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Radiation curing of γ-Al_2O_3 filled epoxy resin

Phil Hyun Kang, Dong Jin Kim and Young Chang Nho

Radiation Application Research Division, Korea Atomic Energy Research Institute
Daejon 305-600, Korea

Abstract

Epoxy resins are widely utilized as high performance thermosetting resins for many industrial applications but characterized by a relatively low toughness. Recently, the incorporation with rigid inorganic was suggested to improve the mechanical properties of epoxy resins. In the present work, an attempt has been taken to disperse nano-sized γ-Al_2O_3 particles into diglycidyl ether of bisphenol-A (DGEBA) epoxy resins for improvement of the mechanical properties. These hybrid epoxy-alumina composites were prepared using by the γ-ray curing technique that was conducted with 100kGy under nitrogen at room temperature. The composites were characterized by determining gel content, UTM (Instron model 4443), SEM, FT-IR studies.

Keywords: Epoxy resin, nano- sized γ-alumina, γ-ray curing, and flexural properties.

1. Introduction

Epoxy resins are very useful polymer materials because of their good mechanical, thermal, and electrical properties [1-3]. Accordingly, the epoxy resins are widely being used as a matrix 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 due to their highly cross-linked structure, which has led to extensive research efforts to improve their low toughness. In order to improve mechanical properties of epoxy resins, elastomeric materials have been used for last few decades. However, these show the lower flexural strength and Young's modulus. Recently, several works have investigated the improvement on the mechanical properties of epoxy resins by the incorporation of rigid inorganic filler [4-8]. In these particulate filled systems, the interface 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 of epoxy resin, in the present work, an attempt has been taken to disperse nano-sized Al_2O_3 particles into epoxy resin and the particulate epoxy resin was cured by γ-ray radiation using cationic initiator. γ-ray irradiation has a number of advantages such as shorter curing time, low energy consumption, low cure temperature, and dimensional stability, reduced manufacturing cost compared to the conventional thermal curing [13]. Moreover, a silane-coupling agent was used to investigate the particle-matrix adhesion and its effects were studied.

2. Experimental

2.1. Materials

Diglycidyl ether of Bisphenol-A epoxy (DGEBA; YD128, viscosity: 11500~13500cps, density: 1.16~1.18g/cm3, EEW: 184~190g/eq) produced by the Kukdo Chemical Co., Ltd. Korea was used as a matrix. Triarylsulphonium hexafluroantimonate (TASHFA) was purchased from Aldrich Chemical Co. USA used as a cationic initiator. γ-Al_2O_3 (Gamma alumina B; micro polished) with an average particle size of 50nm from BUEHLER Co. USA was selected as an inorganic filler particle. As coupling agents, Dow corning Z-6030 (3-Methacryloxypropyl trimethoxysilane) silane-coupling agent from Dow Corning Co., Ltd. USA was used. Fig. 1 shows the schemes of the DGEBA, TASHFA and Z6030 silane-coupling agent.

2.2. Surface treatment of alumina particles

The ethanol was first adjusted to pH of 4.0~4.5 with acetic acid. 0.1 to 0.5% silane concentrated solutions were produced, by adding the silanes while stirring. Then alumina particles were added into the silane solution. The mixture was stirred for 30 min for the hydrolysis and immigration of silanes with hydroxyl groups of alumina surface. The solution was filtrated and the filter cakes were dried at the oven for 24hour for the condensation process of silanes to siloxanes.

2.3. Fabrication of composites

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

2.4. 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 24hr, and then it was dried in vacuum at 80^oC to a constant weight. The surface treated alumina was confirmed by FT-IR (SENSE IR: Travel Co. USA). The mechanical properties of the manufactured epoxy composites were evaluated by a flexural test. An Instron 4443 universal test machine was used for measuring the flexural strength, Young’s modulus and toughness at room temperature. The epoxy composites were cut into pieces of size 50x25mm, and then the specimens were tested by the 3-point bending method (ASTM D790; span: 25mm, cross speed: 0.8mm/min).

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

3. Results and discussion

3.1. Gel fraction of epoxy-alumina composites

Influence of contents of alumina particles and initiator TASHFA on the gel fraction of the epoxy-alumina composites was shown in Fig.2. It was observed that gel fraction of epoxy composite increased as increase of concentration of TASHFA. It is a natural result because higher concentration of initiator causes the increases of radicals. Therefore, the increases of radicals contribute to the curing reactions of on epoxy resin. Fig.3 shows the scheme of curing reaction of epoxy by cationic initiator [14]. According to Fig. 2, the gel fractions of composites were decreased with an increase of contents of alumina particles. It was shown that an increase in alumina filler suppressed the curing reactions of epoxy resin system. There might be two possible mechanisms, which cause this phenomenon. One is the decrease of propagation reaction speed, and the other is inhibition of the propagation reaction, for example, the chain-transfer reaction. Besides, the chain-transfer reaction of growing cation might also occur by the -OH groups remaining in the alumina particles [15].

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

3.2. FT-IR study on alumina particles.

To examine the extent of bonding between the surface of alumina particles and the silane- coupling agents, Infrared spectra was used. Fig. 4 shows the IR spectra of the Z6030 silane-coupling agents, the alumina particles and the alumina particles treated by Z6030 silanes. As shown in Fig. 4, the peaks of Z6030 silane-coupling agent were observed at the peak of treated alumina particle. These changes of peaks demonstrate that the silane groups react with –OH groups of the surface of alumina particles. The treatment was also confirmed by a floating test on water. The treated alumina particles were not wet by water because the surface of alumina particles was changed from hydrophilic to hydrophobic.

3.3. Mechanical properties

Fig. 5 shows the stress of composites filled with the treated alumina particles as a function of the contents of the initiator and filler. The stress of composite increased with suitable contents of alumina particles. It can be seen that the slope of stress curves is steep as increasing with concentration of initiators, and gentle as increasing with alumina particles. The composite containing more initiator caused the increase in strength, while the composites containing more filler led to the increases in toughness. Fig. 6 shows the influences of silane-coupling agents and alumina particle on the stress-strain characteristics of composites. As expected, the composites containing alumina particles treated by silane coupling agent have higher toughness than those containing the untreated alumina particles or a bare-epoxy resin. It means that the silane-coupling agent make a strong adhesion between alumina and epoxy resin. The scheme of mechanism for reaction between epoxy matrix and silane treated alumina particle was shown in Fig. 7.

Fig. 8 and 9 show the Young’s modulus of the composites. The composite containing the higher concentration of TASHFA showed higher modulus value. The modulus of the composites containing treated alumina particles was increased alike in the flexural strength. However, the composite containing untreated alumina particles decreased with increasing alumina particle. This phenomenon might be caused by the difference in adhesion between epoxy matrix and alumina particles. Improvement of flexural strength and modulus by addition of nano-filler into matrix can be attributable to the facts that the stress transfers from matrix to the particles [16]. This transfer takes place well in strong adhesion between matrix and filler. Therefore, the composite mixed with surface treated alumina reveals the higher modulus than untreated one. Fig. 10 and 11 show the fracture toughness of composites as a function of the contents of TASHFA and the alumina particles. The toughness had a similar tendency with flexural strength and modulus.

The toughness of composites was increased up to 2wt% of TASHFA. However, it was shown that toughness of composite containing above 3wt.% of TASHFA was reduced. It might be described that the composite was improved in strength rather than toughness because the degree of cross-linking of composite was extremely high in large concentration of initiator. Increases in 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 composite improved as increase in contents of alumina particles. The composite containing surface treated alumina particle showed high toughness. The interfacial adhesion influenced not only strength and modulus but also toughness.

3.4. Morphology of the flexural surfaces of composites

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

4. Conclusion

Hybridization of the epoxy composites by nano-sized γ-Al_2O_3 fillers showed the improvement of mechanical properties. The nano-sized alumina fillers treated by silane-coupling agents improved the adhesion between alumina and epoxy matrix. This strong interfacial bonding contributes the reduction of the damages from a percussion and improvement in modulus. Although the dispersion of filler particles were not perfectly homogeneous, incorporation of γ-Al_2O_3 filler results in higher fracture toughness by crack deviating by the presence of filler particles. The hybrid composites containing over 5-weight percentage of filler showed low gel fraction because of the inhibition of propagation reaction due to the chain transfer and the residual hydroxyl group of the alumina particle.

Acknowledgements

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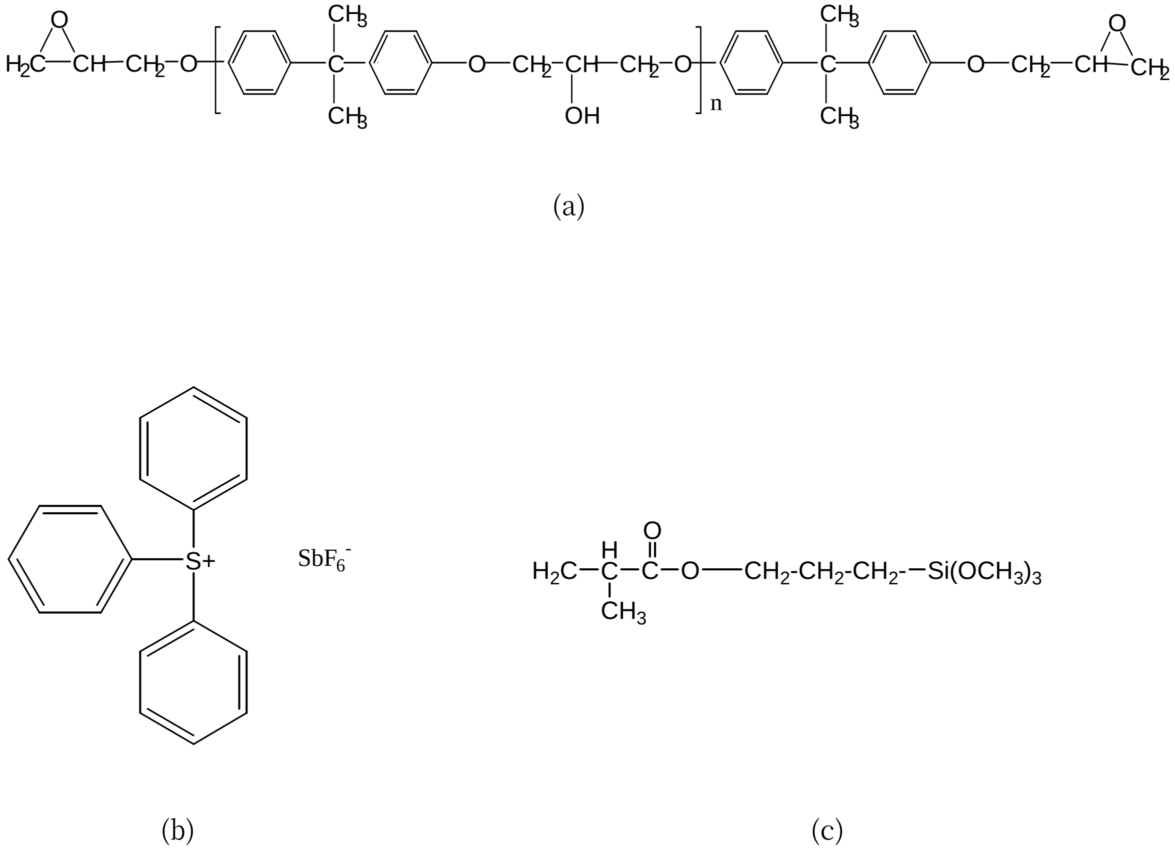


(a)

(b)

(c)

Fig. 1 The scheme of starting materials; (a) DGEBA, (b) TASHFA, (c) Silane-coupling agent.

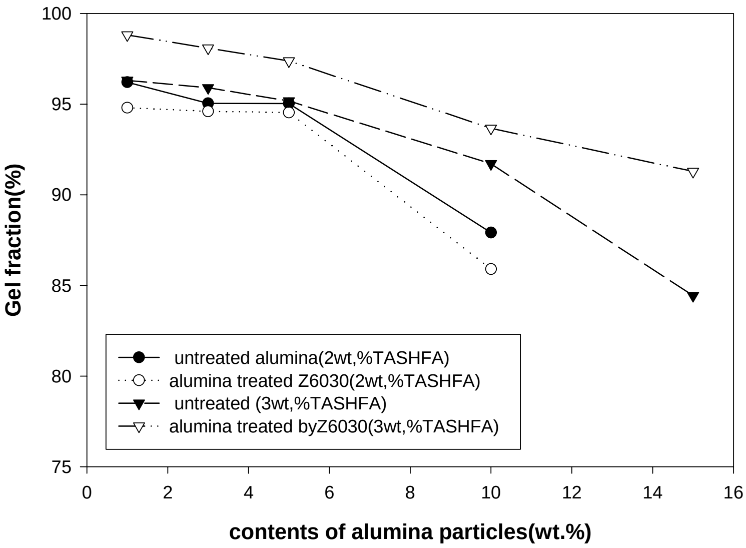


Fig. 2 Gel contents of the hybrid epoxy composites as a function of the contents of alumina particles.

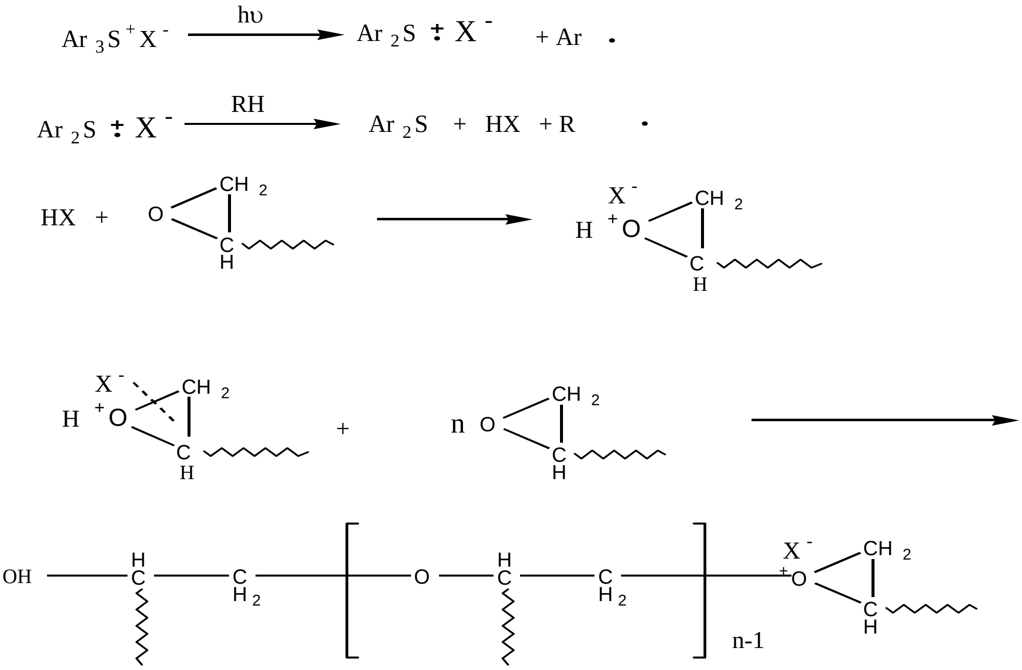


Fig. 3 The scheme of a cationic curing reaction of epoxy by sulfonium salt as an initiator.

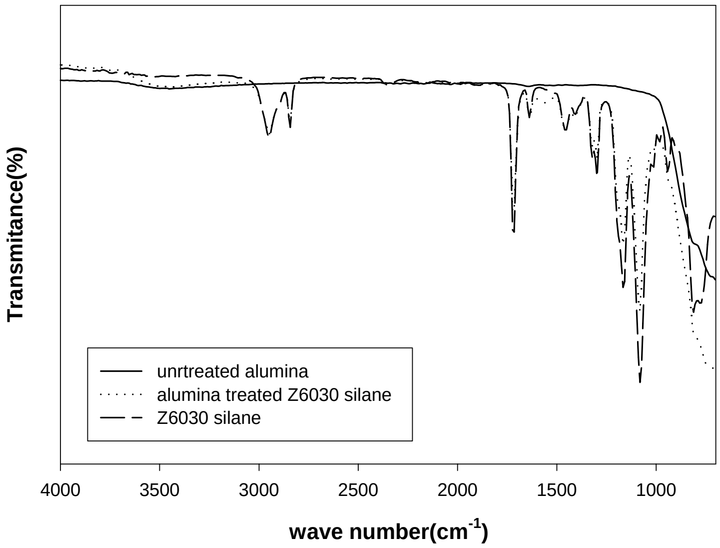


Fig. 4. The IR-spectra of alumina, silane coupling agent and alumina treated by silane.

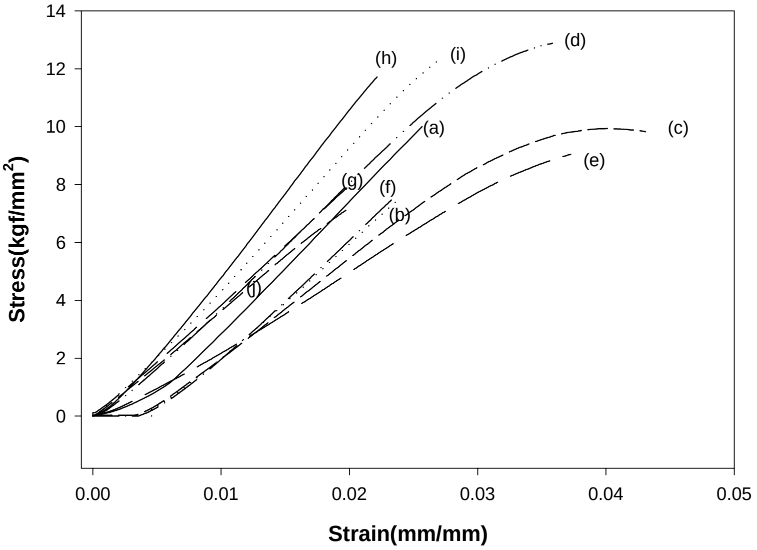


Fig 5. S-S curves of the composites contain; (a) 2wt% TASHFA, (b) 2wt.%TASHFA, 1wt.%alumina, (c) 2wt.%TASHFA, 3wt.%alumina (d) 2wt.%TASHFA, 5wt.%alumina, (e) 2wt.%TASHFA, 10wt.%alumina, (f) 3wt.%TASHFA, 1wt.%alumina, (g) 3wt.%TASHFA, 3wt.%alumina, (h) 3wt.%TASHFA, 5wt.%alumina, (i) 3wt.%TASHFA, 10wt.%alumina, (j) 3wt.%TASHFA, 15wt.%alumina.

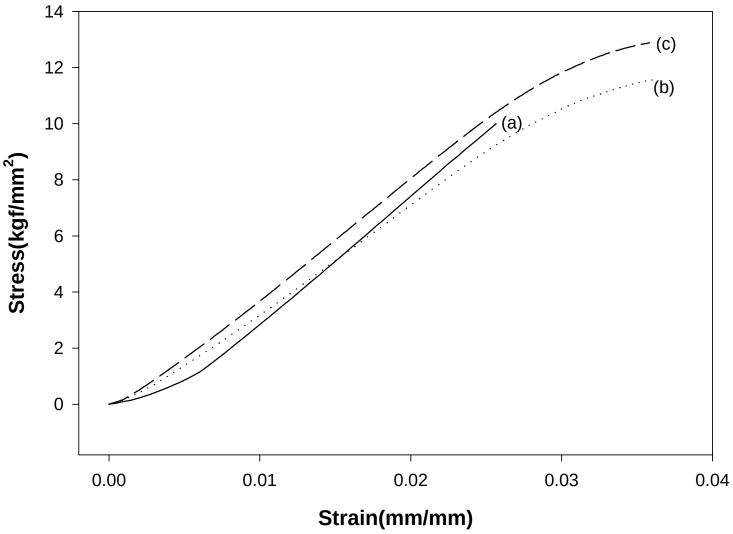


Fig. 6. S-S curves of the composites containing 5wt.% of the alumina particles that were; (a) non alumina particles, (b) non-treated alumina particles, (c) alumina particles treated by Z6030 silane-coupling agent.

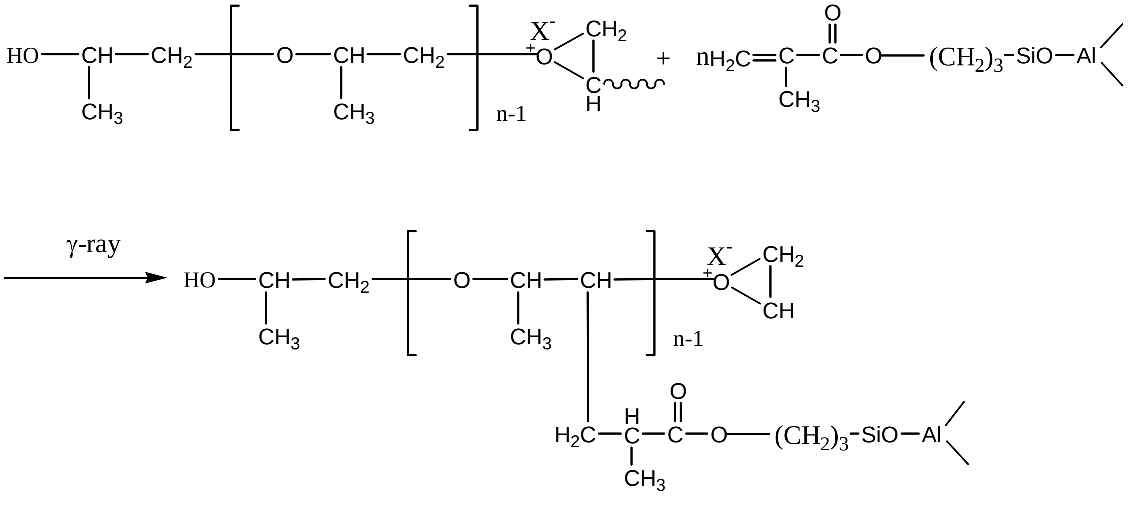


Fig. 7. The scheme of mechanism for reaction between epoxy matrix and silane treated alumina particle.

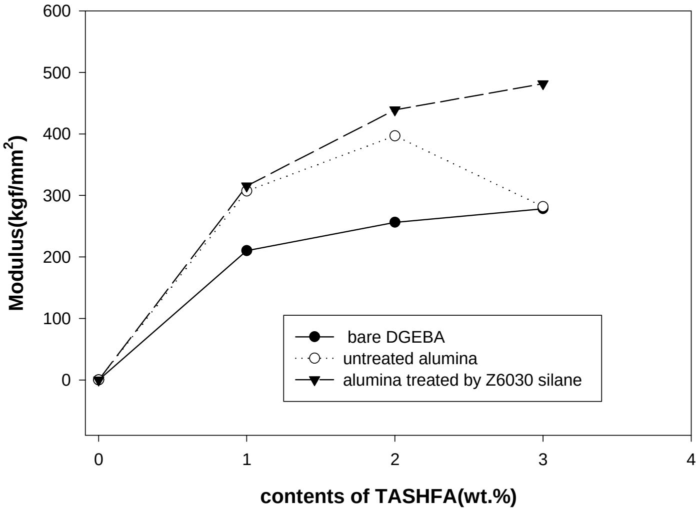


Fig. 8. Young's Modulus of the composites containing 5wt.% of alumina particles as a function of contents of TASHFA.

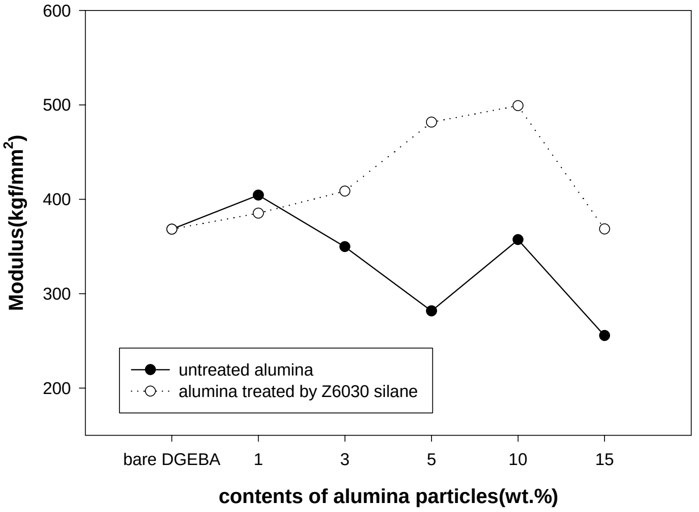


Fig. 9. Young's Modulus of the composites as a function of contents of alumina particles.

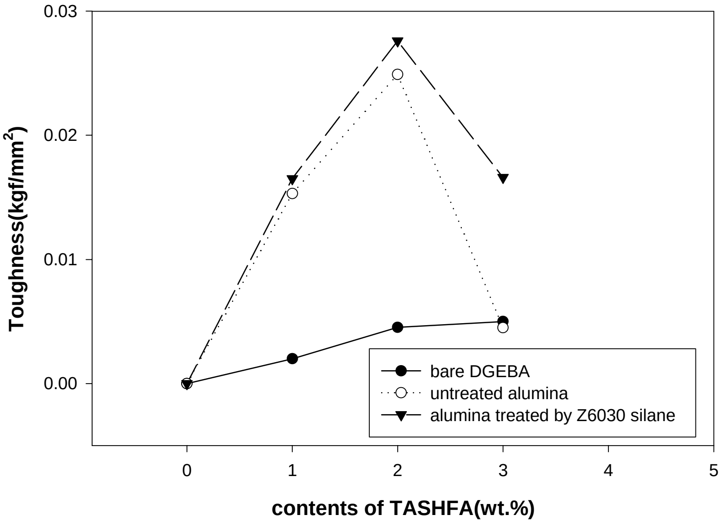


Fig. 10. Toughness of the composites containing 5wt.% alumina particles as a function of the contents of initiator.

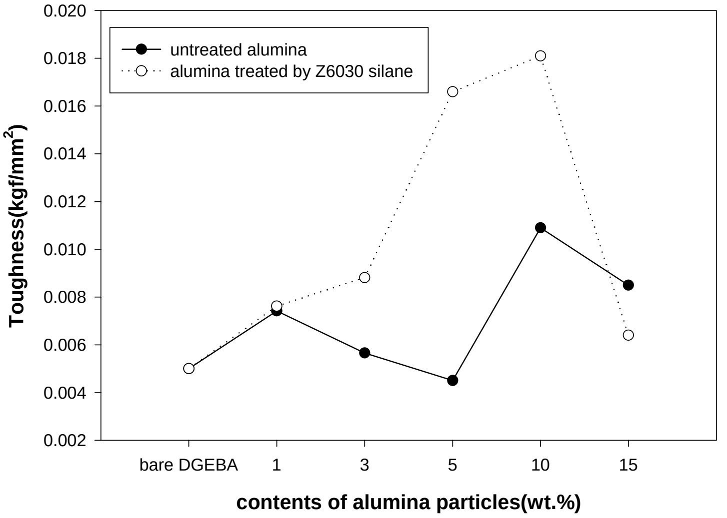
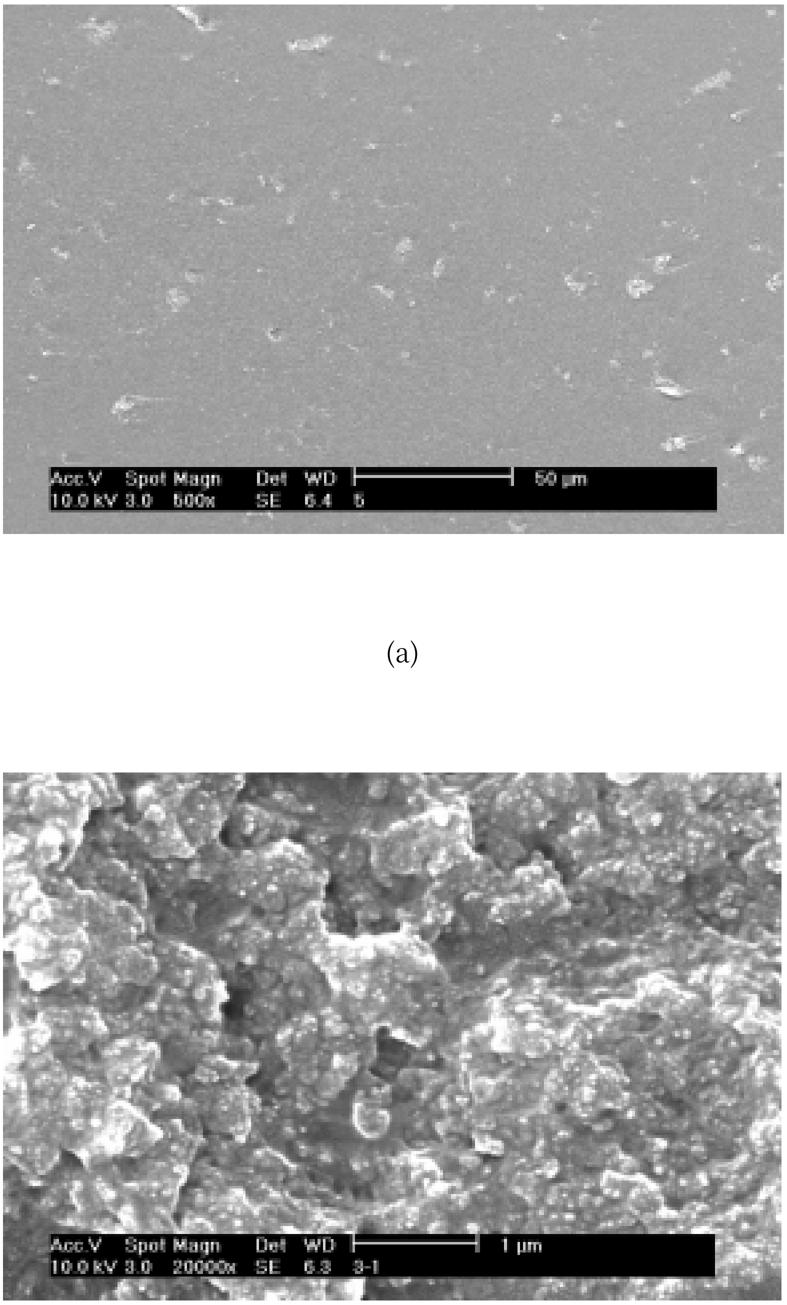


Fig. 11. Toughness of the composites containing 3wt.% of TASHFA as a function of the contents of alumina particles.



(a)

(b)

Fig. 12. SEM images of (a) the fractural surface of the composite and (b) magnified part of alumina in the composite.