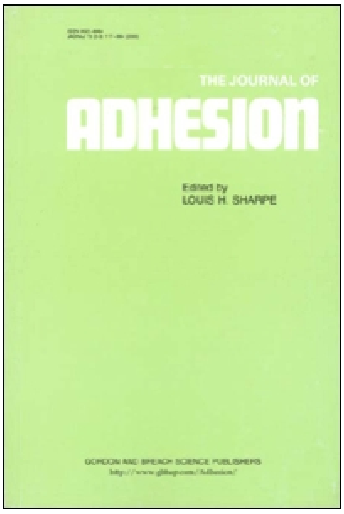

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Determination of Water Diffusion Coefficients and Dynamics in Adhesive/Carbon Fiber-Reinforced Phenolic Resin Composite Joints

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Determination of Water Diffusion Coefficients and Dynamics in Adhesive/Carbon Fiber–Reinforced Phenolic Resin Composite Joints

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Energy-dispersive X-ray spectroscopy analysis (EDX) is an easy and exact method for determination of water diffusion coefficients and dynamics. Here we have calculated the water diffusion coefficients and dynamics in adhesive/carbon fiber–reinforced phenolic resin composite joints subjected to different surface treatments with both EDX and elemental analysis. The water diffusion coefficients and dynamics in the adhesive joints determined with EDX analysis are almost the same as those determined with elemental analysis. The durability of the adhesive joints with carbon fiber–reinforced phenolic resin composites subjected to silane coupling agent treatment is better than those subjected to sandpaper burnishing and chemical oxidation treatment.

Keywords: Adhesive/carbon fiber–reinforced phenolic resin composite joints; Diffusion coefficients; Dynamics; Elemental analysis; Energy dispersive X-ray spectroscopy

1. INTRODUCTION

The significant weakening of adhesive joints as a result of both plasticisation and swelling is associated with the absorption of water, and such materials are regarded, in certain cases, as unsuitable for structural application. Moisture may penetrate and affect the adhesive

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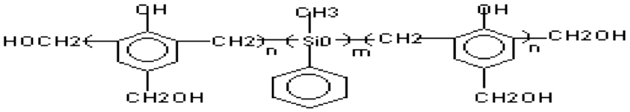

FIGURE 1 Schematic diagram of the structure of thermosetting phenolic resin modified by polyphenylmethyl siloxane.

joints by one or a combination of the following processes: diffusion through the adhesive, transport along the interface, and capillary action through cracks and crazes in the adhesive [1–13]. There are continuing efforts to improve the interfacial adhesion in adhesive joints using surface treatment methods, such as silane coupling agents.

Because water consists of oxygen and hydrogen, the water uptake in the adhesive in adhesive/carbon fiber–reinforced phenolic resin composite joints (adhesive/C-PF composite joints) can be obtained with both elemental analysis and energy dispersive X-ray spectroscopy (EDX) analysis from the changes in the content of oxygen in the adhesive during humidity aging.

A one-component adhesive for C-PF composite joints consisting of thermosetting phenolic resin modified by polyphenylmethyl siloxane, which can be cured at 180°C for 1 h, has been developed by our research group. In this study, water diffusion coefficients and dynamics in adhesive/C-PF composite joints subjected to different surface treatments are determined by both EDX and elemental analysis. The structure of thermosetting phenolic resin modified by polyphenylmethyl siloxane is shown in Figure 1.

2. EXPERIMENTAL

2.1. Materials and Adhesion Process

Carbon fiber–reinforced phenolic resin composites were provided by Aerospace Materials Institute of China (Beijing, China), in which the composite matrix was a thermosetting phenolic resin and the reinforcement was polyacrylonitrile-based carbon fiber, which was of the 12 K uncoated high-strength type, namely, T-600S provided by Toray Corporation (Tokyo, Japan).

Before adhesion, the surfaces of C-PF composite joints were treated by the following procedures: (1) Sandpaper burnishing treatment: burnished by 60-screen sandpaper; (2) chemical oxidation treatment:

burnished by 60-screen sandpaper, heated at 80°C for 1 h in an oxidizing agent ($K_2Cr_2O_7/H_2SO_4/H_2O$ = 1:3:10), then washed by water; and (3) silane coupling agent treatment: burnished by 60-screen sandpaper, heated at 80°C for 1 h in an oxidizing agent ($K_2Cr_2O_7/H_2SO_4/H_2O$ = 1:3:10), washed by water, coated by silane coupling agent [$H_2NCH_2CH_2CH_2Si(OC_2H_5)_3$], and then heated at 150°C for 1 h.

After the C-PF composites were treated by this process, the samples of the adhesive/C-PF composite joints were prepared according to ASTM D-1002. The adhesive/C-PF composite joints were cured at 180°C for 1 h at a pressure of 0.15–0.3 MPa. The thickness of the adhesive in the joints was controlled by the pressure.

2.2. Chemical and Structural Characterization

For humidity aging, the samples were held in a humidity cabinet SRLH-2 made by Harbin Instrument Corp. (Harbin, Heilongjiang Province, China) at 70°C and 98–100% relative humidity (RH) for time periods up to 800 h; 80°C and 98–100% RH for time periods up to 400 h; and 90°C and 98–100% RH for time periods up to 150 h.

EDX analysis on the joint samples was performed at room temperature with an ISIS-300 (Link Corp., Cambridge, UK) an EDX spectrometer. Figure 2 shows the schematic diagram for observing the adhesive in the joints with EDX analysis. The adhesive joints, after

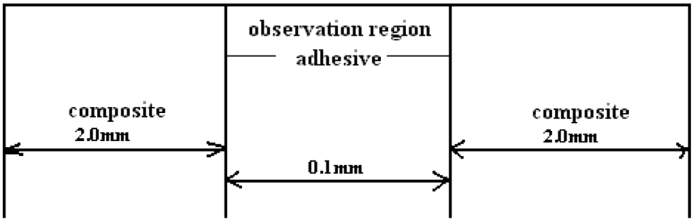

FIGURE 2 Schematic diagram for observing the adhesive in the joints with the EDX analysis method.

exposure to the conditions and for the times given previously, were sputter coated with gold prior to analysis.

Elemental analysis of the samples was performed at room temperature on a PE2400 elemental analyzer (PE Corp., Wellesley, MA, USA).

All data in figures are average values of ten samples. Standard deviation of the data was 10%.

2.3. Determination of Water Uptake in the Adhesive/C-PF Composite Joints

2.3.1. Determination of Water Uptake in the Joints from EDX Analysis

If the water diffusion speed in the adhesive is presumed to be constant, the water uptake can be determined from the changes in oxygen in the adhesive in humidity aging, because water contains oxygen and hydrogen. The water uptake formula of the adhesive is described as follows:

$$C'' = (C \times R - C_0) \times \frac{M_{H_2O}}{M_0}, \tag{1}$$

where C'' is the water uptake in the adhesive joints; C is the percentage of oxygen in the total of carbon and oxygen in the adhesive, which is obtained with EDX; C_0 is the uptake of oxygen in the adhesive before aging; and R is the sum of carbon and oxygen elements in the adhesive before aging. In this study, C_0 is 3.94%, and R is 93.15%; both are determined by chemical structure characteristics of the adhesive and obtained with elemental analysis. M_{H_2O} and M_0 are molecular weights of H_2O and oxygen, respectively.

2.3.2. Determination of Water Uptake in the Joints from Elemental Analysis

If the water penetration rate in the adhesive is assumed to be constant, the water uptake of the adhesive is calculated with elemental analysis:

$$C'' = (C' - C_0) \times \frac{M_{H_2O}}{M_0}. \tag{2}$$

Here, C' is the uptake of oxygen element in the adhesive joints, which is obtained with elemental analysis. Other symbols are the same as in Equation (1).

3. RESULTS AND DISCUSSION

3.1. Determination of Water Diffusion Coefficients in the Adhesive Joints

By Fick's second law, the differential mass transfer equation of water diffusion at a different direction is expressed as [13]

$$\frac{\partial C}{\partial t} = D\left(\frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} + \frac{\partial^2 C}{\partial z^2}\right), \tag{3}$$

where C is the concentration of water, D is the diffusion coefficient, $\partial C/\partial x$ is the concentration gradient of water, x is the diffusion distance, and t is time. Here, only mass diffusion caused by concentration difference is discussed; free diffusion arising from thermal movement is not considered. Assuming the diffusion coefficient and polymer volume are invariable in all diffusion processes and no chemical reaction occurs, then the mass-transfer Equation (3) is simplified to Equation (4) in the x axis direction:

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2}. \tag{4}$$

If equilibrium between the bath and the surface of the film is established instantaneously upon immersion, integration of Equation (5) yields Equation (6):

$$\frac{\Delta C}{C_{\max}} = \frac{4}{b}\sqrt{D\frac{t}{\pi}} \tag{5}$$

as

$$D = \frac{\pi b^2}{16}\left(\frac{\Delta C}{C_{\max}} \times \frac{1}{\sqrt{t}}\right)^2 \tag{6}$$

In these equations, ΔC and $C_{\max}$ are the water uptake of adhesives at time t and after saturation, respectively. The width of the joints is b ($=20\,\text{mm}$) because the diffusion is considered to be one dimensional. Accordingly, the diffusion coefficient D can be calculated using EDX and elementary analysis.

Thus, Equation (6) indicates that a plot of mass uptake versus $t^{1/2}$ should be initially linear, and the diffusion coefficient can be calculated from the gradient.

The diffusion coefficients obtained from the slopes of the linear regions using Equation (6) are collected in Table 1. Table 1 shows that the values of water diffusion coefficients calculated from EDX analysis are almost the same as those calculated with elemental analysis under

TABLE 1 Water Diffusion Coefficients in the Joints in Different Humidity Aging Conditions

Surface treatment method	Temperature (°C)	Water diffusion coefficients D ($\times 10^{-12}m^2/h$) EDX analysis	Elemental analysis	Relative difference (%)
Silane coupling agent treatment	70	1.017	0.996	2.06
	80	2.011	1.951	2.98
	90	5.465	5.657	3.51
Chemical oxidation treatment	70	1.182	1.136	4.05
	80	2.350	2.293	2.49
	90	7.382	7.624	3.28
Sandpaper burnishing, washing	70	1.501	1.445	3.73
	80	3.200	3.207	0.22
	90	10.188	9.805	3.91

the same humidity aging conditions. EDX analysis is as good as elemental analysis in calculating the water diffusion coefficient in the adhesive in the joints.

Table 1 also shows that the values of water diffusion coefficients in the joints treated with the silane coupling agent is lower than those subjected to sandpaper burnishing treatment or chemical oxidizing treatment. Compared with sandpaper burnishing treatment, the chemical oxidizing treatment produces chemical groups that increase the adhesive strength. Silane coupling agent is a surface treatment by which the composites are grafted through the silane coupling agent, which reduces the water penetration rate in the adhesive.

3.2. Determination of Water Diffusion Dynamics in the Adhesive Joints

Because of the lack of more mechanistic descriptions, the relation between the diffusion dynamics and activation energy is usually described by the following equations:

$$-\frac{dc}{dt} = kf(c), \qquad f(c) = c'' \tag{7}$$

$$k = Ae^{-\frac{E}{RT}} \tag{8}$$

$$\frac{k_1}{k_2} = \exp\left[-\frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right] \tag{9}$$

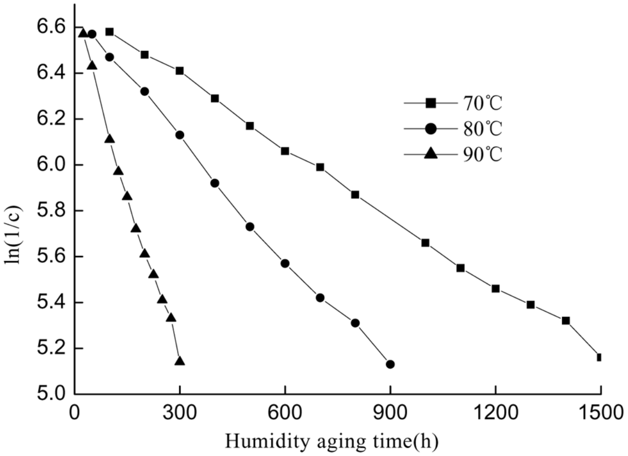

FIGURE 3 Plot of water uptake ln(1/c) versus humidity aging time for the joints treated with the silane coupling agent, based on the EDX analysis.

In Equation (7), c is the water uptake in the adhesive joints at time t, k is the diffusion rate constant, n is the diffusion reaction order, and t is the diffusion time. Equation (8) is the Arrhenius formula, where E is diffusion activation energy, A is the Arrhenius frequency factor, R is the universal gas constant, and T is temperature. The

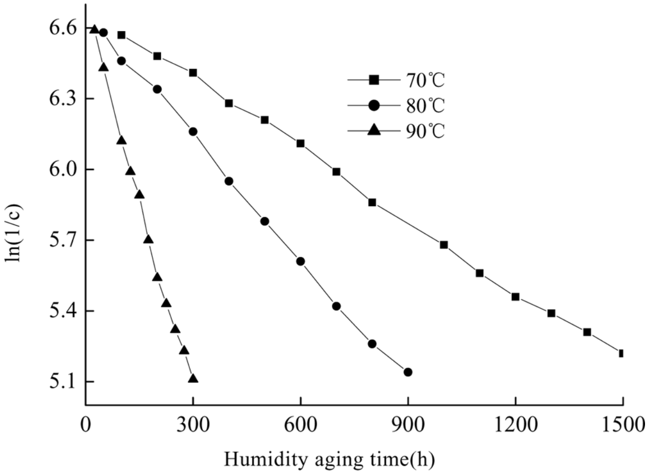

FIGURE 4 Plot of water uptake ln(1/c) versus humidity aging time for the joints treated with the silane coupling agent, based on elemental analysis.

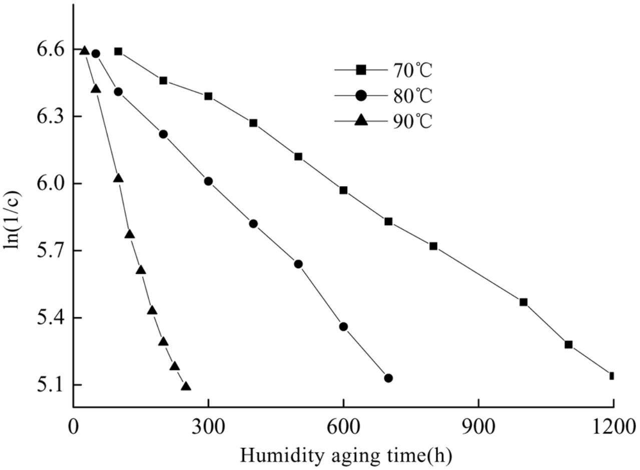

FIGURE 5 Plot of water uptake ln(1/c) versus humidity aging time for the joints subjected to chemical oxidation treatment, based on EDX analysis.

diffusion rate constant *k* can be determined from the relation of the water uptake in the adhesive and time *t* in Equation (8). If the plots of ln(1/c) against time are linear, the diffusion process is first order; therefore, *k* can be calculated from the slopes of the straight lines.

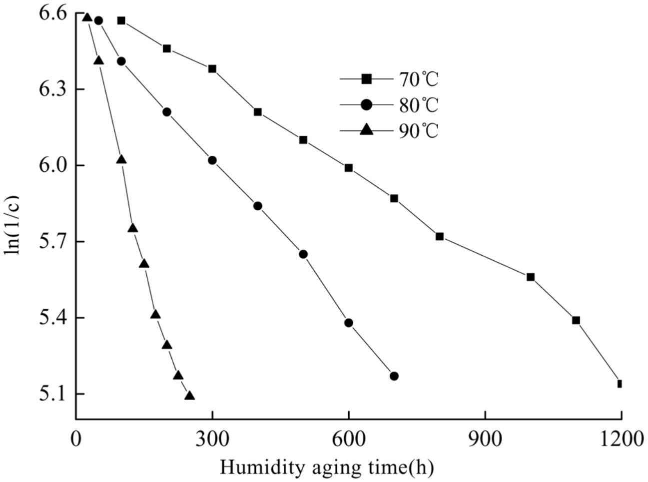

FIGURE 6 Plot of water uptake ln(1/c) against humidity aging time for the joints subjected to chemical oxidation treatment, based on elemental analysis.

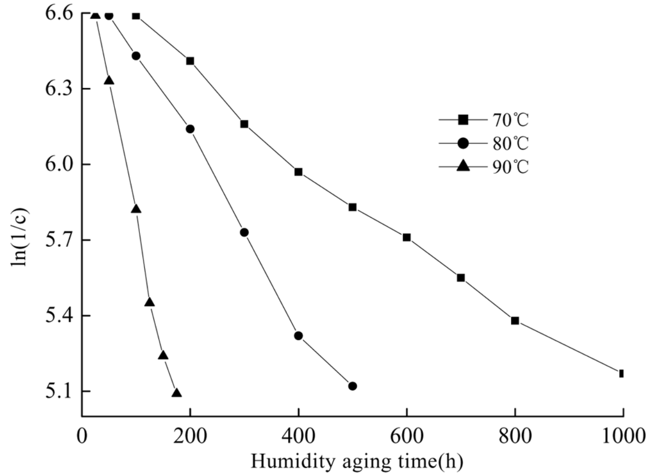

FIGURE 7 Plot of water uptake ln(1/c) versus humidity aging time for the joints subjected to sandpaper burnishing, based on EDX analysis.

Finally, water diffusion activation energy can be determined from Equation (9).

As discussed previously, plots of ln(1/*c*) against time are linear (Figures 3–8). This indicates that the water diffusion is a first-order

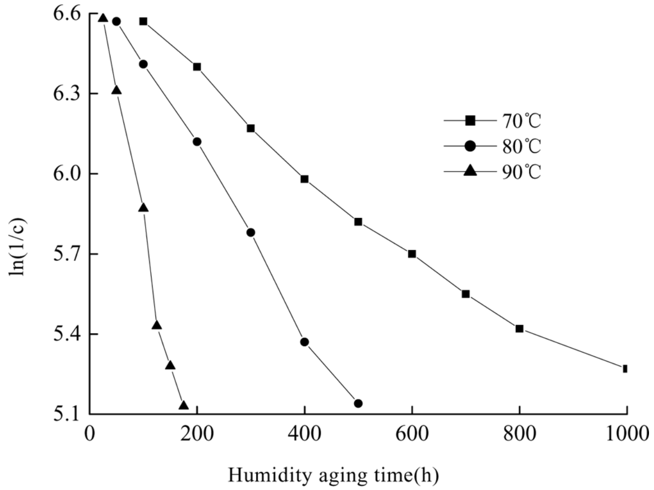

FIGURE 8 Plot of water uptake ln(1/c) versus humidity aging time for the joints subjected to sandpaper burnishing, based on elemental analysis.

TABLE 2 Effective Diffusion Rate Constant k ($\times 10^{-4}s^{-1}$) at Different Humidity Aging Temperatures

	EDX analysis			Element analysis		
Treatment	70°C	80°C	90°C	70°C	80°C	90°C
Silane coupling agent treatment	10.1	17.1	50.1	10.0	17.3	54.2
Chemical oxidation treatment	13.2	21.5	69.4	12.4	20.9	69.2
Sandpaper burnishing, washing	15.9	34.2	104.1	14.9	32.7	100.6

reaction, so the diffusion rate constant and diffusion activation energy can be calculated using Equation (9). The calculation results are listed in Tables 2 and 3, respectively. The values of the effective diffusion rate constant k at different humidity aging temperatures are shown in Table 2. Table 3 shows that the values of water diffusion energy in the joints subjected to different surface treatments calculated from EDX analysis are almost the same as those calculated from elemental analysis. This shows that the EDX analysis is as good as the elemental analysis in calculating the water diffusion energy in the adhesive in the joints.

3.3. Influences of Different Surface Treatments on the Water Diffusion Dynamics in the Adhesive in the Joints

The values of the water diffusion energy are shown in Table 3. Table 3 shows that the value of water diffusion energy in the joints subjected to silane coupling agent is less than for those subjected to the chemical oxidizing treatment or the sandpaper burnishing treatment. The durability of the adhesive joints treated with silane coupling agent is better than those subjected to sandpaper burnishing and chemical oxidation treatment.

TABLE 3 Water Diffusion Energy in the Joints

	Water diffusion energy (kJ/mol)		
Surface treatment methods	EDX analysis	Elemental analysis	Relative difference (%)
Silane coupling agent treatment	83.47	87.42	3.53
Chemical oxidation treatment	86.61	89.69	3.56
Sandpaper burnishing, washing	97.65	99.23	1.62

4. CONCLUSIONS

EDX is a simple and exact method for investigating the water diffusion coefficients and dynamics in the adhesive in the joints.

The durability of the joints of the composites treated with the silane coupling agent is better than those subjected to sandpaper burnishing or chemical oxidizing treatment.

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