bonding is believed to be enhanced through entanglements between the thermoplastic polymer chains and the network structure of the adhesive. Optimization of this bonding process requires an understanding of the rate of diffusion of the adhesive prepolymers into the thermoplastic.

BACKGROUND

The diffusion of small molecules into polymers is often investigated using gravimetric methods. However, several challenges exist when using this technique to study the diffusion of high-viscosity liquids such as epoxy resins and amine curing agents. These challenges include difficulty in removing the liquids from the surface of the polymer prior to weighing, difficulty in determining how much of the weight gain is due to surface polymer and how much to diffusion, and the length of time it takes to complete the experiments due to the macroscopic dimensions of the samples and the low diffusivities of the molecules. However, other techniques can be used to study penetrant diffusion. For example, FTIR-ATR has recently been used to study transport phenomena in polymer materials [2, 3, 4].

FTIR-ATR is an internal reflection technique in which an optically dense medium (the internal reflection element, or IRE) is used as a waveguide to obtain an infrared spectrum. The infrared radiation above the critical angle is totally reflected at the crystal/sample interface. An evanescent wave is formed at the crystal/sample interface. This wave decays exponentially from the surface through the penetration depth. The penetration depth is given by the following equation and is defined as the distance at which the electric field formed by the evanescent wave diminishes by a factor of 1/e [5]:

$$dp = \frac{\lambda}{2\pi n_2\left(\sin^2\theta - \left(\frac{n_1}{n_2}\right)^2\right)^{1/2}} \tag{1}$$

where λ is the wavelength of light in vacuum, θ is the angle of incidence, and n_1 and n_2 are the refractive indices of the IR crystal and the sample, respectively.

If the sample absorbs in the infrared, the evanescent wave interacts with the material causing attenuation of the total reflection of the propagating beam inside the IR crystal. An IR spectrum of the sample is obtained by detecting the attenuated radiation. The absorbance, A, is given by the following equation, which is the equivalent to the Beer-Lambert law for transmission [3]:

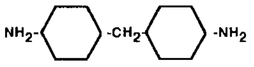
$$A = \int_0^\infty aSC(z)\exp\left(-\frac{2z}{d_p}\right)dz \tag{2}$$

where z is the distance from the surface, a is the oscillator strength, $C(z)$ is the concentration, S is the cross-sectional area, and d_p is the penetration depth. This expression represents a weighted average of the concentration of the absorbing species; thus, the majority of the signal is obtained from the material closest to the IRE interface.

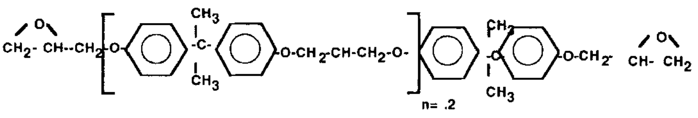
EXPERIMENTAL

Materials

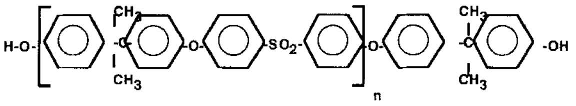
PSU was the amorphous thermoplastic selected for the study because earlier work [6] showed it to be compatible with the DGEBA (diglycidyl ether of bisphenol A) epoxides. Other researchers have added PSU to epoxy to improve the fracture toughness and increase ductility [7, 8]. The DGEBA epoxy resin chosen for this work was Shell Epon 828,™ which has a functionality of two; an aliphatic diamine PACM-20, was selected as the curing agent. The kinetics of this epoxy/amine system has been extensively studied by other researchers [9, 10]. The chemical structure of all materials can be found in Figure 1. Table I lists some material properties.



Diamine Curing Agent
(PACM 20)



Epoxy Resin
(EPON 828)



Polysulfone

FIGURE 1 Chemical structure of PSU, PACM-20 and Epon 828.

TABLE I Molecular weight, density and molar volume of materials

Material	*Molecular Weight (g/mole)*	*Density (g/cm^2)*	*Molar Volume (cm^3/mole)*
PSU	6400–10,000	1.24	
Epon 828	370–384	1.162	318–331
PACM-20	210	0.95	221

Procedure

Diffusion couples were formed directly on the IRE's as shown schematically in Figure 2. Trapezoidal germanium internal reflection elements with an incident angle of 60 degrees and dimensions of 50 mm × 5 mm × 1 mm were used in this work. Thin films of PSU were obtained by spin coating the germanium crystals with a 5% by weight solution of PSU in methylene chloride. Three coats at 5000 rpm for 30 seconds consistently produced 10-micron films. The coated crystal was then placed next to a Teflon® fluid boat in a heated sample holder. The entire assembly was heated to a constant temperature before the pre-heated penetrant was injected into the bath. Figure 3 shows a schematic of the experimental set-up.

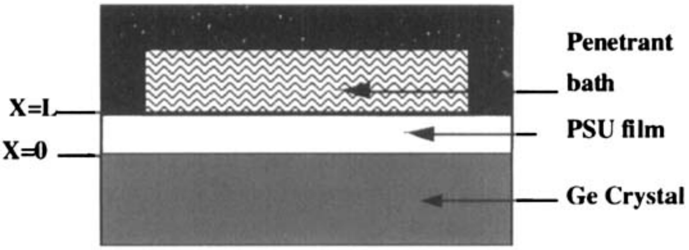


FIGURE 2 Experimental geometry used to solve diffusion equation.

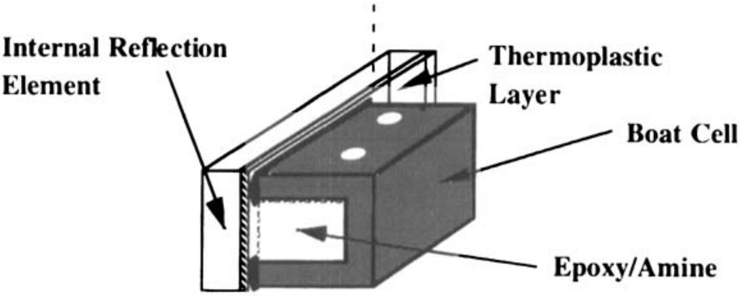


FIGURE 3 Schematic of diffusion experiment set-up.

Peak Selection, Identification and Monitoring

The FTIR-ATR technique provides information through the change in peak height or peak area with time. In order to use this technique to study diffusion, there must be detectable and distinguishable peaks in the spectra of each of the components in the system being studied. Infrared spectra of the pure components were obtained to determine which absorbance peaks could be monitored to study the diffusion of epoxy and amine into PSU. The peak at 1151 cm^{-1} corresponds to the S=O stretching [11]. In the epoxy, the 915 cm^{-1} peak, which is assigned to the epoxide ring deformation, and the 1032 cm^{-1} peak, which is assigned to the aromatic deformation, were monitored throughout the diffusion experiment. The 2916 cm^{-1} peak in the amine spectrum corresponds to the C—H stretching of the diamine cyclohexane ring. Table II lists some of the bands tracked in this work.

Spectra were taken in real time at regular intervals until the system reached equilibrium. The epoxy experiment was performed at 80°C and 60°C. (The epoxy experiment was attempted at 50°C, but the diffusion was too slow to complete the experiment in a reasonable period of time.) The diffusion of amine into PSU was investigated at 80°C, 60°C, and 50°C. The change in peak height was recorded as a function of time. For example, the evolution of the epoxy peak due to diffusion is shown in Figure 4.

RESULTS

Data Analysis

The data generated by the FTIR-ATR experiments are peak height as a function of time. The diffusivity is determined by solving Fick's

TABLE II Peaks monitored during diffusion experiment

Polymer	*Band*	*Group*
Epon 828	915	Epoxide Deformation
	1036	Aromatic Deformation
PACM 20	2916	C—H Stretching of diamine cyclohexane ring
PSU	1151	S=O Stretching
PSU	1488	CH_3 Deformation

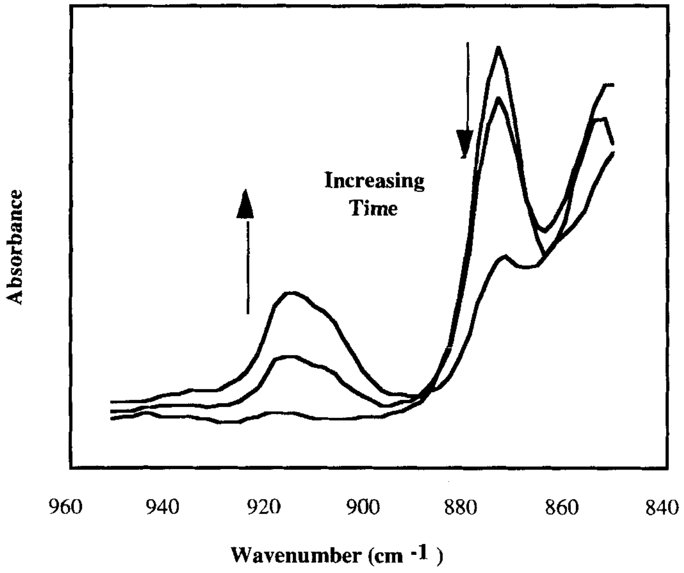


FIGURE 4 Schematic of the evolution of the epoxy peak due to diffusion.

second law with the appropriate boundary conditions [12]. The expression for concentration is put into Eq. (2) to determine the absorbance. The expression in nondimensionalized form below is fit to the experimental absorbance data [13].

$$\frac{A(t)-A_\infty}{A_0-A_\infty} = \frac{\sum_{n=0}^{\infty} F_n \exp\left(-\left(\frac{(2n+1)\pi}{2l}\right)^2 Dt\right)}{\sum_{n=0}^{\infty} F_n} \tag{3}$$

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

Epoxy Diffusion in Polysulfone

The diffusion of epoxy resin into PSU was investigated at 80°C and 60°C. The height of the epoxy bands increased over time as the height of PSU peaks decreased. The absorbances of both achieved a constant value once equilibrium was reached. The data were normalized to the final absorbances of epoxy, and Eq. (3) was used to fit the normalized absorbance data to determine the diffusion coefficients of epoxy in PSU at each temperature. Diffusivity was the only fitting parameter used in the analysis. Figure 5 shows the fit to the 1151 cm^{-1} PSU peak and the 915 cm^{-1} epoxy peak during the 80°C experiment. The diffusion coefficients determined from the 1151 cm^{-1} peak absorbance data are summarized in Table III. The error listed in Table III corresponds to the error of the fit to Eq. (3).

Generally the data are well represented by the Fickian model. Overall, the model slightly underestimates the rate of diffusion at early times and overestimates the rate at intermediate times at both temperatures tested. This phenomenon may be due to the boundary condition, which assumes that equilibrium is instantaneously achieved at the penetrant/bath interface. More likely, there is a delay associated with equilibrium.

The results indicate that epoxy does diffuse into PSU at the temperatures studied, and the assumptions made in the Fickian analysis are valid for this system. An Arrhenius relationship exists for the diffusivities of epoxy into PSU.

Amine Diffusion of Polysulfone

The diffusion of amine curing agent into PSU was studied at 80°C, 60°C, and 50°C. The peaks associated with amine groups increased with time, while those associated with PSU groups decreased over time, indicating that diffusion is occurring at these temperatures.

Unlike the absorbance of the epoxy peaks, the absorbance of the amine peaks did not reach a constant equilibrium value. Therefore, it was not possible to obtain a goot fit to the normalized experimental absorbance data using Eq. (3). The equation was rewritten as follows such that the final absorbance is a second fitting parameter:

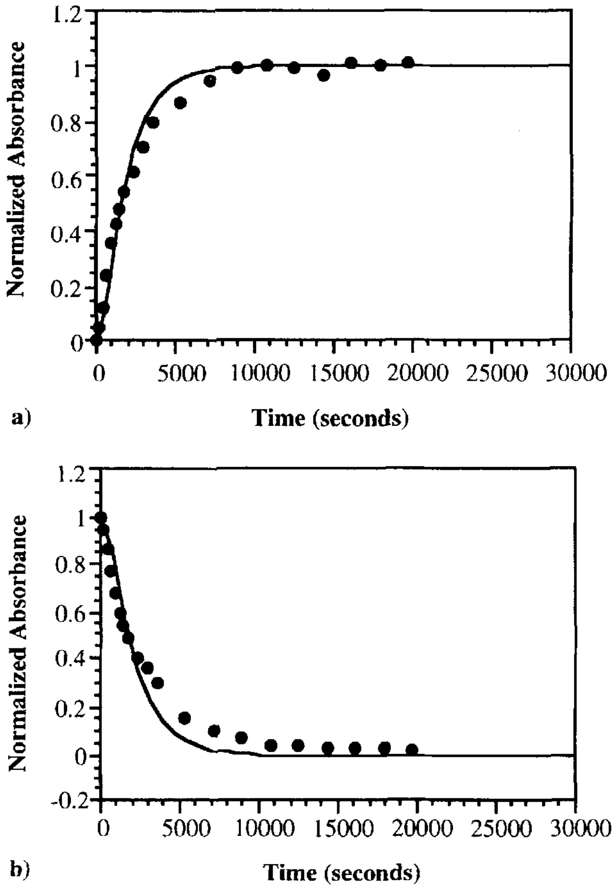


FIGURE 5 Normalized absorbance of the a) 915 cm^{-1} and b) 1151 cm^{-1} peaks during the 80°C epoxy/PSU diffusion experiment.

TABLE III Experimentally determined diffusivities

Temperature (°C)	*D Epoxy (cm^2/s)*	*Error (%)*	*D Amine (cm^2/s)*	*Error (%)*
80	2.31 E-10	6.7	6.63 E-09	16
60	1.11 E-11	8.1	3.25 E-10	13
50			5.47 E-12	21

$$A(t) = \left(\left(\frac{\sum_{n=0}^{\infty} F_n \exp\left(-\left(\frac{(2n+1)\pi}{2l} \right)^2 Dt \right)}{\sum_{n=0}^{\infty} F_n} \right) (A_0 - A_\infty) \right) + A_\infty \quad (5)$$

In order to obtain an apparent diffusivity value the above equation was fit to the initial absorbance data. Figure 6 shows an example of the experimental amine data. The top graph shows the fit of Eq. (5) the 1151 cm^{-1} peak at each temperature. The lower graph shows the absorbance of the 2915 cm^{-1} amine peak for the entire duration of

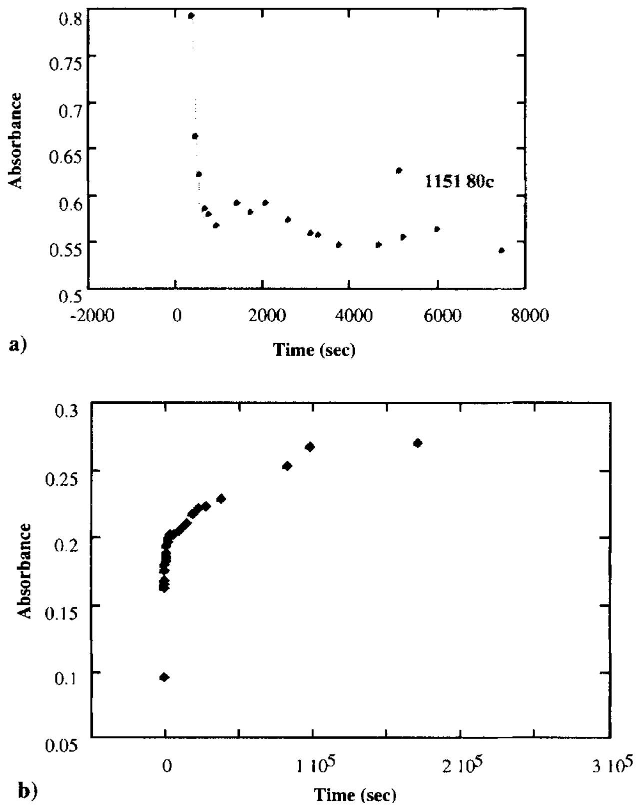


FIGURE 6 a) Absorbance of 1151 cm^{-1} PSU peak with associated fit during amine experiment at 80°C and b) absorbance of 2915 cm^{-1} amine peak.

the experiment. The diffusion coefficients at each temperature are listed in Table III.

The results show that the amine diffusion is not truly Fickian. The effects of swelling were ignored in the Fickian analysis, and it is suspected that the amine swells the PSU network as it diffuses.

Temperature Dependence of Diffusivities

The experimentally determined epoxy and amine diffusivities were fit with an Arrhenius type of equation as follows:

$$D = D_0 \exp\left(\frac{-E_0}{RT}\right) \tag{6}$$

where D is the diffusivity, D_0 is the pre-exponential constant, and E_0 is the activation energy. The results of the fit are shown in Figure 7. Additional experiments are required to determine the constants associated with the epoxy fit more accurately; however, the pre-exponential terms and the activation energies listed in Table IV can be used to predict the diffusivities at other temperatures.

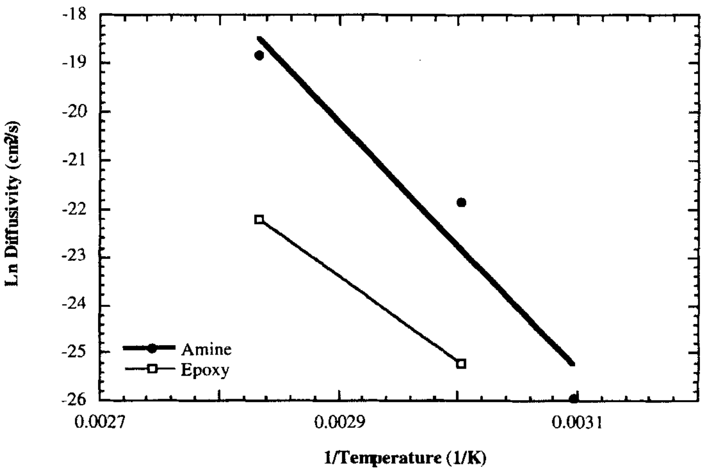


FIGURE 7 Arrhenius plot for diffusivities of epoxy and amine in PSU.

TABLE IV Activation Energy and pre-exponential Constant

Diffusant	*Activation Energy (kcal/mole)*	*Pre-exponential (cm^2/s)*
Epoxy	2.1	4.86 E-13
Amine	3.1	1.67 E-24

DISCUSSION

This work has produced many significant results. Most importantly, it has been confirmed by the changes in absorbance over time that diffusion is indeed occurring. Previously it was only suspected that diffusion was one of the mechanisms responsible for bond strength.

The diffusion coefficients of epoxy and amine in PSU provide further insight into polymer diffusion. The magnitudes of the epoxy and amine diffusivities (10^{-9}–10^{-12}) into PSU are consistent with the reported diffusivities of other molecules. For example, water diffuses into polymers at 10^{-8} cm^2/sec [14], and reptation, the diffusion of high polymers, occurs at 10^{-13}–10^{-14} cm^2/sec [15].

The diffusivity of amine is an order of magnitude greater than that of epoxy at a given temperature. This result is expected in part due to the smaller molar volume of amine as compared with epoxy. Furthermore, it is suspected that the amine swells the PSU network, which creates more free volume and facilitates diffusion [16]. The difference between diffusion coefficients may cause large stoichiometric gradients that may result in compromised thermal and mechanical properties at the interphase. Furthermore, unreacted amine may be present in the interphase, affecting long-term durability and aging behavior.

The diffusivities were fit to an Arrhenius relationship. More experiments must be conducted to get a more accurate measure of the activation energy and pre-exponential term.

Epoxy and amine monomers exhibited different diffusion behavior in addition to different diffusion coefficients. The epoxy diffusion into PSU shows Fickian behavior over the entire length of the experiment at all temperatures. A constant equilibrium absorbance value was achieved, and diffusivity was the only fitting parameter needed to obtain a good fit to the Fickian model. The assumptions made in the analysis, such as penetrant diffusion and the presence of a stationary diffusion front, seem to be valid for the epoxy/PSU system.

Amine diffusion appears to deviate from Fickian behavior at intermediate and long time scales. Even though the duration of the amine experiments was greater than that of the epoxy experiments at the same temperature, a constant equilibrium absorbance was not obtained, and a second fitting parameter was necessary to determine the diffusivity. The assumptions made in the diffusion analysis are not valid for the amine/PSU system.

It is suspected that the amine molecule acts like a solvent in PSU, and swelling is responsible for the anomalous diffusion. The physical reason for the deviation from Fickian behavior is the time-dependent properties of a glassy polymer due to the finite rate of adjustment of the polymer chains in the presence of the penetrant [17]. Solvent penetration involves both diffusion of molecules through the polymer matrix and local relaxation of polymer segments. The solvent enhances the mobility of polymer chains by converting the glassy matrix to a swollen rubbery material [16].

Case II is the term used to describe diffusion when the penetrant swells the matrix. The role of both diffusion and swelling must be considered in analyzing data, as the diffusion behavior is determined by the relative time scales for diffusion and swelling. The latter is determined by the characteristic relaxation time of the glassy polymer in the presence of the solvent.

The Fickian behavior that was observed at short times is consistent with the assumption of Case II diffusion. Research has indicated that a small amount of solvent is present ahead of the front for Case II diffusion, and the concentration profile looks Fickian [18]. Furthermore, a certain solvent concentration must be reached before Case II diffusion occurs [19]. An induction time is needed to create sites in the polymer for the penetrant.

CONCLUSIONS

Much was learned about the diffusion of epoxy and amine into PSU through this study. FTIR-ATR was proven to be a good experimental technique to determine the diffusivity of epoxy and amine in PSU and, thereby, to gain a better understanding of the diffusion-enhanced bonding process.

The diffusivities of epoxy and amine as a function of temperature were determined. Epoxy and amine appear to behave differently in the presence of PSU. The epoxy shows Fickian behavior, while the amine diffusion is more non-Fickian. It appears that the amine swells the PSU as it diffuses through. Furthermore, the diffusivity of amine is an order of magnitude greater than the diffusivity of epoxy at a given temperature. The diffusivities show an Arrhenius relationship.

Acknowledgements

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