Effects of Particle Size on Mechanical and Impact Properties of Epoxy Resin Filled with Spherical Silica

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SYNOPSIS

Effects of particle size on the mechanical and impact properties of cured epoxy resins are studied. This resin was filled with spherical silica particles prepared by hydrolysis of silicon tetrachloride. Particles were sorted into five kinds of different mean sizes in the range from 6–42 μm. A static flexural and tensile tests and an instrumented Charpy type impact test were carried out. Flexural strength, tensile strength, and impact-absorbed energy increased with a decrease in the particle size. Fractured surfaces were observed using a scanning electron microscope to clarify the initiation point of fracture.

INTRODUCTION

The drawback of epoxy resin is still "low toughness," i.e., cured epoxy resin is a rather brittle polymer that has poor resistance to cracking. This crack is derived from the internal stress generated by shrinkage in the cooling process from cure temperature to room temperature.

In a series of investigations,[1-6] we have been able to reduce internal stress. For this purpose, the formation of a two-phase structure in which soft acrylic polymer particles were dispersed as domains (second phase) in the cured epoxy matrix was carried out. As a result, the effects of the domain size[1] and the domain/matrix interaction[2-6] on the reduction of the internal stress were clarified.

Many researchers[7-18] have reported that the addition of rigid filler particles is useful for toughening cured epoxy resin. Most of these studies were carried out using glass beads, but a few studies were made using irregularly shaped silica particles ranging from 60–300 μm in diameter.[15] Recently, cured epoxy resin filled with irregularly shaped and spherical silica particles ranging in size from submicron to about 100 μm were used as encapsulating materials for integrated circuits.[19,20] In the previous articles,[21-23] the effect of particle size on fracture toughness was studied using such irregularly shaped[21,22] and spherical silica particles[22,23] having different mean sizes in the range from 2 to about 50 μm.

Mechanical and impact properties of the particles are also important for application of these materials. Some researchers have reported these properties using glass beads[13,15] or the above-mentioned larger, irregularly shaped silica particles.[14,15] In the previous articles,[24-26] effects of particle size on mechanical[24,25] and impact properties[26] were studied using the same irregularly shaped silica particles.

In this study, subsequently, we report the effects of particle size on the mechanical and impact properties of epoxy resin filled with spherical silica.

EXPERIMENTAL

Materials

Spherical silica particles (Excelica ML-801, Tokuyama Soda Co., Ltd.) were prepared as follows. Agglomarated SiO_2 was produced by hydrolysis of silicon tetrachloride through the following reaction:

$$SiCl_4 + 2H_2O \rightarrow SiO_2 + 4HCl \quad (1)$$

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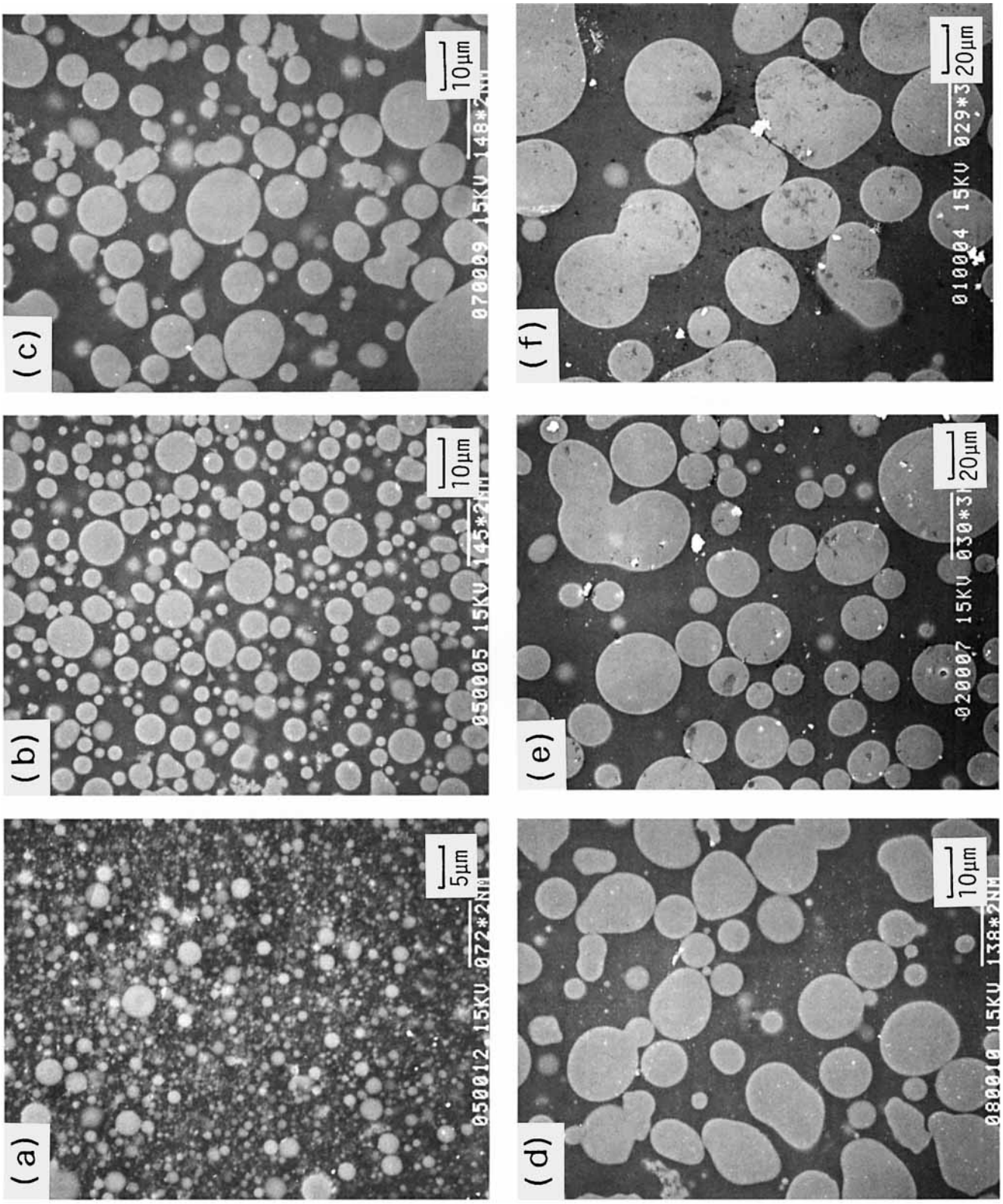
(a)
5μm
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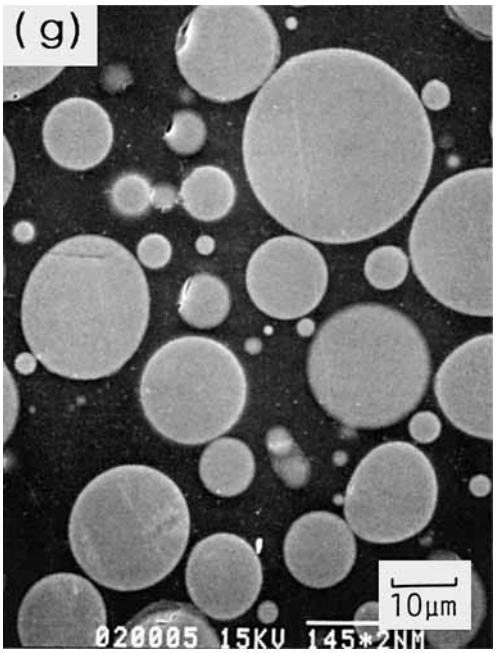

Figure 1 *(continued from previous page)*

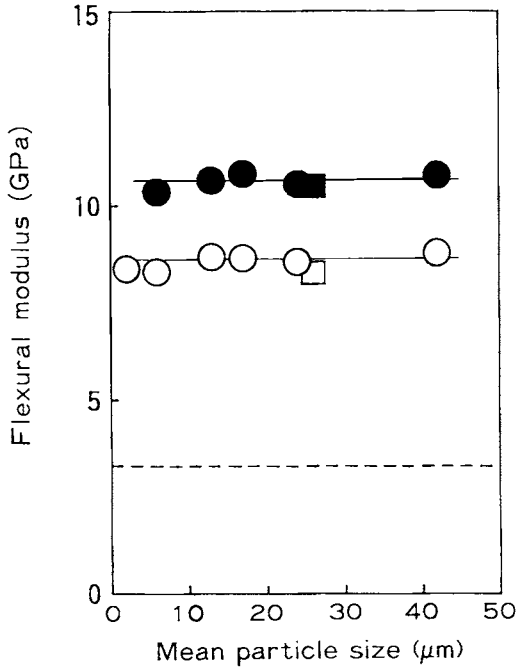

Figure 2 Effect of particle size on flexural modulus of cured epoxy resins filled with (□, ■) unsorted original and (○, ●) sorted spherical silica particles with particle contents of (□, ○) 55 and (■, ●) 64 wt %. Broken line indicates the flexural modulus value for unfilled cured epoxy resin.

Subsequently, agglomarated SiO_2 was fused in a flame of hydrogen and oxygen; as a result, spherical particles were obtained. Particles were sorted into five groups by air separation. The mean sizes of sorted particles are 6, 13, 17, 24, and 42 μm. In addition, the finest silica particles (Adoma-fine SO-32H type, mean particle size 2 μm, supplied by Tatsumori Ltd.), prepared by fusing of metallic Si powder in a flame of oxygen at 4000°C (vaporize metallic conversion method), were used without sorting. Scanning electron microscope (SEM) photographs of these silica particles and their size distribution curves obtained using a laser-beam type of size distribution analyzer are shown in previous articles.[23,25] The specific surface area of each silica particle was measured according to BET equation.

The epoxy resin used was bisphenol-A type epoxy resin (Epikote 828, Shell Chemical Co., equivalent weight per epoxy group 190 ± 5, average molecular weight 380). 1,2-Cyclohexanedicarboxylic anhydride and tri-*n*-butylamine were used as a hardener and an accelerator for curing of the epoxy resin, respectively.

Sample Preparation

Silica particles (204 or 296 parts per hundred resin by weight, phr) were dispersed in the mixture of the epoxy resin (100 phr) and the hardener (66 phr) by stirring at room temperature for 1 h under vacuum degassing. Accelerator (0.5 phr) was added to the mixture under stirring for 10 min. The final mixture was cured in a mold (4 × 10 mm, height 100 mm, dumbbell-shaped type, thickness 2 mm, and 15 × 15 mm, height 140 mm) at 120°C for 2 h followed by 140°C for 21 h.

Figure 1 SEM photographs of polished surfaces of cured epoxy resins filled with (b–f) sorted and (a, g) unsorted original spherical silica particles with particle contents of (a) 55 and (b–g) 64 wt %. Mean particle size of filled silica: (a), 2 μm; (b), 6 μm; (c), 13 μm; (d), 17 μm; (e), 24 μm; (f), 42 μm; (g), 25 μm.

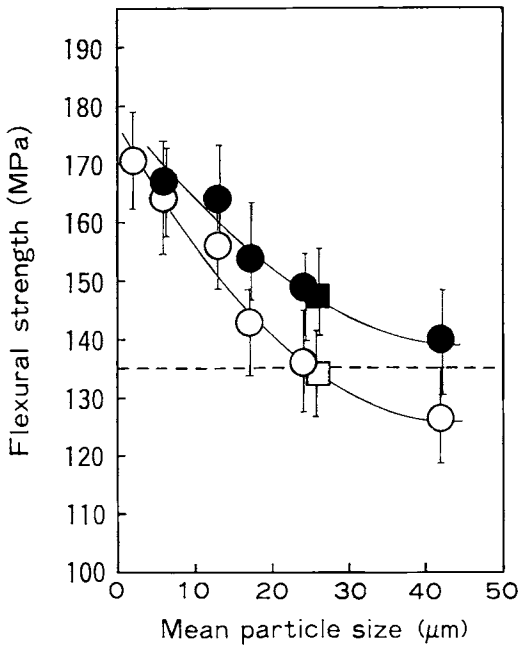

Figure 3 Effect of particle size on flexural strength of cured epoxy resins filled with (□, ■) unsorted original and (○, ●) sorted spherical silica particles with particle contents of (□, ○) 55 and (■, ●) 64 wt %. Broken line indicates the flexural strength value for unfilled cured epoxy resin.

Static Mechanical Test

The static mechanical properties of the cured epoxy resin filled with silica particles were measured by the following methods described in detail in the previous article.[24]

Flexural Test

The three-point bending flexural test specimens are 4 × 10 × 80 mm and the support span is 64 mm. The load–time curve was recorded using a tensile testing machine at a displacement rate of 5 mm/min at room temperature. The flexural modulus (E_f) and the flexural strength (σ_f) were calculated from following equations (ASTM D-790):

$$E_f = \frac{S^3}{4B \cdot W^2} \cdot m \tag{2}$$

$$\sigma_f = \frac{3P_c \cdot S}{2W \cdot B^2} \tag{3}$$

where P_c is the load at specimen break, W is the specimen width, B is the specimen thickness, S is the support span, and m is slope of the tangent to the initial straight-line portion of the load–time curve.

Tensile Test

The shape and dimension of the tensile test specimen (dumbbell-shaped type) were shown in the previous article.[24] The test was carried out with a displacement rate of 5 mm/min. The tensile strength (σ_t) was calculated from the following equation:

$$\sigma_t = \frac{P_c}{A} \tag{4}$$

where A is the cross-sectional area of the dumbbell specimen.

Impact Properties

The impact test specimens are 15 × 15 × 90 mm. A U-shaped blunt notch with depth of 2 mm and radius

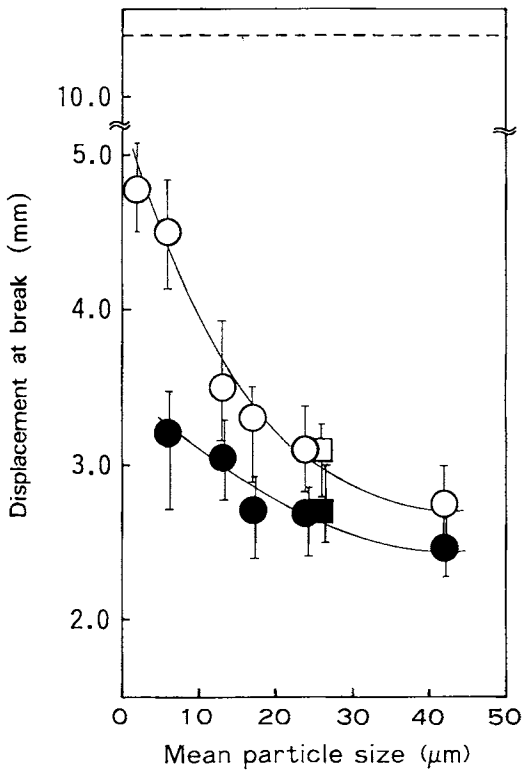

Figure 4 Effect of particle size on displacement at break measured by flexural test of cured epoxy resins filled with (□, ■) unsorted original and (○, ●) sorted spherical silica particles with particle contents of (□, ○) 55 and (■, ●) 64 wt %. Broken line indicates the displacement at break value for unfilled cured epoxy resin.

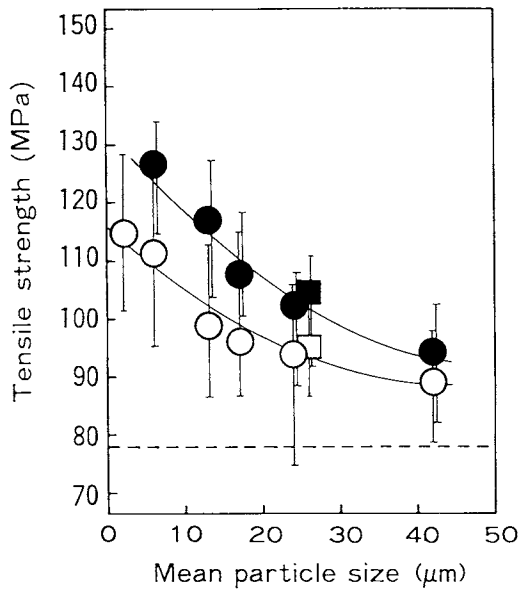

Figure 5 Effect of particle size on tensile strength of cured epoxy resins filled with (□, ■) unsorted original and (○, ●) sorted spherical silica particles with particle contents of (□, ○) 55 and (■, ●) 64 wt %. Broken line indicates the tensile strength value for unfilled cured epoxy resin.

of 1 mm was machined at the center part of the specimen. The support span was 70 mm. Impact properties were measured by the instrumented Charpy type impact tester[27-30] (CAI-AC5-CZ(A) type, Japan Sensor Corp., capacity 14.7 J) at room temperature. The weight of the hammer is 6 kg and the length of the hammer arm is 0.6 m. In the condition employed in this study, the hammer speed at strike was 1.10 m/s. This apparatus and the measurements for the load and displacement at impact specimen break and impact-absorbed energy were described in detail in the previous article.[26]

RESULTS AND DISCUSSIONS

Figure 1 shows SEM photographs for the polished surfaces of cured epoxy resins filled with unsorted original (a, g) and sorted (b–f) spherical silica particles at particle contents of (a) 55 and (b–g) 64 wt %. Those indicate that particles were well dispersed in the cured epoxy matrix.

Figure 2 shows the effect of particle size on flexural modulus. The modulus increased with an increase in particle content, whereas it did not depend on particle size. There was no difference in the values between unsorted (□, ■) and sorted particles (○, ●) at particle contents of 55 and 64 wt %.

Figures 3–5 show the effects of particle size on flexural strength, displacement at break in flexural test, and tensile strength, respectively. These values increased with a decrease in the particle size. These phenomena were in accordance with results obtained in the cured epoxy resin filled with irregularly shaped silica particles having similar sizes reported in the previous article[24] and with those reported by Cantwell et al.[16] using larger irregularly shaped silica particles (mean size: 60–300 μm).

Figures 6–8 show the effects of particle size on the load at specimen break, displacement at specimen break, and impact-absorbed energy measured by the instrumented Charpy type impact test, respectively. These values increased with decrease in the particle size. These phenomena were also in accordance with results obtained in the irregularly shaped silica-filled system reported in the previous article.[26]

From the above results, it was clarified that both static and impact properties are improved with decrease in particle size.

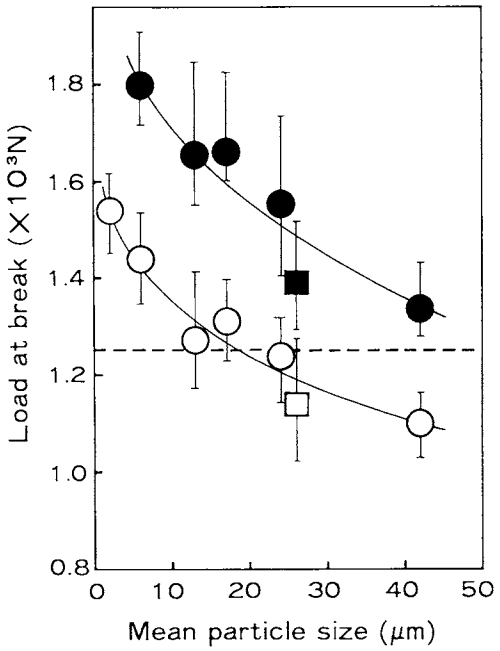

Figure 6 Effect of particle size on load at break measured by instrumented Charpy type impact test of cured epoxy resins filled with (□, ■) unsorted original and (○, ●) sorted spherical silica particles with particle contents of (□, ○) 55 and (■, ●) 64 wt %. Broken line indicates the load at break value for unfilled cured epoxy resin.

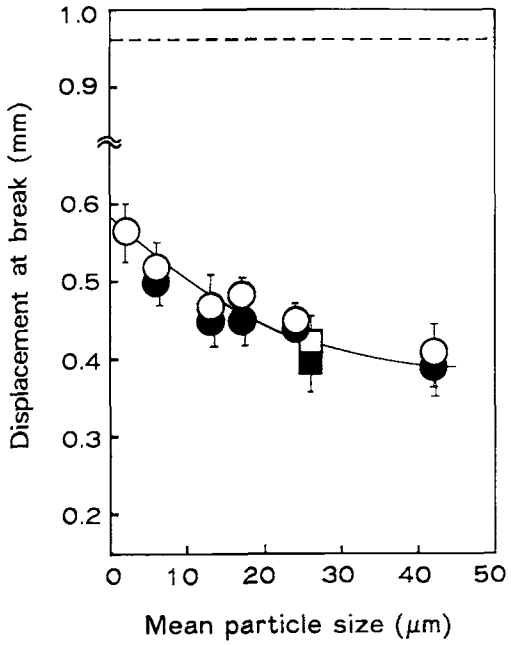

Figure 7 Effect of particle size on displacement at break measured by instrumented Charpy type impact test of cured epoxy resins filled with (□, ■) unsorted original and (○, ●) sorted spherical silica particles with particle contents of (□, ○) 55 and (■, ●) 64 wt %. Broken line indicates the displacement at break value for unfilled cured epoxy resin.

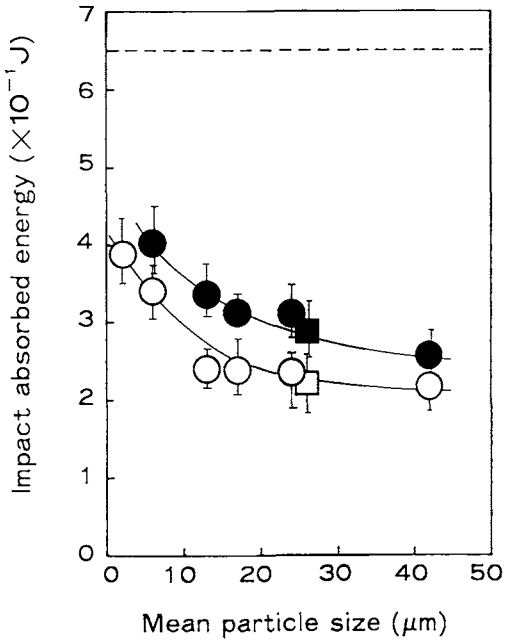

Figure 8 Effect of particle size on impact absorbed energy measured by instrumented Charpy type impact test of cured epoxy resins filled with (□, ■) unsorted original and (○, ●) sorted spherical silica particles with particle contents of (□, ○) 55 and (■, ●) 64 wt %. Broken line indicates the impact-absorbed energy for unfilled cured epoxy resin.

Figure 9 shows the relationship between flexural strength value and the specific surface area of filled silica particles. Good relation between both values was obtained. This indicates that the increase of specific surface area of filled particles increases their flexural strength. Similar relation was obtained in the tensile strength.

Figure 10 shows SEM photographs of fractured surfaces of flexural specimens filled with the particles in the sizes of (a) 6 μm, (b) 17 μm, or (c) 42 μm. In all specimens, the fracture was started from the lower part of specimen (under tensile mode). In these fractured surfaces, the initiation point was surrounded by a relatively smooth, small semicircular zone. Further, this zone was surrounded by a rough zone in which fractured marks started radiately from the initiation point. These observations were the same as those of the flexural[24] and impact test specimens[26] of cured epoxy resin filled with irregularly shaped silica particles shown in our previous articles[24,26] and those of others.[16,17] Next, the region around the initiation point of fracture was magnified to clarify the effect of particle size on their initiation of fracture.

Figure 11 show the results. Figure 11(a) shows that the defect that had existed at the specimen sur-

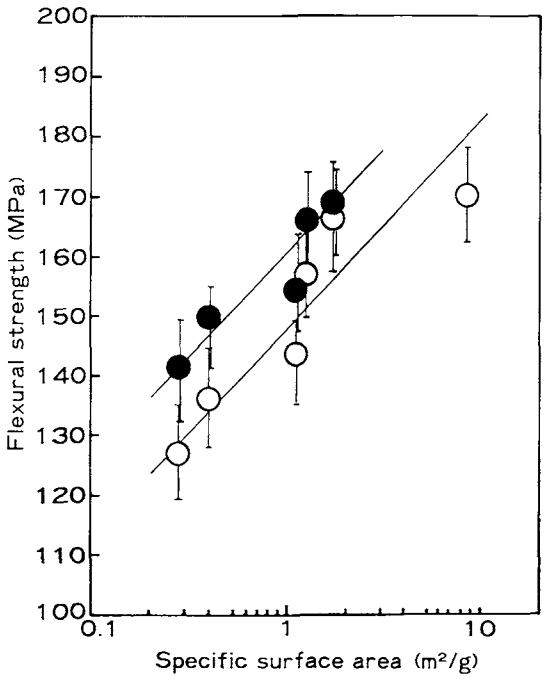

Figure 9 Flexural strength of cured epoxy resins filled with spherical silica particles having different mean sizes with particle contents of (○) 55 and (●) 64 wt % vs. specific surface area of filled silica particles.

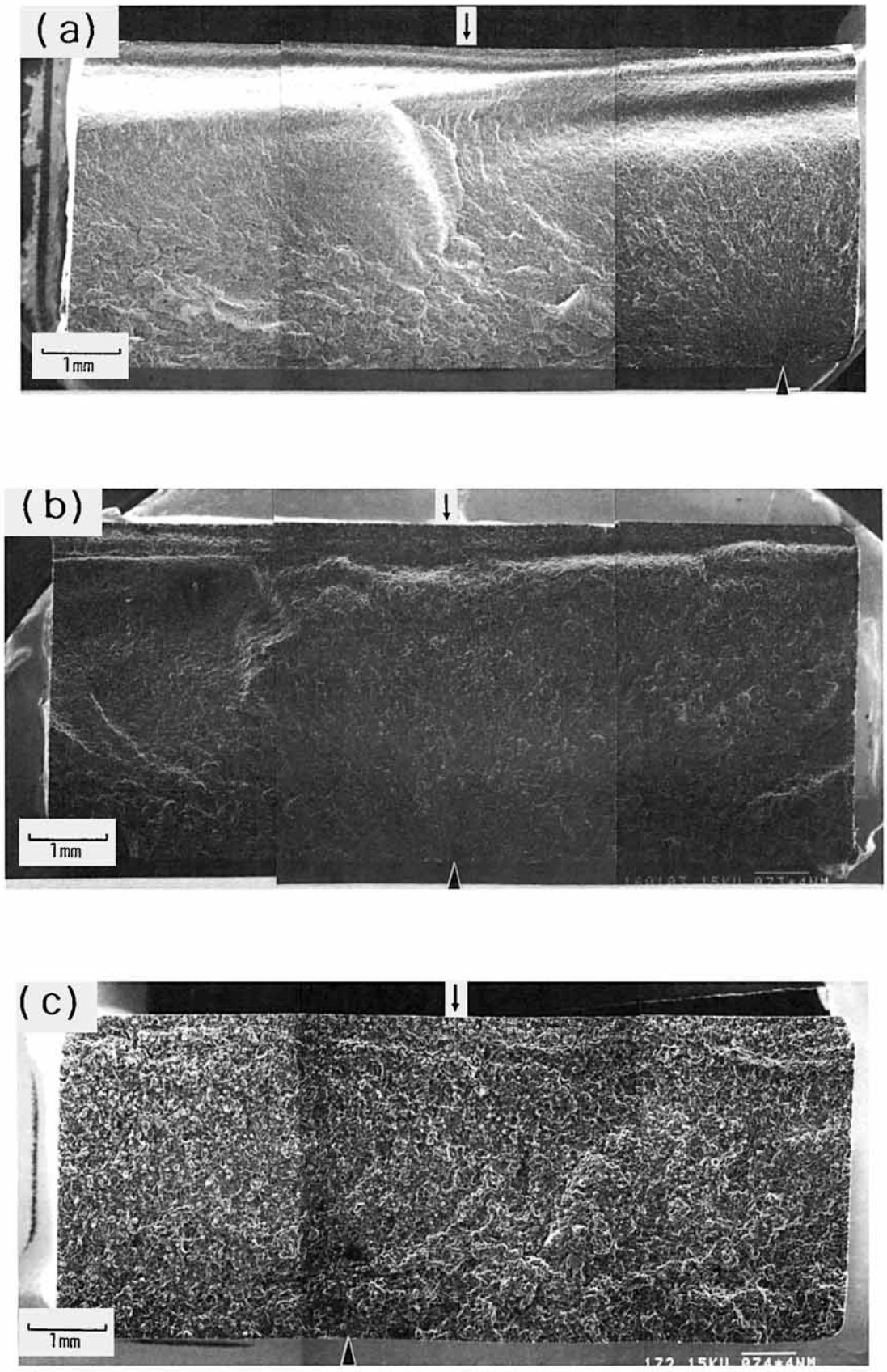

Figure 10 Fractured surfaces for flexural test specimens of cured epoxy resins filled with spherical silica particles with a particle content of 64 wt % observed by SEM. Mean particle size of filled silica: (a), 6 μm; (b), 17 μm; (c), 42 μm. Arrow indicates the direction of applied load and triangle indicates the initiation point of fracture.

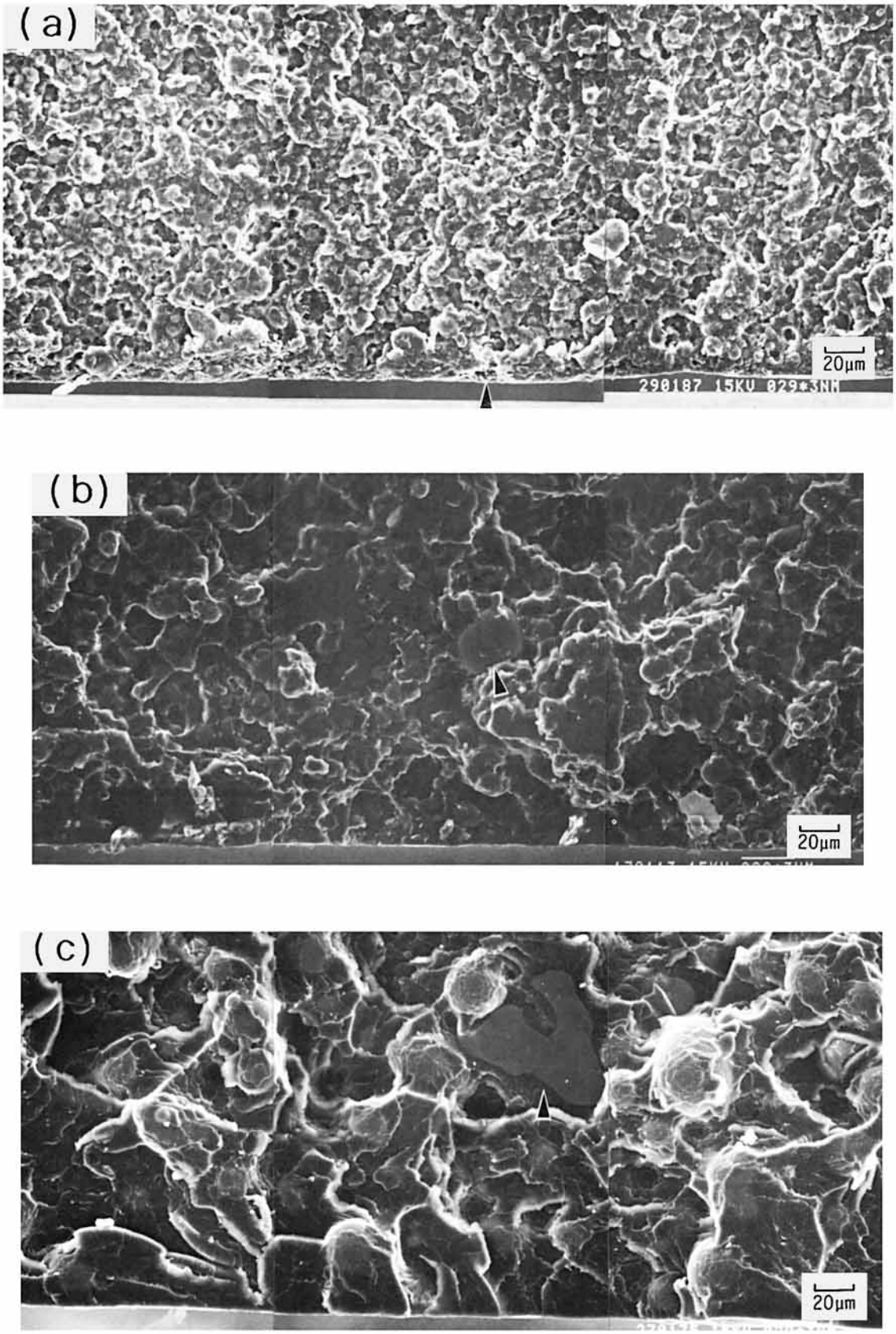

Figure 11 Regions around the initiation point of fracture for fractured flexural test specimens of cured epoxy resins filled with spherical silica particles with a particle content of 64 wt % observed by SEM. Mean particle size of filled silica: (a), 6 μm; (b), 17 μm; (c), 42 μm. Triangle indicates the initiation point of fracture.

face was the initiation point of fracture in the cured epoxy resin filled with small particles (mean size: 6 μm). In all tested specimens for the unfilled cured epoxy resin and those filled with 2- and 6-μm particles, similar observations were obtained. In resin filled with medium particles (mean size: 17 μm), a relative larger particle than their mean size existed at the initiation point of fracture [Fig. 11(b)]. This suggests that the fracture is initiated from the delaminated interface. In resin filled with the largest particles (mean size: 42 μm), it was initiated from a fractured particle [Fig. 11(c)]. With an increase in particle size above 6 μm, the portion of the initiation point that was due to the particle fracture increased. In resins filled with 24- and 42-μm particles, fractures were initiated from the particle fracture in all tested specimens. The spherical silica particles used in this study were fused in a flame during the preparation process as mentioned in the experimental section. In this process, a portion of the particles agglomerated, resulting in "irregular" particles. It is clear from Figure 1 that increasing particle size causes the shape of agglomerated particles to become more irregular. The agglomerated irregular particles may be cracked easily when the load is applied. Similar observations were obtained in the fractured surfaces of impact test specimens.

From the above results, it was concluded that the possibility of particle fracture that initiates the specimen break increases with particle size in the spherical particle-filled system used in this study, although it is difficult to distinguish strictly between the effects of size and shape because of the agglomeration of the particles.

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