Calculation the water diffusion coefficient and dynamics in site of adhesive/c-c composites joints

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ABSTRACT

In this paper, water diffusion coefficient and dynamics in site of adhesive/c-c composites joints are calculated with EDX analysis methods. This method is much easier than elemental analysis method in calculation water diffusion coefficient and dynamics. Until now this method is not introduced in calculation the water diffusion coefficient and dynamics of adhesive joints or polymer composites. This paper not only calculates the water diffusion coefficient and dynamics of adhesive/c-c composites joints with EDX analysis and elemental analysis, but also calculates water diffusion coefficient and dynamics of adhesive/c-c composites joints treated by different surface treatment methods. It is indicated that the water diffusion speed in adhesive/c-c composites joints treated by silane couple agent is the slowest than that treated by chemical oxidation and by sand paper burnishing respectively.

Keywords: calculation, diffusion coefficient, diffusion dynamics, in site of, adhesive/c-c composites joints

1. INTRODUCTION

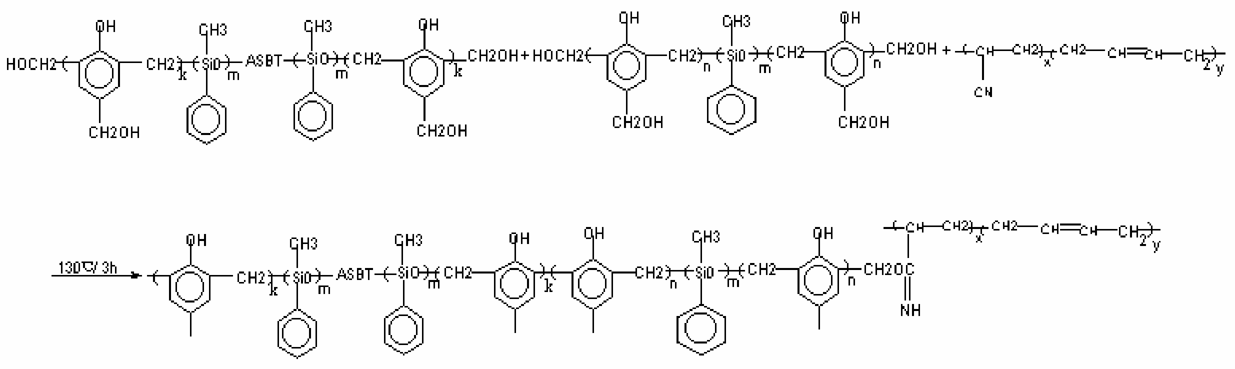
C-C composites are widely used in aerospace and airplane industries because of theirs excellent heat-resistance property. For C-C composites joints, the research of the adhesive and its heat-resistance property have been reported, but the durability for adhesive/c-c composites joints in water are seldom found [1-12]. It is well known that the water absorption have significant effect on the properties of the adhesive joints. Both accelerated environmental tests and long-term exposure to warm/moist environments have shown conclusively the potentially disastrous results which can result from the use of adhesive joints components in moist environments [13-16].

A kind of one component structural adhesive for C-C composites, consisting of thermosetting phenolic resin modified by polyphenylmethylsiloxane, asbestos modified by polyphenylmethylsiloxane terminated by thermosetting phenolic resin, butadiene-acrylonitrile rubber and curing accelerator, which can be cured at 130℃ for 3h, have been developed by our research group. In this paper the diffusion coefficient and dynamics of the adhesive/C-C composites joints under water are calculated with EDX analysis method and elemental analysis method respectively. Compared with elemental analysis method, the EDX analysis method does not broken the adhesive joints, so it is very easy to calculation the water diffusion coefficient and diffusion dynamics of the adhesive joints.

2. EXPERIMENTAL

2.1 Materials and adhesion process

The adhesive consisting of a thermosetting phenolic resin modified by polyphenylmethyl siloxane, asbestos(ASBT) modified by polyphenylmethylsiloxane terminated by thermosetting phenolic resin, butadiene-acrylonitrile rubber (NBR) and curing accelerator in ratio of 100:10:5:5. The curing reaction procedures is described as follows ：



Three directional C-C composites are provided by Aerospace Materials Institute of China, which the carbon matrix is derived from pitch and the reinforcement used in this paper is polyacrylonitrile based carbon fiber.

Before adhesion, the surface of C-C composites are treated by the following procedures respectively: (1) sand paper burnishing treatment: burnished by 60# sand paper; (2) chemical oxidation treatment: burnished by 60# sand paper, heated at 80℃ for 1h in an oxidation agent($K_2Cr_2O_7$: H_2SO_4: H_2O=1:3:10), washed by water; (3) silane coupling agent treatment: burnished by 60# sand paper, heated at 80℃ for 1h in an oxidation agent ($K_2Cr_2O_7$: H_2SO_4: H_2O=1:3:10), washed by water, dabbed by silane coupling agent($H_2NCH_2CH_2CH_2Si(OC_2H_5)_3$), and then heated at 150℃ for 1h.

The adhesive/C-C composites joints are bonded by the above adhesive, and cured at 130℃ for 3h with the pressure of 0.15-0.3MPa.

2.2 Chemical and structural characterization

For water aging, the joints samples immersed in water at 40℃ for 1200h, 50℃ for 500h and 90℃ for 100h respectively, are obtained.

EDX of the joint samples are performed at room temperature on ISIS-300 (Link Corp.) energy dispersive X-ray spectroscopy. The adhesive joints, after in water aging as the above, are spurted coating with gold for analysis. Fig.1 shows schematic diagram of observing the interlayer and the surface of the joints.

The water uptake of the adhesive joints samples are calculated with elementary analysis method and EDX analysis method respectively.

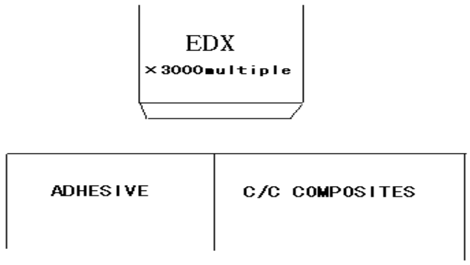


Fig.1 Schematic diagram of the calculation the elements content on the adhesive joints surface

2.3 Calculation methods of the water diffusion coefficient and dynamics in site of adhesive/c-c composites joint

The solution to Fick's second equation for case of an initially dry thin film of thickness *l* in an infinite bath is given by equation (1) [10]:

$$\frac{C}{C_\infty} = 1 - \frac{4}{\pi}\sum_{n=0}^{\infty}\frac{(-1)^n}{(2n+1)e^{\frac{-D(2n+1)^2\pi^2 t}{l^2\cos(n+1)\frac{\pi x}{l}}}} \qquad (1)$$

Here, *C* is the concentration at points at a distance x from the center of the film and $C_{(\infty)}$ is the at concentration equilibrium. *D* is the diffusion coefficient and *t* is time. It is assumed that equilibrium between the bath and the surface of the film is established instantaneously on immersion. Integrating this equation to give the total water content gives equation (2):

$$\frac{M}{M_\infty} = 1 - \sum_{n=0}^{\infty}\frac{8}{(2n+1)^2\pi^2 e^{\frac{-(2n+1)^2\pi^2 Dt}{l^2}}} \qquad (2)$$

As short times, this equation simplifies to:

$$\frac{\Delta G}{G_{\max}} = \frac{4}{b}\sqrt{D\frac{t}{\pi}} \qquad (3)$$

as

$$D = \frac{\pi b^2}{16}\left(\frac{\Delta G}{G_{\max}}\times\frac{1}{\sqrt{t}}\right)^2 \qquad (4)$$

In these equations, ΔG and G_{max} are the water uptake at time *t* and at equilibrium respectively. *b* is the width of the samples, which indicates that a plot of mass uptake against $t^{1/2}$ should be initially linear and the diffusion coefficient may be calculated from the gradient.

2.4 Calculation the water uptake

2.4.1 EDX methods

The water uptake of the adhesive is calculated with EDX. If the water penetrative speed in the adhesive is presumed constant, water uptake formula of the adhesive is described as follows：

$$G'' = \left(G \times R - G_0\right) \times \frac{M_{H2O}}{M_O}$$

G'': water uptake in the adhesive joints

G: the uptake of oxygen element in the general of carbon and oxygen elements in the adhesive, which is obtained with EDX.

R: the general uptake of carbon and oxygen elements in the adhesive before humidity aging, it is 89.06%, which is determined by chemical structure characteristics of the adhesive and obtains with elementary analysis.

Go: the uptake of oxygen element in the adhesive before humidity aging, it is 7%, which is determined by chemical structure characteristics of the adhesive and obtained with elementary analysis before water aging.

M_{H2O} and *Mo*: molecular weight of H_2O and oxygen, respectively.

2.4.2 Elements analysis methods

The water uptake of the adhesive is calculated with elementary analysis:

$$G'' = \left(G' - G_0\right) \times \frac{M_{H2O}}{M_O}$$

G'': water uptake in the adhesive joints

G': the uptake of oxygen element in the general of the adhesive joints, which is obtained with elemental analysis.

Go: the uptake of oxygen element in the adhesive before humidity aging, it is 7%, which is determined by chemical structure characteristics of the adhesive and obtained by elementary analysis before water aging.

M_{H2O} and Mo: molecular weight of H_2O and oxygen, respectively.

3.RESULTS AND DISCUSSION

3.1Calculation the water diffusion coefficient in the adhesive joints

Water uptake in the adhesive joints and the value of the water diffusion coefficient are showed in table1 and table2. Table1 and table2 show that the value of water diffusion coefficient calculated with EDX method are almost the same as that calculated with elemental analysis method. Because EDX spectra of the adhesive joints samples, whose detected depth is 20nm, are performed; the water uptake on the joints surface is higher than that in the joints, but the samples are spurted coating with gold for analysis in vacuum, a little water are emanated from the joints surface, since the errors of water uptake are counteracted.

Table1 Water diffusion coefficient in the joints by different surface treatments with EDX analysis method

surface treatment methods	water uptake of the joints in different water aging time (%)							D ($10^{-12}m^2/h$)
	0h	100h	200h	300h	400h	450	500h	EDX analysis
silane couple agent	0	0.160	0.219	0.279	0.338	0.366	0.392	2.153
chemical oxidation	0	0.161	0.221	0.283	0.342	0.404	---	2.230
sand paper burnishing	0	0.166	0.233	0.289	0.359	---	---	2.252

Table2 Water diffusion coefficient in the joints by different surface treatments with elemental analysis method

surface treatment methods	water uptake of the joints in different water aging time (%)							D ($10^{-12}m^2/h$)
	0h	100h	200h	300h	400h	450	500h	Elemental analysis
silane couple agent	0	0.161	0.220	0.279	0.337	0.365	0.391	2.154
chemical oxidation	0	0.161	0.222	0.281	0.341	0.402	---	2.228
sand paper burnishing	0	0.165	0.234	0.287	0.361	---	---	2.250

Table1 and table2 also show that the value of the water diffusion coefficient in the joints treated by silane coupling agent is the lowest than that treated by sand paper burnishing and chemical oxidation. Compared with sand paper burnishing treatment, chemical oxidation treatment can oxidized the surface of C-C composites that resulted micropores produced which increases adhesion area and formed mechanism lockpin structure with the adhesive during curing process. Silane coupling agent treatment is a surface treatment method on the base of chemical oxidation treatment, which can graft with a little of activity groups produced by chemical oxidation on the surface of C-C composites at high temperature that conduces polarity groups on the surface of C-C composites such as $-O-Si-R-NH_2$ groups increasing and forming transition layer which can weaken water penetrative speed in the adhesive joints.

3.2 Calculation the dynamics of adhesive/c-c composites joints

3.2.1 The different calculation methods of the dynamics of adhesive/c-c composites joints

Diffusion reaction is often described using an expression of the following formula:

$$-\frac{dc}{dt} = kf(c), \quad f(c) = c^n \tag{5}$$

$$k = Ae^{-\frac{E}{RT}} \tag{6}$$

$$\frac{K_1}{K_2} = \frac{e^{\left(-\frac{E}{RT_1}\right)}}{e^{\left(-\frac{E}{RT_2}\right)}} \tag{7}$$

C is the mass increasing degree, *n* is the reaction order, *k* is the influences reaction rate, *E* is the activation energy of the diffusion reaction, *A* is the Arrhenuis frequency factor, *R* is the universal gas constant, *T* is the temperature.

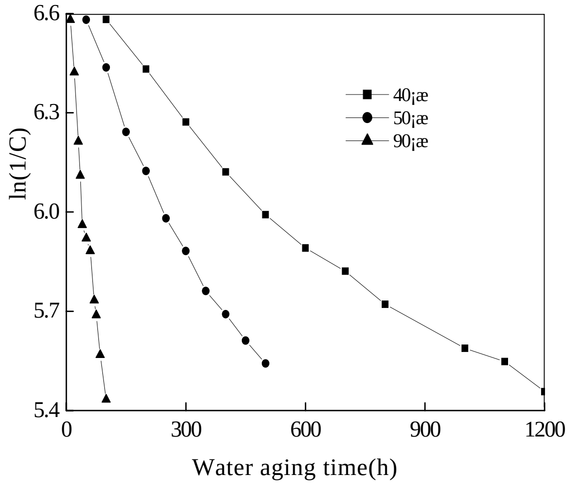


Fig.2 EDX analysis of ln(1/C) against water aging time

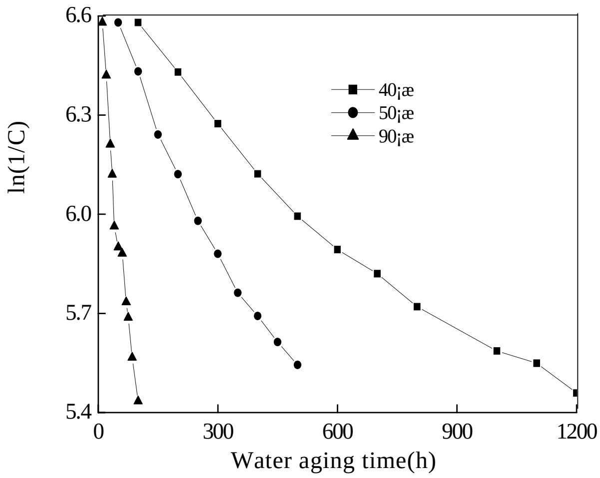


Fig.3 Elemental analysis of ln(1/C) against water aging time

Table3 Reaction speed parameter *k* at different temperature

name	EDS analysis			Elemental analysis		
temperature(℃)	40	50	90	40	50	90
K ($10^{-4}s^{-1}$)	12.9	23.1	122.3	12.8	23.0	122.4

Fig.2 and Fig.3 show that the water diffusion reaction is one order, since the curves are analyzed by ploting ln(1/c) against time from equation(5) to give a linear plot with slope. The influences reaction rate *k* are showed in Table3. From the relation of equation（7）, the value of the diffusion dynamics of adhesive/c-c composites joints in water is -40.98kJ/mol with EDX, the diffusion dynamics of adhesive/c-c composites joints in water is -41.12kJ/mol with elemental analysis. It showed that the EDX method is almost the same as elemental analysis method, because of the above reason.

3.2.1 The influences of different surface treatment methods in water diffusion the dynamics of adhesive/c-c composites joints

The joints treated by sand paper burnishing and chemical oxidation respectively in water for 500h，ploting ln(1/c) against time are showed in Fig.4 and Fig.5, and the influences reaction rate *k* are showed in table4. Fig.4, Fig.5 and table4 show that the water diffusion reaction is one order. From the relation of equation（7）, the diffusion dynamics of adhesive/c-c composites joints treated by chemical oxidation in water is –44.026kJ/mol, the diffusion dynamics of adhesive/c-c composites joints treated by sand paper burnishing is –44.83kJ/mol. It is indicated that the durability property of the joints treated by silane is the best than that, because of the above reasons.

Table4 Reaction speed parameter at different temperature

name	Sand paper burnishing			chemical oxidation		
Temperature (℃)	40	50	90	40	50	90
K (s^{-1})	12.9	26.3	129.4	12.6	25.6	122.5

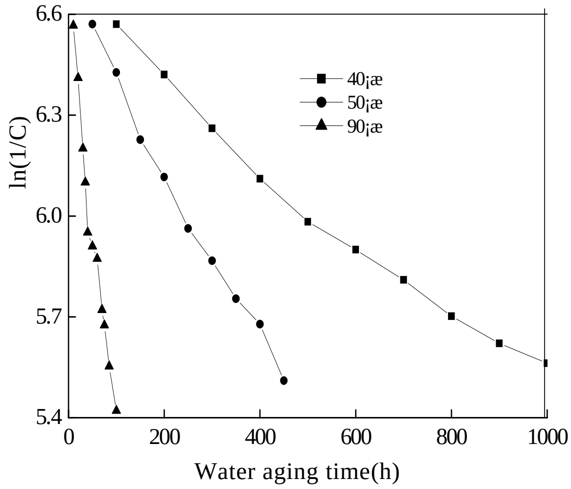


Fig.4 ln(1/C) against water aging time of the joints treated by chemical oxidation

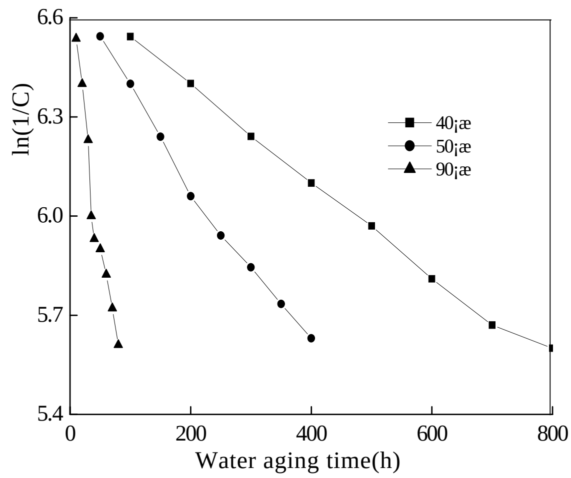


Fig. 5 ln(1/C) against water aging time of the joints treated by sand paper burnishing

4.CONCLUSIONS

The calculation of the water diffusion coefficient and diffusion dynamics of the adhesive joints with EDX method is a much easier than that of elemental analysis method, because the EDX method can not broken the joints. This methods not only calculates the water diffusion coefficient and diffusion dynamics of the adhesive joints, but also calculates the water diffusion coefficient and diffusion dynamics of the between fiber and matrix resin, which well be introduced in other papers.

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