Effects of pH, Strain Rate and Fiber Volume Fraction on Fracture Energy of Carbon Fiber/Epoxy Composites

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(Received January 10, 1995, Accepted February 7, 1995)

Abstract: The effects of pH, strain rate and fiber volume fraction on the fracture energy of carbon fiber/epoxy composites were investigated. The range of strain rate was from $2.37 \times 10^{-3}$ sec$^{-1}$ to $23.67 \times 10^{-3}$ sec$^{-1}$, that of pH was 2 to 12 and fiber volume fraction was 0 to 0.09. Fracture of the specimen was carried out by three point bending test and fiber debonded length and pull-out length were measured by Zeiss projection microscope. Pull-out energy gave a major contribution to the fracture energy. The fracture energy at pH 7 was larger than those at pH 2 and pH 12. Fracture energy increased with the increase of strain rate and fiber volume fraction.

1. Introduction

Fiber-reinforced epoxy composite systems exhibit high specific strength, high specific modulus and also high specific toughness. Because of those properties, they are applied in fields, such as aircraft, automobiles, structural component, etc.[1, 2]. However, these materials are subjected to environmental conditions, such as pH, strain rate, stress, moisture, temperature, etc.[3, 4]. So it is very important to interpret the fracture mechanism of the composites under these conditions. For the interpretation of fracture mechanism is necessary to get proper properties and to design optimum process.
It has been well known that there are three factors in mechanisms of microfracture of fiber reinforced composites. They are debonding energy, post debond friction energy and pull-out energy, and these values are various with the kinds of fibers[5, 6]. In the epoxy system reinforced with carbon fiber, pull-out energy gives a major contribution to the fracture energy[7, 8].

In this study, the effects of strain rate, pH and fiber volume fraction in the view of fracture mechanism for carbon fiber/epoxy composites were investigated.

2. Experimental

2.1. Materials

A general-purpose DGEBA type epoxy resin, Epon 828 supplied by Shell Co. was used in this study. Curing agent was MDA(4,4'-methylenedianiline) and a reactive additive was SN (succinonitrile). These were supplied by Fluka Chemie AG. And, HQ(hydroquinone) as a catalyst was obtained from Hayashi Pure Chemical Ind. Ltd.. The properties of carbon fiber is in Table 1.

Table 1. Properties of Carbon Fiber

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile Strength (GPa)</td>
<td>3.43</td>
</tr>
<tr>
<td>Young's Modulus (GPa)</td>
<td>230.3</td>
</tr>
<tr>
<td>Diameter (×10⁻⁷m)</td>
<td>7.59</td>
</tr>
</tbody>
</table>

2.2. Specimen Preparation and Test Method

Carbon fiber arranged unidirectionally in mold was wetted by the mixture of DGEBA/MDA (30phr)/SN(10phr)/HQ(2.5phr). Roving numbers were 1 to 5. And, it was cured at 150°C for 1hr after curing at 80°C for 1.5hr. Specimen of 10×30×4(mm) was cut from the mold and notch was done. The depth of notch was 1.5mm and the width of that was 1mm.

To investigate the influence of pH, specimen which had 5-rovings of carbon fiber was exposed to the solution of pH 2, 5, 7, 9 and 12, respectively at 25°C for 48hr. These solutions were prepared by HCl and NaOH.

Specimen was fractured by three point bending test. Strain rates were 2.37×10⁻³, 4.73×10⁻³, 11.83×10⁻³ and 23.67×10⁻³ sec⁻¹. From this test, macroscopic fracture work was measured.

Fiber debonded length and fiber pull-out length were measured by Zeiss Projection Microscoping method[9] and theoretical fracture energy could be calculated. The fractured specimen through three point bending test was observed by microscope at 40 magnitude. The debonded zone and pull-out zone were shown clearly at this magnitude. After tracing these zone like in Fig. 1, the areas of debonded zone (white) and pull-out zone (black) were measured. And, debonded length and pull-out length were obtained by dividing these regions by the diameter of carbon fiber.

3. Results and Discussion

Composites consist of two or more constituent materials, so fracture energy of the composites was influenced at the same time by the individual and complex properties of the constituent materials. So, the fracture energy of the fiber reinforced composites should be investigated by the rule of mixture [10]. The rule of mixture for this system is described as

\[ \gamma_f = V_f \cdot \gamma_f + V_m \cdot \gamma_m \]

Where, $\gamma$ is fracture energy, $V$ is volume fraction and subscripts, $c$ and $m$ are for carbon fiber and matrix, respectively. But, the fracture energy of the matrix compared to that of the carbon fiber is so small that the term of $\gamma_n \cdot V_n$ in Eq.(1) can be ignored, with the assumption that matrix serves only to bind the fibers[9].

The fracture energy of the fiber-reinforced composites can be calculated by the next equations[9, 11, 12].

$$\gamma_f = \frac{\sigma_f \cdot \gamma_{max}}{4 E_l} : \text{debonding energy}$$

(2)

$$\gamma_{mf} = \frac{\sigma_f \cdot \gamma_{max} \cdot \varepsilon_l}{8 l_{ave}} : \text{post debond friction energy}$$

(3)

$$\gamma_p = \frac{\sigma_f \cdot l_{ave}}{6} : \text{pull-out energy}$$

(4)

where, $\sigma_f$: tensile strength of carbon fiber, $E_l$: Young's modulus of carbon fiber, $\varepsilon_l$: differential failure strain of carbon fiber, $\gamma_{max}$: maximum debonded length and $l_{ave}$: average pull-out length. And, total theoretical energy becomes

$$\gamma_t = \gamma_f + \gamma_{mf} + \gamma_p$$

(5)

$\sigma_f$ and $E_l$ are shown in Table 1, and $\gamma_{max}$ and $l_{ave}$ can be measured by the method of Fig. 1. $\varepsilon_l$ of carbon fiber is 0.014.

Fig. 2 shows the effect of pH on the fracture energy of carbon fiber-DGEB/A/MDA/SN/HQ system. Fracture energy for this system is mainly composed with pull-out energy, and debonding energy and post debond friction energy can be ignored. As external stress was given to the system, debonding on the interface between fiber and matrix occurred at the propagating crack tip. Fibers failed randomly at weak points and a section of the fiber was pulled-out from the matrix socket as the crack surface separated. In these processes, interfacial strength of carbon fiber-epoxy resin was small, and debonding energy and post debond friction energy were small. But, the friction between fiber and matrix took place during the process of the fiber pull-out, and then pull-out energy was the main fracture energy.

The fracture energy of pH 7 was larger than those of pH 2 and pH 12. And, the fracture energy of pH 2 was larger than that of pH 12. It is because carbon fiber and matrix are attacked by HCl and NaOH, the interfacial strength between carbon fiber and matrix decreases.

It is confirmed by SEM photographs. As shown in Fig. 3, corroded appearance is found on the fracture surface of the specimens treated with HCl and NaOH, and the effect of corrosion is larger at pH 12 than at pH 2. The corrosion of carbon fiber decreases the fiber pull-out length and the wear of matrix decreases the friction on the interface. Therefore, fiber pull-out energy decreases.

And, it is important to remember that the total theoretical energy overestimated the experimental fracture work.

The effect of strain rate upon the fracture energy is shown in Fig. 4. Fracture energy is slightly increased with the increase of strain rate. As strain rate increases, shear stress on the interface between
Fig. 3. SEM photographs of the surface of pull-out fibers after undergoing fracture at $23.67 \times 10^{-1} \text{ sec}^{-1}$ of strain rate.
(a) pH 2, (b) pH 7, (c) pH 12

Fig. 4. Fracture energy according to strain rate for carbon fiber-DGEBA/MDA/SN/HQ system at pH 2: work of fracture(), pull-out energy(), debonding energy() and total theoretical energy().

matrix and carbon fiber increases. So, experimental fracture work which is related to interfacial friction energy increases. On the contrary, pull-out energy in Eq.(4) would decrease with the increase of strain rate, but this energy increases with the increase of strain rate in practice. The relationship of shear stress to average pull-out length of carbon fiber can be expressed as $\tau/d = \alpha/8\text{l}_{\text{p}}[9, 13]$, where $\tau$ is shear stress and $d$ is the diameter of carbon fiber. Shear stress increases with the increase of strain rate and was inverse proportional to average pull-out length of carbon fiber. So, the above result can not be completely explained and more investigation are needed. It may be because of the decrease of interfacial strength by corrosion on the interface. The same tendency at each pH is found in Fig. 5.

The relationship between fracture energy and fiber volume fraction is shown in Fig. 6. Fracture energy increases linearly with the increase of the fiber volume fraction. In this case, specimen was not treated with chemical solution but exposed to
Fig. 5. Pull-out energy according to strain rate for carbon fiber-DGEBA/MDA/SN/HQ system at various pHs: pH 2(○), pH 5(●), pH 7(□), pH 9(▲) and pH 12(△).

Air for 48hrs at 25°C. The fracture energy of untreated specimen was 107.17 kJ/m² and that of treated specimen of pH 7 was 95.15 kJ/m², which is smaller about 10%. It means that carbon fiber-epoxy composites were degraded by humidity.

4. Conclusions

The fracture energy for carbon fiber-DGEBA/MDA/SN/HQ system was investigated and the following results were obtained.

1. In three forms of fracture energy, pull-out energy was the main contributor and debonding energy and post debond friction energy were ignored.

2. The fracture energy at pH 7 was larger than that of pH 2 and 12. The fracture energy of pH 12 was larger than that of pH 2.

3. The fracture energy increased with the increase of strain rate.

4. Carbon fiber-epoxy resin composites were degraded by humidity.

Fig. 6. Fracture energy according to fiber volume fraction for carbon fiber-DGEBA/SN/HQ system untreated with chemical solution at $2.37 \times 10^{-3}$ sec⁻¹: work of fracture(●), pull-out energy(□), debonding energy(▲) and total theoritical energy(○) at pH 2.

Acknowledgement

This work was financially supported by Sun Kyong group.

References

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