Fracture energy of nano- and micro-silica particle-filled epoxy composites

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Abstract: The effects of particle size on the surface energy of the fracture surface and elastic moduli of nano- and micro-spherical silica-particle-filled epoxy composites were investigated experimentally. The Young’s modulus and shear modulus of the composites agreed well with the results evaluated by Lewis and Nielsen’s equation and were shown to be dependent on only the volume fraction of the particle. Surface energies of the fracture surface were evaluated from the critical energy release rates and the surface areas including the unevenness. The surface energies were shown to be constant regardless of the volume fraction of the particle.
Keywords: fracture energy; nano-composite; particle-filled composite; silica particle; epoxy composite; surface energy; energy release rate; particle size effect; mechanical property.


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1 Introduction

Polymer materials can be reinforced by filling with several kinds of particles or fibres to make composite materials. It is well known that the size and content of particles strongly affect the mechanical properties of composites (Nielsen and Landel, 1994; Hashin, 1983), especially their fracture toughness (Moloney et al., 1987; Rice, 2000). Nano-composites filled with particles smaller than the micrometre level are believed to have superior mechanical properties due to the size effect of the particles.

Several researchers have considered the effects of particle size or volume fraction on the fracture toughness of polymer matrix composites. Studies by Adachi et al. (2008, 2010) have suggested a mixture law of the fracture toughness including the effects of diameter and volume fraction of particles and confirmed the validity of the law for spherical silica-filled epoxy composites. In the studies, the importance of the interphase surrounding the particles in the composites was pointed out in connection with fracture toughness because the crack propagates not along the particle surface but into the matrix resin and along the interface between the interphase region and the matrix. The interphase region is specific for small-particle-filled composites, and it does not exist in large-particle-filled composites. Several researchers have investigated the interphase region in the composites. Nakamura et al. (2001) found that the particle size and interfacial slope structure affected the mechanical and fracture properties of
Zhang et al. (2006) reported that the interphase constructed a three-dimensional physical network in nano-composites formed by a sol-gel process, which would dominate mechanical performance. Sun et al. (2006) analysed the stress-strain behaviours of particle-reinforced composite considering interphase region by using the finite-element method. Esmaeili and Tomita (2006) used a multi-scale model to calculate the mechanical responses of particle-blended polymer with an interphase layer. Therefore, the role of the matrix resin near the particles and on the fracture surface must be clarified to understand the reinforcement mechanics for fracture of the particle-filled composites, especially nano-composites.

In this research, the effects of particle size on the surface energy of the fracture surface of nano- and micro-spherical silica-particle-filled epoxy composites were investigated experimentally to consider the mechanism of crack propagation and the reinforcement mechanics of the composites. First, composite materials to be used as specimens were prepared by mixing bisphenol A type epoxy resin and spherical silica particles of various particle diameters ranging from microsize to nanosize, i.e., 1.56 µm to 240 nm, and volume fractions ranging from 0 to 0.15. The fracture toughness of the composites, namely critical energy release rates, was measured by a three-point bending test after a tensile test was conducted to determine Young’s and shear moduli. The fracture surface areas including the unevenness were evaluated based on three-dimensional images created from two-dimensional images observed by a scanning electron microscope (SEM). Finally, the surface energy on the fracture surface of the composite was calculated from the fracture toughness and the fracture surface area including the unevenness to consider the effect of the particle size on the fracture energy of the composites.

2 Materials

Several silica-particle-filled epoxy composites were prepared by adding different spherical silica particles to epoxy resin. The epoxy resin was a bisphenol A-type epoxide resin (Japan Epoxy Resin, Epikote 828) with methyl-tetrahydro-phthalic anhydride (Hitachi Chem., HN-2200) as the curing agent and 2,4,6-tris(dimethyl aminomethyl) phenol (Daito Curar, DMP-30) as the accelerator. The weight ratio of the resin, agent, and accelerator was determined as 100 : 80 : 0.5 on the basis of stoichiometry.

Specific surface areas of the silica particles were calculated as shown in Figure 1. The surface areas of particles with diameters less than 500 nm increase drastically. For fillers for the composites in the experiment, we selected spherical silica particles with median diameters, \( D_m \), of 1.56 µm (Tatsumori, SO-C5), 560 nm (Tatsumori, SO-C2), and 240 nm (Tatsumori, 1-FX). The diameter distributions of the particles in the composites are also plotted in Figure 2. The surfaces of the particles were not chemically coated. The particles with volume fractions of 0, 0.05, 0.10, and 0.15 were added to the epoxy resin as matrix material to produce composites.
The silica particles were compounded into a blend of the epoxy resin, the hardener, and the accelerator with a mixing machine until any cohesion of particles in the matrix resin disappeared, and the mixtures were poured into a Teflon-coated mould made from aluminium alloy after being fully agitated and degassed by vacuuming. The mould was 260 mm long, 5 mm wide, and 180 mm deep. The curing was done in two steps. First, the composite was kept at 353 K for 3 h to gel the matrix resin (pre-curing). In the second step, post-curing, which greatly affects the crosslinking reaction of the resin, was done at 413 K for 10 h. The heating rate from pre-curing to post-curing was constant at 72 K/h (Adachi et al., 2008). After curing, densities at different positions of the composites were measured by weighing in water (JIS Z8807) to confirm uniform particle
dispersion. The measured distributions of the densities in the composites are shown in Table 1. The difference of the densities for each composite was below 1%. Uniform dispersion of particles for each composite was confirmed since the differences of the volume fractions evaluated from the densities were also approximately below 1%.

<table>
<thead>
<tr>
<th>Particle size</th>
<th>Volume fraction of particle</th>
<th>Position from bottom of mould</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.56 µm</td>
<td></td>
<td>150 mm</td>
</tr>
<tr>
<td>0.05</td>
<td>1.26 × 10^3</td>
<td>1.26 × 10^3</td>
</tr>
<tr>
<td>0.10</td>
<td>1.31 × 10^3</td>
<td>1.32 × 10^3</td>
</tr>
<tr>
<td>0.15</td>
<td>1.36 × 10^3</td>
<td>1.36 × 10^3</td>
</tr>
<tr>
<td>560 nm</td>
<td></td>
<td>150 mm</td>
</tr>
<tr>
<td>0.05</td>
<td>1.26 × 10^3</td>
<td>1.26 × 10^3</td>
</tr>
<tr>
<td>0.10</td>
<td>1.31 × 10^3</td>
<td>1.31 × 10^3</td>
</tr>
<tr>
<td>0.15</td>
<td>1.36 × 10^3</td>
<td>1.36 × 10^3</td>
</tr>
<tr>
<td>240 nm</td>
<td></td>
<td>150 mm</td>
</tr>
<tr>
<td>0.05</td>
<td>1.26 × 10^3</td>
<td>1.26 × 10^3</td>
</tr>
<tr>
<td>0.10</td>
<td>1.32 × 10^3</td>
<td>1.31 × 10^3</td>
</tr>
<tr>
<td>0.15</td>
<td>1.37 × 10^3</td>
<td>1.37 × 10^3</td>
</tr>
</tbody>
</table>

3 Experimental procedures

3.1 Tensile test

Tensile tests of specimens were conducted to measure the elastic moduli: Young’s modulus and shear modulus. The specimens were 120 mm long, 10 mm wide, and 5 mm thick. Longitudinal and transverse strains were measured by using biaxial strain gauges (Kyowa, KFG-5-120-D16) in which tensile loads were applied by a universal testing machine (Instron, 8501). The loading rate was 0.01 kN/s for each specimen. From the measured stress-strain curves of each composite, Young’s and shear moduli were determined.

3.2 Fracture test

Three-point bending tests on pre-cracked specimens were conducted to measure the mode I fracture toughness at room temperature (298 K) according to ASTM standard D5045 (Figure 3). The specimens were machined from the cured plates to the required size. A slot-notch was cut in the specimen with a saw, and a sharp crack was initiated with a razor blade. The specimen was 90 mm long, 20 mm wide, and 5 mm thick. The lengths of the pre-crack and span were 10 mm and 80 mm, respectively. The tests were carried out under a constant displacement rate of 2 µm/s at the loading point with the universal testing machine (Instron, 8501). From the measured deflection-load curves, critical energy release rates of the specimens, $G_{IC}$, were evaluated as fracture toughness according to ASTM D5045:
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\[ G_{IC} = U/(BW\phi), \]  

where

\[ \phi = A + 18.64 \frac{dA}{d\alpha}, \quad \alpha = \frac{a}{W}, \]

\[ A = \frac{16x^2(1 - \alpha)^3}{3} \left[ 8.9 - 33.717\alpha + 79.616\alpha^2 - 112.952\alpha^3 + 84.815\alpha^4 - 25.672\alpha^5 \right]. \]

B, W, and a are the thickness, width, and crack length of the specimen, respectively. U is the corrected energy given from the deflection-load curve, and \( \phi \) is the energy calibration factor. The corresponding crack length was measured by observing the fracture surface of each specimen with an optical microscope after the bending test. The average value of \( G_{IC} \) of each blended resin was determined using at least five results.

**Figure 3** Three-point bending test (mm)

3.3 Observation of fracture surface

After the fracture tests, the fracture surfaces of the specimens were observed with an SEM (Keyence, VE-8800) to evaluate their geometrical properties visually and quantitatively. Three-dimensional images of the fracture surfaces were created from two-dimensional images observed in different directions by the SEM. The geometrical properties of the fracture surfaces were evaluated using the three-dimensional images. The regions of the three-dimensional images were \( L_{OC} \times L_{OT} = 10.20 \times 7.61 \mu m \) at 3 mm from the pre-crack tip on the centre line of the specimen (Figure 4(a)), where \( L_{OC} \) and \( L_{OT} \) were side lengths along the crack propagation and transverse directions, respectively. The surface profiles were measured on each of the seven lines of the images along the propagation direction of the crack and the transverse direction of the crack propagation (Figure 4(b)). The line lengths along both directions including the unevenness of the surfaces, \( L_C \) and \( L_T \), which were line lengths along the crack propagation and the transverse directions, were evaluated from the surface profiles. The resolutions of the three-dimensional images along the in-plane and out-of-plane directions were 19 nm and 10 nm, respectively. Finally, the areas of the fracture surfaces including the surface unevenness, \( A_S \), were calculated approximately as \( A_S = L_C \times L_T. \)
Figure 4 Measurement of surface profile: (a) position observed by SEM and (b) scanning lines of surface profiles. Solid line: scanning along crack propagation. Broken line: scanning along transverse direction of crack propagation.

The surface energies of the composites, $\gamma_S$, were evaluated from the critical strain energy release rates, $G_{IC}$, and the areas of the fracture surfaces, $A_S$, as follows

$$\gamma_S = \frac{G_{IC}}{2A_S}$$

(2)

4 Results and discussion

4.1 Elastic properties

Figure 5 shows Young’s and shear moduli of the composites. It was reported that the elastic moduli of the particle-filled composites were dependent on only the volume fraction of the particles (Kwon et al., 2006, 2008; Adachi et al., 2008, 2010). In Figure 5, the results evaluated by Lewis and Nielsen’s mixture law (Nielsen, 1970) are plotted to compare with the experimental results. Lewis and Nielsen’s mixture law is
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\[ E_c = \frac{1 + AB\phi}{1 - B\psi\phi} E_m, \]  

where

\[ A = \frac{7 - 5\nu_m}{8 - 10\nu_m}, \quad B = \frac{(E_p/E_m) - 1}{(E_p/E_m) - A}, \quad \psi = 1 + \left( 1 - \frac{\phi_{\text{max}}}{\phi_{\text{max}}} \right) \phi, \]

\[ E \] and \( \nu \) are the elastic modulus and Poisson’s ratio. The subscripts \( c, m, \) and \( p \) denote the composite, matrix, and particle, respectively. \( \phi \) and \( \phi_{\text{max}} \) are volume fraction and closest volume fraction of the particle, respectively.

**Figure 5** Elastic moduli: (a) Young’s modulus and (b) shear modulus

The experimental results agreed well with the results evaluated by Lewis and Nielsen’s equation. Young’s and shear moduli were not affected by the particle size.
4.2 Fracture toughness

Figure 6 plots fracture toughness, $G_{IC}$, of the composites. The fracture toughness of the composites increased as the volume fractions increased. The fracture toughness of the composites filled with the smallest particle of 240-nm-diameter was larger than that of the other composites. The differences of the fracture toughness were not large since the volume fractions were relatively low in the experiment. Therefore, the fracture toughness, namely the critical energy release rate, was shown to be strongly dependent on the volume fraction and the particle size.

Figure 6  Fracture toughness

4.3 Fracture surface

After the fracture tests, the fracture surfaces were observed by SEM as shown in Figure 7. The unevenness of the fracture surfaces increased as the volume fractions of the particle increased or the particle size decreased. No particles were found to be on the fracture surface. This means that the particles were surrounded by a polymer region, namely the interphase region (Zhang et al., 2006). Adachi et al. (2008) also showed this on the basis of observation and estimation by SEM and microscopic Raman spectroscopy. Therefore, the fracture surface energy is dependent on the properties of the polymer matrix or the interface between the interphase region and the matrix of the epoxy.
Figure 7 Fracture surface: (a) particle size 1.56 µm, volume fraction 0.05; (b) particle size 560 nm, volume fraction 0.05; (c) particle size 240 nm, volume fraction 0.05; (d) particle size 1.56 µm, volume fraction 0.15; (e) particle size 560 nm, volume fraction 0.15 and (f) particle size 240 nm, volume fraction 0.15

Figure 8 shows the line lengths, including the unevenness on the surfaces, along the crack propagation and transverse directions, \( L_C \) and \( L_T \). In the figure, the line lengths were normalised by the line lengths of the straight lines on the projected plane: \( L_0C \) or \( L_0T \). The plots and the error bars denote the average values of the line lengths and their standard deviations. The line lengths along the propagation direction were approximately the same as those along the transverse direction, although the relationship between the line lengths and the volume fraction of the particle is not seen clearly in Figure 8.

Figure 8 Line lengths in region observed by SEM
The fracture surface areas that included the unevenness were evaluated approximately from the product of both line lengths, \( A_s = L_0 \times L_0 \). Figure 9 shows the surface areas of the fracture surfaces including the unevenness. In the figure, the areas are normalised by the areas projected to the plane, \( A_{s0} = L_{0c} \times L_{0t} (=10.20 \times 7.61 \mu m) \). The areas were dependent on the diameters and the volume fractions of the particles. The area of the small-particle-filled composite was relatively larger.

**Figure 9** Normalised area of fracture surface

### 4.4 Surface energy

Surface energies of the composites were evaluated by equation (2). The results are shown in Figure 10. The surface energies of the composites were constant regardless of the volume fraction of the particle. The surface energies for the composites filled with the particles of 1.56-mm and 560-nm diameter were approximately the same, and the surface energy for the composite with 240-nm-diameter particles was larger. The energies were dependent on only the particle diameter regardless of the volume fractions of the particles although the fracture toughness was affected by both the diameter and the volume fraction, as shown in Figure 6. The surface energy for the particle sizes correlated well with the specific surface area in Figure 1. Therefore, the interphase region surrounding the particles in the composite plays an important role in the fracture phenomena.
5 Conclusion

The effects of particle size on the surface energy of fracture surface of nano- and micro-spherical silica-particle-filled epoxy composites were investigated experimentally. Young’s modulus and shear modulus of the composites agreed well with the results evaluated by Lewis and Nielsen’s equation. The elastic moduli were confirmed to be dependent on only the volume fraction of the particles. The fracture toughness, namely critical energy release rates, was dependent on the volume fraction and size of the particles. The surface energies of the fracture surface were evaluated from the critical energy release rates and the surface areas including the unevenness. The surface energies of the composites were constant regardless of the volume fraction of the particles.

References


