

Characterization of Mechanical Properties of $\gamma\text{Al}_2\text{O}_3$ Dispersed Epoxy Resin Cured by γ -Ray Radiation

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ABSTRACT: Epoxy resins are widely utilized as high performance thermosetting resins for many industrial applications, but they are characterized by relatively low toughness. Incorporation of rigid inorganics is suggested to improve the mechanical properties of epoxy resins. An attempt is made to disperse nanosized $\gamma\text{-Al}_2\text{O}_3$ particles into diglycidyl ether of bisphenol A epoxy resins for the improvement of the mechanical properties. These hybrid epoxy–alumina composites are prepared using by the γ -ray curing technique

conducted at 100 kGy under nitrogen at room temperature. The composites are characterized by determining the gel content, flexural strength, Young's modulus, and toughness at room temperature using scanning electron microscopy and FTIR studies. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 1898–1903, 2004

Key words: epoxy resin; nanosized γ -alumina; γ -ray curing; flexural properties

INTRODUCTION

Epoxy resins are very useful polymer materials because of their good mechanical, thermal, and electrical properties.^{1–3} Accordingly, epoxy resins are being widely used as matrices in structural applications such as high performance fiber reinforced composites (CFRP) for aerospace, automobiles, and surface coatings materials. However, the main drawback of epoxy resins is their inherent brittleness because of their highly crosslinked structure, which has led to extensive research efforts to improve their low toughness. Elastomeric materials have been used to improve the mechanical properties of epoxy resins for the last few decades. However, these materials have lower flexural strength and Young's modulus. Several recent works have investigated the improvement of the mechanical properties of epoxy resins by the incorporation of rigid inorganic fillers.^{4–8} In these particulate filled systems, the interfacial bonding or adhesion between the filler and the matrix has a great effect on the mechanical properties, which was controlled by using coupling agents.^{9–12}

In order to improve the mechanical properties, we attempted to disperse nanosized Al_2O_3 particles into an epoxy resin and the resulting particulate epoxy resin was cured by γ -ray radiation using a cationic

initiator. γ -Ray irradiation has a number of advantages such as a shorter curing time, low energy consumption, a low cure temperature, dimensional stability, and reduced manufacturing cost compared to conventional thermal curing.¹³ A silane-coupling agent was used to investigate the particle–matrix adhesion, and its effects were studied.

EXPERIMENTAL

Materials

Diglycidyl ether of bisphenol A (DGEBA) epoxy (YD128, viscosity = 11,500–13,500 Pa s, density = 1.16–1.18 g/cm³, epoxy equivalent weight = 184–190 g/eq, Kukdo Chemical Co., Ltd.) was used as a matrix. Triarylsulfonium hexafluoroantimonate (TASHFA) was purchased from Aldrich and used as a cationic initiator. $\gamma\text{-Al}_2\text{O}_3$ (Gamma alumina B, micropolished, Buehler Co.) with an average particle size of 50 nm was selected as an inorganic filler particle. 3-Methacryloxypropyl trimethoxysilane (Z6030, Dow Corning) was used as a silane-coupling agent. Figure 1 shows the schemes of DGEBA, TASHFA, and the Z6030 silane-coupling agent.

Surface treatment of alumina particles

Ethanol was first adjusted to pH 4.0–4.5 with acetic acid. Then, 0.1–0.5% silane concentrated solutions were produced by adding the silanes while stirring. Alumina particles were added into the silane solution. The mixture was stirred for 30 min for hydrolysis and immigration of silanes with the hydroxyl groups of

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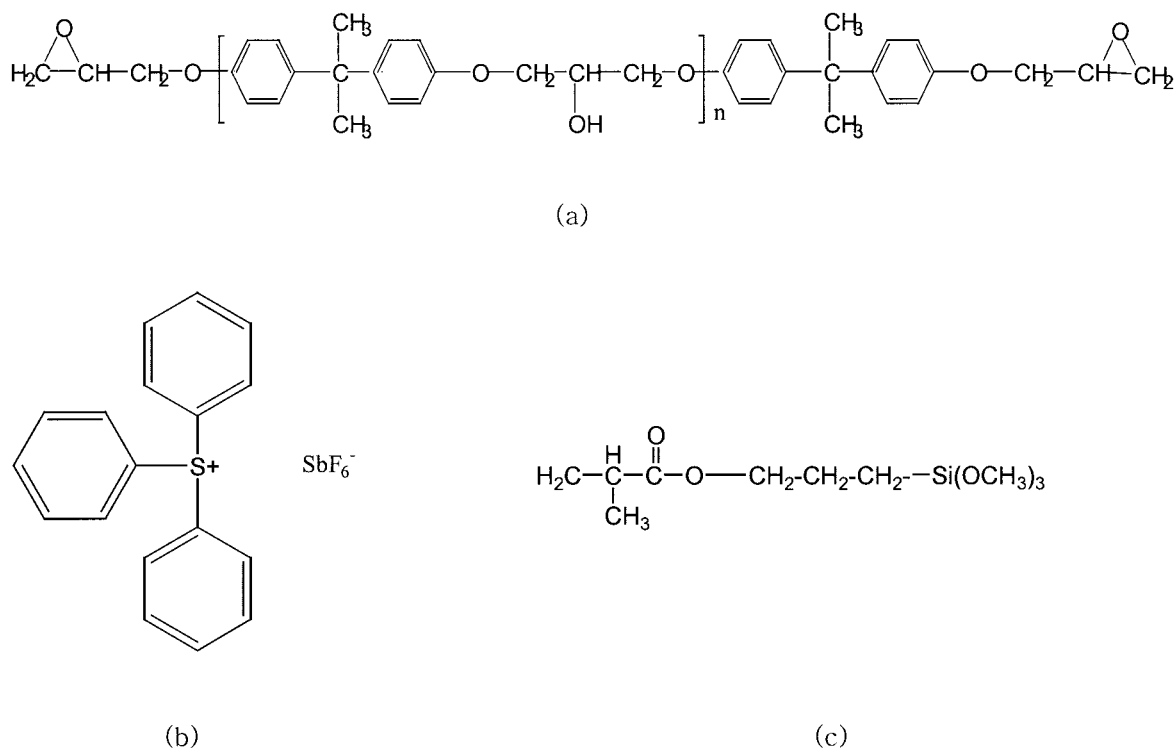


Figure 1 The scheme of the starting materials: (a) DGEBA, (b) TASHFA, and (c) silane-coupling agent.

the alumina surface. The solution was filtrated and the filter cakes were dried in an oven for 24 h for the condensation process of silanes to siloxanes.

Fabrication of composites

Silane or nontreated alumina particles and the photo-initiator were mixed with epoxy resins. Sonic agitation was performed to disperse the particles homogeneously. The mixture was poured into an aluminum mold that was treated with a releasing agent and then cured by γ -rays. Irradiation was carried out at a dose rate of 10 kGy/h from a Co^{60} source. Irradiation was performed up to 100 kGy under a nitrogen atmosphere at room temperature.

Characterization

After curing, the gel fraction of irradiated epoxy composite was determined by the Soxhlet method. The pieces of the composites were extracted with boiling acetone for 24 h, and then they were dried in a vacuum at 80°C to constant weight. The surface treated alumina was confirmed by FTIR (Sense IR, Travel Co.). The mechanical properties of the manufactured epoxy composites were evaluated by a flexural test. An Instron 4443 universal testing machine was used for measuring the flexural strength, Young's modulus, and toughness at room temperature. The epoxy com-

posites were cut into 50 × 25 mm pieces, and the specimens were tested by the 3-point bending method (ASTM D 790; 25-mm span, 0.8 mm/min crosshead speed).

The dispersion of particles in the composites and the fracture surface were observed by scanning electron microscopy (SEM; XL30S, Philips Co.).

RESULTS AND DISCUSSION

Gel fraction of epoxy–alumina composites

The influence of the contents of alumina particles and TASHFA initiator on the gel fraction of the epoxy–alumina composites are shown in Figure 2. The gel fraction of the epoxy composite increased as the concentration of TASHFA increased. This is a natural result because a higher concentration of initiator causes the increase of radicals. Therefore, the increase of radicals contributes to the curing reactions of an epoxy resin. Figure 3 shows the scheme of the curing reaction of the epoxy by a cationic initiator.¹⁴ According to Figure 2, the gel fractions of the composites were decreased with an increase of the contents of alumina particles. An increase in alumina filler suppressed the curing reactions of the epoxy resin system. There might be two possible mechanisms that cause this phenomenon. One is the decrease of the propagation reaction speed, and the other is inhibition of the

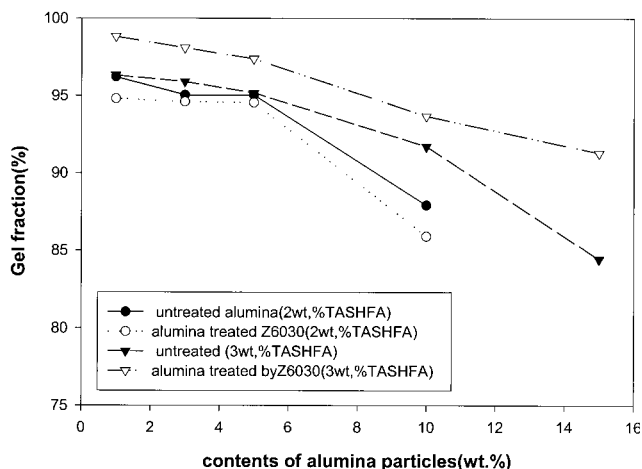


Figure 2 The gel contents of the hybrid epoxy composites as a function of the contents of alumina particles.

propagation reaction, for example, the chain-transfer reaction. In addition, the chain-transfer reaction of a growing cation might also occur via the —OH groups remaining in the alumina particles.¹⁵

If the chain-transfer reaction occurred, the propagation reaction would be inhibited and the gel time of the epoxy resin system would become longer.

FTIR study on alumina particles

IR spectra were used to examine the extent of bonding between the surface of the alumina particles and the silane-coupling agents. Figure 4 shows the IR spectra of the Z6030 silane-coupling agents, the alumina particles, and the alumina particles treated with Z6030 silanes. The peaks of the Z6030 silane-coupling agent are observed at the peak of the treated alumina particle in the figure. These changes of peaks demonstrate that the silane groups react with t—OH groups of the surface of alumina particles. The treatment was also

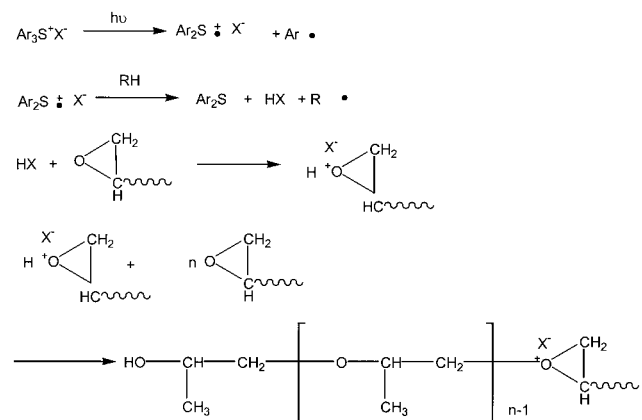


Figure 3 The scheme of a cationic curing reaction of epoxy with sulfonium salt as an initiator.

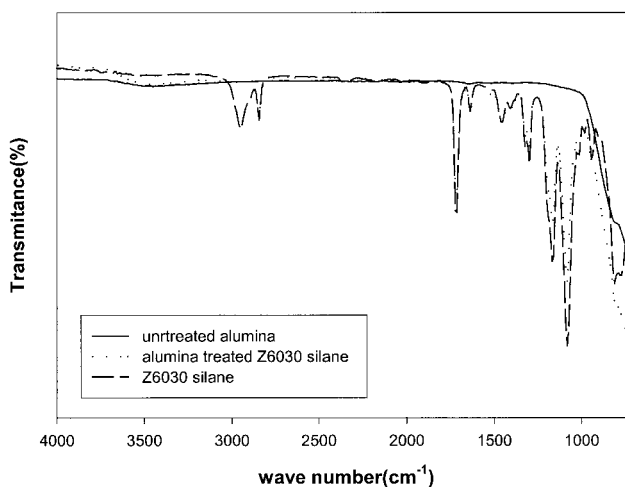


Figure 4 The IR spectra of alumina, silane-coupling agent, and alumina treated with silane.

confirmed by a floating test on water. The treated alumina particles were not wet by water because the surface of the alumina particles was changed from hydrophilic to hydrophobic.

Mechanical properties

Figure 5 shows the stress of the composites filled with the treated alumina particles as a function of the contents of the initiator and filler. The stress of the composite increased with suitable contents of alumina particles. The slope of the stress curves is steep and increases with the concentration of the initiators and

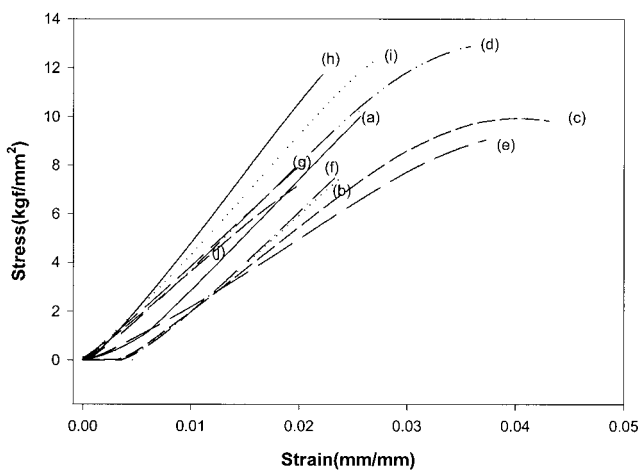


Figure 5 Stress-strain curves of the composites containing (a) 2 wt % TASHFA, (b) 2 wt % TASHFA and 1 wt % alumina, (c) 2 wt % TASHFA and 3 wt % alumina, (d) 2 wt % TASHFA and 5 wt % alumina, (e) 2 wt % TASHFA and 10 wt % alumina, (f) 3 wt % TASHFA and 1 wt % alumina, (g) 3 wt % TASHFA and 3 wt % alumina, (h) 3 wt % TASHFA and 5 wt % alumina, (i) 3 wt % TASHFA and 10 wt % alumina, and (j) 3 wt % TASHFA and 15 wt % alumina.

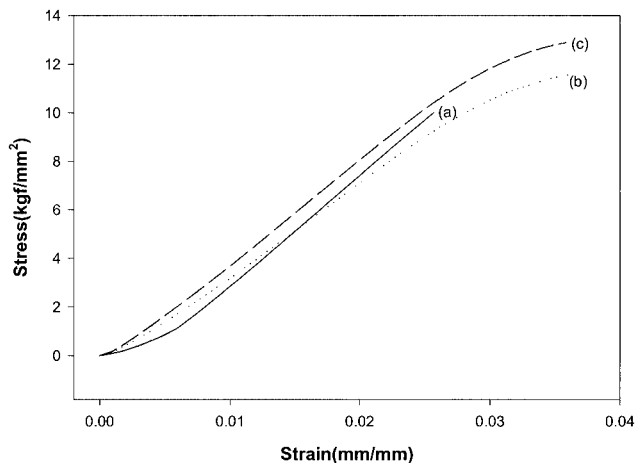


Figure 6 Stress-strain curves of the composites containing nonalumina particles (curve a), 5 wt % nontreated alumina particles (curve b), and 5 wt % alumina particles treated by Z6030 silane-coupling agent (curve c).

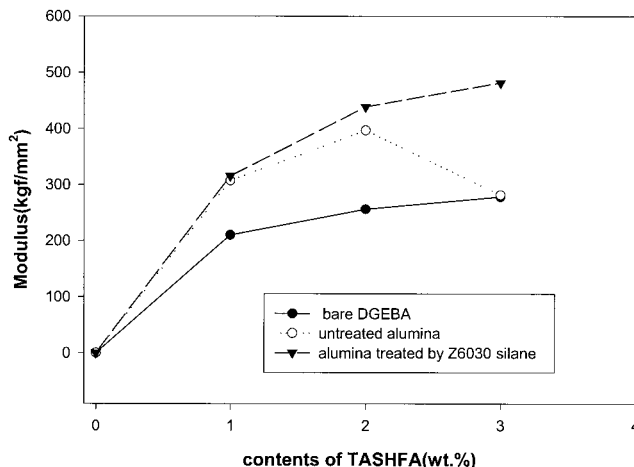


Figure 8 The Young's modulus of the composites containing 5 wt % alumina particles as a function of the contents of TASHFA.

much less steep with the increase of alumina particles. The composite containing more initiator caused the increase in strength, whereas the composites containing more filler led to the increase in toughness. Figure 6 shows the influence of silane-coupling agents and alumina particles on the stress-strain characteristics of the composites. As expected, the composites containing alumina particles treated by the silane-coupling agent have higher toughness than those containing the untreated alumina particles or the epoxy resin (no alumina particles). This means that the silane-coupling agent made a strong adhesion between the alumina and epoxy resin. The scheme of the mechanism for the reaction between the epoxy matrix and silane treated alumina particles is shown in Figure 7.

Figures 8 and 9 show the Young's modulus of the composites. The composite containing a higher con-

centration of TASHFA showed a higher modulus value. The modulus of the composites containing treated alumina particles was increased like the flexural strength. However, it was decreased with increasing alumina particles in the composite containing untreated alumina particles. This phenomenon might be caused by the difference in adhesion between the epoxy matrix and the alumina particles. Improvement of the flexural strength and modulus by the addition of nanofiller into the matrix can be attributable to the fact that the stress transfers from the matrix to the particles.¹⁶ This transfer is good because of the strong adhesion between the matrix and filler. Therefore, the composite mixed with surface treated alumina reveals a higher modulus than the untreated one. Figures 10 and 11 show the fracture toughness of composites as a function of the contents of TASHFA and alumina par-

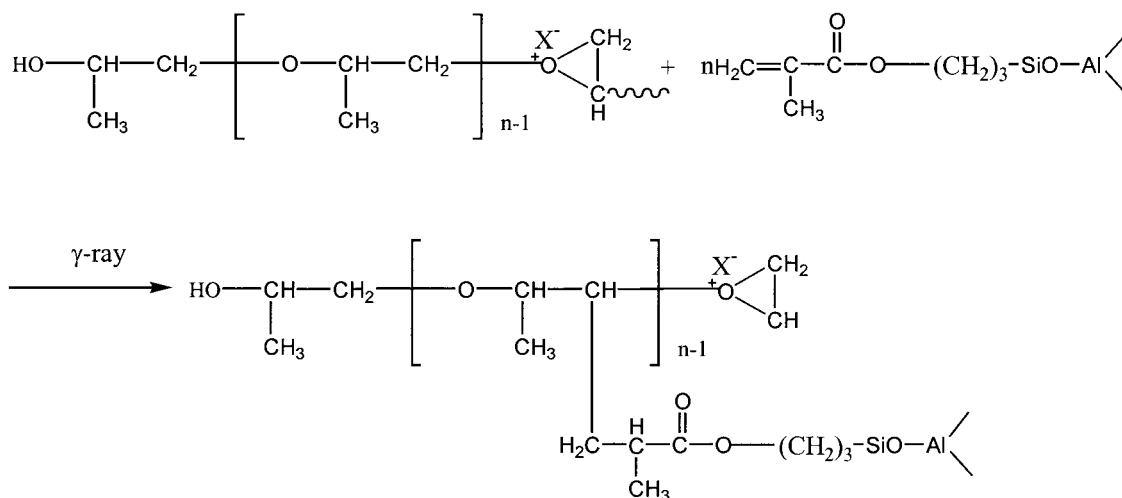


Figure 7 The scheme of the mechanism for the reaction between the epoxy matrix and silane treated alumina particles.

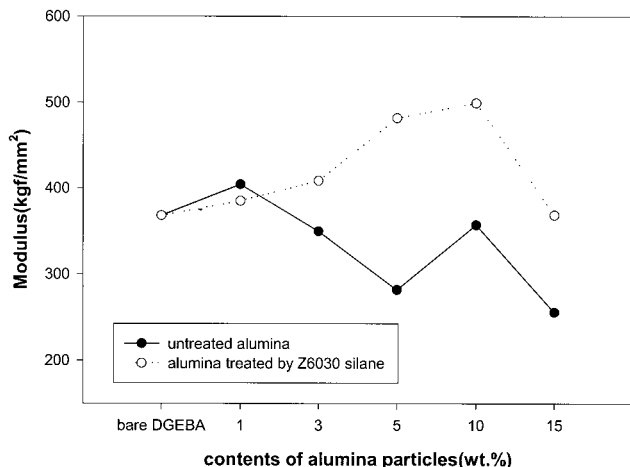


Figure 9 The Young's modulus of the composites as a function of the contents of alumina particles.

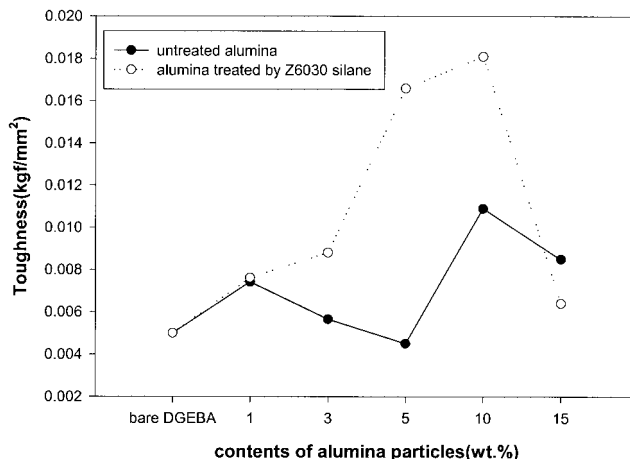


Figure 11 The toughness of the composites containing 3 wt % TASHFA as a function of the contents of alumina particles.

ticles. The toughness had a tendency similar to the flexural strength and modulus.

The toughness of the composites was increased up to 2 wt % TASHFA. However, the toughness of the composite containing over 3 wt % TASHFA was reduced. It may be that the composite was improved in strength rather than toughness because the degree of crosslinking of the composite was extremely high with a large concentration of initiator. Increases in the fractural toughness are due to different crack growth processes. The primary crack might detour around the alumina particles or the crack tips are blunted, which contribute the higher fracture toughness.¹⁶ For that reason, the toughness of the composite improved as the contents of alumina particles were increased. The composite containing surface treated alumina particles showed high toughness. The interfacial adhesion

influenced not only the strength and modulus but also the toughness.

Morphology of flexural surfaces of composites

Figure 12 shows the SEM micrographs of the flexural surfaces of the composite. The images show that the alumina particles are dispersed into the epoxy matrix. However, the particles are not homogenously dispersed into it. Although sonic agitation was performed for uniform dispersion of the particles, the cohesion of the alumina particles and the viscosity of the epoxy resin might hinder the uniform dispersion. In the magnified image of the particle-matrix parts the epoxy resin besieged the particles.

CONCLUSION

Hybridization of epoxy composites by nanosized γ -Al₂O₃ fillers showed improvement of the mechanical properties. Nanosized alumina fillers treated by silane-coupling agents improved the adhesion between the alumina and the epoxy matrix. This strong interfacial bonding contributes the reduction of damage from percussion and improvement in the modulus. Although the dispersion of filler particles was not perfectly homogeneous, incorporation of γ -Al₂O₃ filler results in higher fracture toughness by crack deviation because of the presence of filler particles. The hybrid composites containing over 5 wt % filler showed a low gel fraction because of the inhibition of the propagation reaction due to the chain transfer and the residual hydroxyl group of the alumina particles.

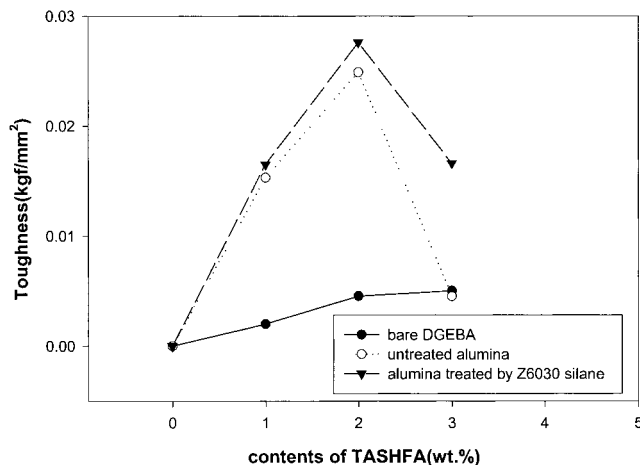
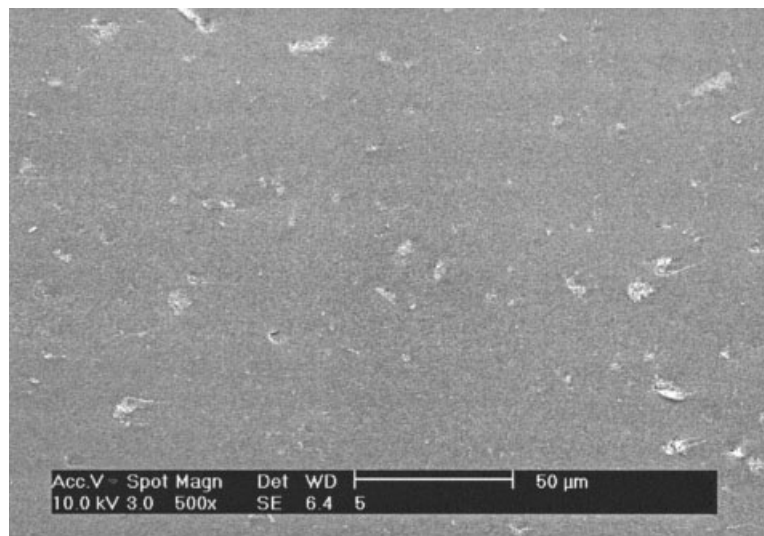
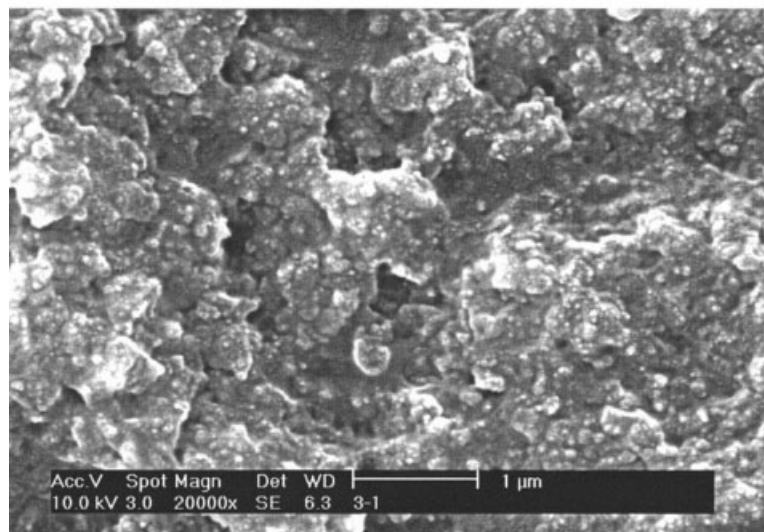


Figure 10 The toughness of the composites containing 5 wt % alumina particles as a function of the contents of the initiator.

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(a)



(b)

Figure 12 SEM images of (a) the fracture surface of the composite and (b) a magnified section of the alumina in the composite.

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