Mass Gain of Carbon Fiber Reinforced Polyimide (CFRP) by Dipping in Hot Distilled Water

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Influence of isothermal dipping in hot distilled water for 200 ks on the mass gain of carbon fiber reinforced polyimide (CFRP) was investigated. Dipping in distilled water raised the mass gain. Based on the kinetics equation, both reaction index (n) and kinetic constant (k) were obtained. Since the n value is approximately 0.6 from 333 to 373 K, the reaction mode was independent on the absorption temperature. Based on the results and discussion, the water absorption was probably the directional mass transport through the fiber/polyimide cylindrical interface. On the other hand, Arrhenius linear relationship between logarithmic (log k) and reciprocal dipping temperature (1/T) was obtained. The apparent activation energy estimated by the slope of water absorption in the CFRP was approximately equal to the activation energy of self-diffusion coefficient of water molecule. Mass gain of CFRP (CF/PI) dipped in distilled water for 100 ks at 373 K probably enhanced the molecules’ density induced by water molecules’ intrusion among polyimide polymers, resulting in enhancement of (dΩ/dΩ)max, and fracture stress. On the other hand, the mass gain by dipping for 200 ks at 373 K enriched the water concentration in polyimide matrix. Thus, it was assumed to enhance the intermolecular distance of polyimide polymers and then to reduce the intermolecular force among polyimide polymers, resulting in a drop of (dΩ/dΩ)max of CFRP dipped for 200 ks. On the other hand, the dipping for 200 ks probably raised the intermolecular force between water molecules and polyimide polymers, resulting in remarkable enhancements of the fracture strain, fracture energy and impact value of the CFRP.


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1. Introduction

Carbon fiber reinforced polymers (CFRP) have been applied as light structural composites materials with high strength.1,2 In order to develop high-speed mover machines with tiny energy consumption, the further strengthening has been always expected. Although carbon fiber reinforced epoxy (CFRP (CF/EP)) is popular to utilize for practical application, the low resistance to heat is the serious point.3,4 On the other hand, polyimide (PI), which monomer is mainly constructed with imide’s bond and aromatic ring (see Fig. 1), is one of the typical thermoset polymers with high heat resistance and high chemical resistance.5 It is generally applied to aerospace parts, machine parts and electrical insulation material.

Since the polyimide (PI) matrix exhibits the highest heat resistance relative to other conventional polymers, this makes it possible for the carbon fiber reinforced polyimide (CFRP (CF/PI)) to be used for the long term above 473 K.5,6 Thus, it has been expected to be utilized for the light structural materials under corrosive environments.6,7 Moreover, it is also expected to be utilized for the spaceship fuel tank materials.8,9

However, water absorption, which causes softening10,11 and high growth rate of fatigue crack,11 is often observed in nylon6. Although water absorption enhances the impact value of nylon6 and its composites,12 the influence of water absorption on expansion and softening is a serious problem, as well as other polymers and their composites.

To confirm the basic work for safety design related to the resistance to environmental corrosion, the water absorption is one of the important factors of CFRP (CF/PI). Therefore, the influence of isothermal dipping in hot distilled water from 333 to 373 K (near the boiling point) on the mass gain of CFRP (CF/PI) has been investigated.

2. Experiment Procedure

2.1 Sample preparation

The CFRP (CF/PI) samples with heat resistance (HA-10, PETI PLATE) were constructed with the plain-weave of commercially used carbon fiber (T300-3k, Toray Industries, Inc.) and polyimide (see Fig. 1, PETI-330, Ube Industries, Ltd.) matrix. Volume fractions of carbon fiber and polymer matrix were 59.0 ± 0.10 and 41.0 ± 0.10 vol%, respectively. CFRP was prepared by lay up method of laminated weave plies, whose polyimides are typically cured at 370°C in an autoclave under vacuum.13 Specimens were then cut from panels. By using a diamond cutter (MC-201, MARUTO), the sample sizes were formed to be 80 × 10 × 2 (mm).

The drying at 423 K reduces the mass change ratio of CFRP (CF/PI), as shown in Fig. 2. Thus, the CFRP (CF/PI) was dried for 20 ks at 423 K (150°C) prior to isothermal dipping in the hot distilled water.

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2.2 Mass measurement of isothermal dipping
To measure water absorption, the dried CFRP (CF/PI) was dipped in the heated distilled water. The mass was measured by using an electric balance (ER-180A, KENSEI-KOUGYO, Japan). The mass was measured at 0, 0.1, 0.2, 0.5, 1.0, 2.0, 5.0, 10, 20, 50, 100 and 200 ks at 333, 343, 353, 363 and 373 K. The mass gain was obtained by eq. (1).

\[
C = \frac{(m_f - m_0)}{m_0} \times 100
\]

Here, \( C \) is the water absorption ratio (%), \( m_0 \) is the mass before dipping in both salt solution and water, and \( m_f \) is the mass after dipping in distilled water.\(^{12}\)

2.3 Bending test
In order to evaluate the stiffness, the flexural moduli of the CFRPs were measured using a standard testing method for three-point bending test (IMADA Co., Ltd. DPU-50N, CFRPs were measured using a standard testing method for MX-500N). The testing speed was 6.5 mm/min.

The flexural modulus \( E_f \) (GPa) was obtained by the following equation.\(^{14,15}\)

\[
E_f = (1/4)(L^3/(bh^2))(P/d)
\]

Here, \( E_f \) is flexural modulus (GPa), and the maximum slope value \((\Delta e/\Delta P)_{\max}\) was determined from the slope of stress-strain curves within elastic deformation of \( \varepsilon = \pm 8.0 \times 10^{-4} \). The distance between supporting points was 20 mm. The testing speed was 6.5 mm/min.

3. Results

3.1 Mass gain of CFRP (CF/PI) dipped in hot water
The influence of dipping in distilled water at constant temperatures on the mass gain of CFRP (CF/PI) has been investigated. Figure 3 plots changes in water absorption ratio (mass%) of CFRP (CF/PI) against water absorption time at each water absorption temperature from 333 to 373 K for 200 ks. Dipping in distilled water raised the mass gain of CFRP (CF/PI).

4. Discussion

4.1 Temperature dependent mass gain
Based on experimental results, the Johnson–Mehl kinetic equation\(^{19}\) was applied to the simple reaction.\(^{17,18}\) Moreover, the evolution of the mass of water versus time (see Fig. 3) was obviously favorable for such a model. When the reaction index \( n \) and kinetic constant \( k \) are defined, the absorption ratio \( X \) of water is expressed by the following equation.\(^{16}\)

\[
X = 1 - \exp[-(kt)^n]
\]

When \( N_0 \) and \( N_\infty \) are the mole fraction \((N_o)\) of the samples after drying before and after water absorption for infinite time, the general reaction ratio \( (X) \) is obtained from the following equation.

\[
X = (N_1 - N_o)/(N_\infty - N_o)
\]

However, when \( N_o \) assumes to be zero, the absorption ratio \( (X) \) of water should be expressed by the following equation.

\[
X = N_1/N_\infty
\]

Figure 4 plots changes in \( X \) of CFRP (CF/PI) against water absorption time at each water absorption temperature. The highest \( X \) value was found in the CFRP (CF/PI) dipped in water at high temperature of 373 K, whereas the lowest \( X \) value was found in the CFRP (CF/PI) dipped in water at low temperature of 333 K.

To obtain the \( n \) and \( k \) values of eq. (5), the linear relationship was obtained by converting to eq. (8).

\[
\log_{10}1 - \ln(1 - X) = n \log_{10}t + n \log_{10}k
\]

When \( N_\infty \) can be determined to be the maximum value of correlation coefficient \((F)\), the highest linearity of plots
according to eq. (8) can be obtained. Figure 5 plots changes in $F$ against the potential $N_\infty$ value ($e^N_\infty$). The $N_\infty$ was determined at the maximum $F$ value.

Figure 6 depicts the linear relationships between $\log_{10}[-\ln(1-x)]$ and logarithmic reaction time $[\log_{10}(t/s)]$ of water absorption. Both $n$ and $k$ values can be obtained by the linear relationships between $\log_{10}[-\ln(1-x)]$ and $[\log_{10}(t/s)]$ with high $F$ of more than 0.998, as shown in Fig. 5.

Since the plots exhibit high correlation coefficients, the dipping was the isothermal treatment. The reaction heat of water absorption was negligible. This relationship corresponded perfectly to the Johnson–Mehl kinetic equation for application to the simple reaction at a constant temperature.16,18)

The slopes of the linear relationships in Fig. 6 correspond to $n$ values. Based on the straight lines, the mean values of $n$ and $k$, which were obtained from the experimental values of all the plots, probably predict the water absorbed mass, dipping time and dipping temperature.

4.2 Reaction index ($n$)

The absorption rate of distilled water has been generally controlled by both diffusion in the nylon6 matrix and mass transfer at the interface in nylon6 composites.20) To control the absorption rate, mechanics of the absorption of polymers and their composites should be precisely determined by using the general kinetic analysis.16-18)

The reaction index ($n$) can be obtained for CFRP (CF/PI). Figure 7 plots the identified reaction index ($n$) of mass gain related to water absorption of CFRP (CF/PI) in distilled water against dipping temperature. The temperature dependence of $n$ (0.59 $\pm$ 0.04) is constant, which is approximately 0.6.

The water molecules cannot mostly diffuse through the inside of carbon fiber and cannot easily diffuse through the inside of the polyimide matrix. Since the interface corrosion

Fig. 4 Changes in reaction ratio ($X$) of CFRP (CF/PI) against water absorption time at each water absorption temperature.

Fig. 5 Changes in correlation coefficient ($F$) against the potential $N_\infty$ value ($e^N_\infty$). The $N_\infty$ was determined at the maximum $F$ value.

Fig. 6 Relationships between $\log_{10}[-\ln(1-x)]$ and logarithmic reaction time $[\log_{10}(t/s)]$ of water absorption.

Fig. 7 Changes in reaction index ($n$) on the water absorption of CFRP (CF/PI) in distilled water versus water absorption temperature.
4.3 Kinetic constant \((k)\)

Based on the kinetics equation, the kinetic constant \((k)\) can be obtained. Figure 8 plots changes in the kinetic constants of the overweight of mass gain related to water absorption of CFRP (CF/PI) in distilled water versus water absorption temperature. The \(k\) value increases at elevated temperatures. The temperature dependence of \(k\) is the Arrhenius linear relationship between logarithmic \(k\) \((\log k)\) and reciprocal temperature \((1/T)\) with high correlation coefficient \((0.996)\). The apparent activation energy \((43 \text{ kJ/mol})\) estimated by the slope of water absorption in CFRP (CF/PI) is approximately equal to the activation energy of self-diffusion coefficient of water molecule \((39 \text{ kJ/mol})\).

4.4 Mechanical properties of CFRP (CF/PI) dipped in water

Figure 9 shows changes in Vickers’ hardness \((H_v)\) at 4.90 N, the maximum hardening modulus \((\text{d}\sigma/\text{d}e)_\text{max}\) at mid-cumulative probability of 0.5, fracture energy \((E_f)\) at mid-fracture probability \((P_f)\) of 0.5, bending strength \((\sigma_b)\) at mid \(P_f\) of 0.5, bending strain at \(\sigma_b^\text{b} (\varepsilon_b^\text{b})\) at mid \(P_f\) of 0.5 and impact value \((a_{\text{ic}})\) at low and mid \(P_f\) of 0.06 and 0.5 of bending test of CFRP (CF/PI) against water absorption time.

Dipping in distilled water for 100 ks at 373 K enhances the \((\text{d}\sigma/\text{d}e)_\text{max}\) which is 3% higher than that before treatment. It simultaneously enhances the fracture stress, fracture energy and impact value, which are 8, 16 and 5% higher than those before dipping. On the contrary, dipping for 100 ks at 373 K reduces the hardness and fracture strain, which are 26 and 2% less than those before dipping.

On the other hand, although dipping in distilled water for 200 ks at 373 K reduces the hardening modulus, a 7%-drop, the dipping for 200 ks raises the fracture strain, fracture energy and impact value, which are 7, 58 and 15% higher than those of CFRP (CF/PI) before dipping, respectively.

4.5 Water absorption model deduced by mechanical properties

As shown in Fig. 9, the mass gain of CFRP (CF/PI) dipped in distilled water at 373 K affects the Vickers’ hardness, elasticity, fracture energy, fracture stress, fracture strain and impact value.

When the water absorption by dipping for 100 ks is assumed to enhance the molecules’ density induced by water molecules’ intrusion among polyimide polymers and then to
enhance the elastic deformation resistivity, the 3% higher \((\text{d}r/\text{d}e)_{\text{max}}\) of CFRP (CF/PI) dipped for 100 ks than that before dipping can be explained. It partly contributes to enhance the fracture stress, fracture energy and impact value which are 8, 16 and 5% higher than those before dipping, respectively.

On the contrary, the hardness drop of 26% indicates the softening resistivity of micro-plastic deformation of CFRP (CF/PI) dipped for 100 ks. The hardness mainly indicates the irreversible plastic deformation with relaxation, rather than the reversible elastic deformation with stiffness. As the intruded water molecules among polyimide polymers are assumed to enhance the intermolecular distance among the polymers and to reduce its attractive intermolecular force, it softens the matrix with the irreversible plastic deformation, resulting in the 26%-hardness drop of CFRP (CF/PI).

The water absorption in CFRP (CF/PI) by dipping for 200 ks enriches the water concentration in polyimide matrix. It is assumed to enhance the intermolecular distance of polyimide polymers and then to reduce the attractive intermolecular force among polyimide polymers, resulting in 7%-drop of \((\text{d}r/\text{d}e)_{\text{max}}\) of CFRP (CF/PI) for 200 ks.

Based on the NMR results, the weak attractive intermolecular force is found between polyimide polymers and water molecules. Therefore, the dipping for 200 ks probably raises the weak attractive intermolecular force between water molecules and polymers, resulting in enhancements (7, 58 and 15%) of fracture strain, fracture energy and impact value of CFRP (CF/PI) for 200 ks, respectively.

5. Conclusion

Influence of isothermal dipping in hot distilled water on the mass gain of carbon fiber reinforced polyimide (CFRP (CF/PI)) was investigated.

(1) Dipping in distilled water raised the mass gain of CFRP (CF/PI).

(2) Based on the Johnson–Mehl kinetics equation, the reaction index \(n\) was obtained with high correlation coefficient. Since the \(n\) was approximately 0.6 at each dipping temperature from 333 to 373 K, the reaction mode was independent on the temperature. The water molecules probably prefer to diffuse through the cylindrical interface rather than inside of carbon fiber and matrix. The water absorption is probably the directional mass transport through the fiber/polyimide cylindrical interface. Consequently, it appears to be the pipe diffusion controlled reaction.

(3) Based on the kinetics equation, the kinetic constant \((k)\) can be obtained. The temperature dependency of \(k\) is Arrhenius linear relationship between logarithmic \(k (\log k)\) and reciprocal temperature \((1/T)\). The apparent activation energy estimated by the slope of water absorption in CFRP (CF/PI) is approximately equal to the activation energy of self-diffusion coefficient of water molecule.

(4) Mass gain by dipping for 100 ks at 373 K was assumed to enhance the molecules’ density induced by water molecules’ intrusion among polyimide polymers, resulting in enhancement of \((\text{d}r/\text{d}e)_{\text{max}}\) and fracture stress of CFRP (CF/PI) dipped in distilled water for 100 ks.

(5) Mass gain by dipping in distilled water for 200 ks at 373 K enriched the water concentration in polyimide matrix. Thus, it was probably assumed to enhance the intermolecular distance of polyimide polymers and to reduce the intermolecular force among polyimide polymers, resulting in a drop of \((\text{d}r/\text{d}e)_{\text{max}}\) of CFRP (CF/PI) dipped in distilled water at 373 K.

(6) Since the water molecules generally attract the polyimide polymers by weak attractive intermolecular force, the dipping for 200 ks probably raises the attractive intermolecular force between water molecules and polyimide polymers, resulting in remarkable enhancements of fracture strain, fracture energy and impact value of CFRP (CF/PI).

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