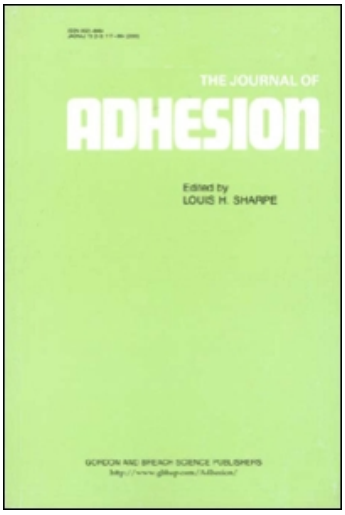

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S. M. Kulkarni[a]; Kishore[a]
[a] Polymer Composites Laboratory, Department of Metallurgy, Indian Institute of Science, Bangalore, India

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EFFECT OF CONTACT AT THE INTERFACE ON THE COMPRESSIVE PROPERTIES OF FLY ASH-EPOXY COMPOSITES

S. M. Kulkarni
Kishore
Polymer Composites Laboratory, Department of Metallurgy,
Indian Institute of Science, Bangalore, India

Particulate composites based on polymer matrices generally contain fillers, especially those that are abundantly available and are cheaper. The inclusion of these, besides improving the properties, makes the system costwise viable. In the present study, fly ash was tried as a filler in epoxy. The filler particle surfaces were modified using three chemical surface treatment techniques in order to elicit the effect of adhesion at the interface on the mechanical properties of these composites. The compatibilizing of the filler with the use of a silane coupling agent yielded the best compression strength values. Scanning Electron Microscopy (SEM) has been used to characterize and supplement the mechanical test data.

Keywords: Epoxy; Filler; Fly ash; Silane coupling and compressive properties

INTRODUCTION

Mechanical properties of particulate composite systems depend on the matrix properties, filler characteristics and polymer/filler interface properties. The nature of the filler or its constituents, and its size,

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Address correspondence to Kishore, Polymer Composites Laboratory, Department of Metallurgy, Indian Institute of Science, Bangalore 560 012, India. E-mail: balkis@metalrg.iisc.in

shape and size distribution greatly influence the properties of composites. It is common to fill polymers with rigid particulate materials such as metal powders [1] and inorganic oxides [2–4] to improve the mechanical, electrical or rheological properties. Abundantly available cheaper materials such as sand [5], chalk dust [6] and wood flour [7, 8] are also used in order to realize a secondary benefit in the form of reduction in the total cost of the system.

Fly ash, a waste product from thermal power plants, possesses very good mechanical properties on account of the constituent phases such as silica and alumina that it contains. Also, fly ash consists of a mixture of solid and hollow spherical (Cenosphere) [9] particles of varying sizes. Typically, fly ash collected at the electrostatic precipitators of thermal power plants displays particles of assorted sizes. These characteristics of fly ash qualify it as one of the good alternatives for use as a filler in polymers, especially in epoxy, and, by virtue of its good mechanical properties and excellent corrosion resistance, it has carved for itself a niche in a variety of engineering applications. Though fly ash was used in earlier studies with different thermoset [10–12] and thermoplastic [13] matrix materials, very little attention was focused on the mechanical properties in general and compressive properties in particular involving the system of epoxy and fly ash.

Also, over the years, scientists and engineers working in the area of newer materials have recognized the importance of interactions at filler/polymer interfaces, especially from the point of view of their influence on the properties of particulate-filled polymers. In this context, the adhesion between the particles and the matrix gains importance as it influences the strength of the system. The size of the interface is generally dependent on the specific surface area of the filler. As regards strength, it is usually modified using the techniques of surface treatments. Surface modification is done in number of ways ranging from simple cleaning or coating to treatments involving bombardment from sources yielding plasma/laser. The preferred method, however, belongs to the chemical surface modification techniques, especially the ones using silane- or non-silane-based coupling agents. Following such treatments, improvement in adhesion of a wide variety of metal powders and inorganic oxides to a number of polymer matrix systems was observed in earlier studies [14, 15]. The present work looks at this aspect of study on the compressive properties of epoxy resin containing fly ash additions having selected surface modifications carried out on them. Features in the interface regions of samples subjected to compression are observed by examining surfaces of failed samples under the Scanning Electron Microscope (SEM).

EXPERIMENTAL

Materials

The matrix system consists of a medium viscosity epoxy resin (LAPOX L-12) and a room temperature curing hardener with a TETA (triethylene tetramine) functional group (K-6) supplied by ATUL India Ltd. The density of cured neat resin was found to be 1.12 g/cc. The filler used, *i.e.*, fly ash, was procured from Neyveli Lignite Corporation Ltd., Neyveli, India. This ASTM class "C" fly ash with bulk density of about 0.9 g/cc was found to consist of a mixture of solid and hollow spheres of different sizes (Figure 1). Particle size analysis using a Malvern laser particle size analyzer shows grossly bimodal distribution (Figure 2) with about 77% of larger-sized particles and 23% of smaller-sized ones. As regards the compositional aspect, energy dispersive spectroscopy of the fly ash sample revealed the main constituents to be silica and alumina of about 63% and 26% by weight, respectively. Other oxides present were Fe_2O_3-(7%) and TiO_2-(2.5%).

Laboratory reagents used for the surface modification were acetone and paraffin liquid supplied by Qualigens fine chemicals, Mumbai, India and Chemix fine chemicals, Bangalore, India, respectively. The silane coupling agent used with the filler was 3-(triethoxysilyl)-pro-

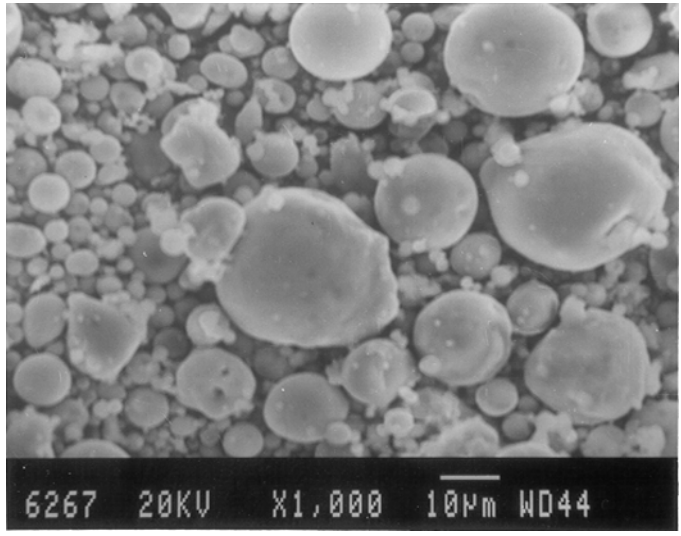

FIGURE 1 Fly ash particles with assorted sizes.

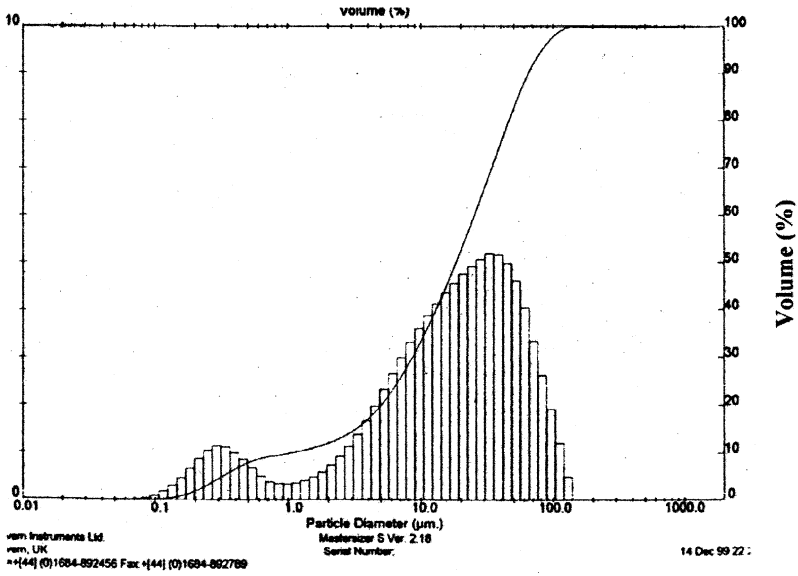

FIGURE 2 Size distribution of fly ash particles.

pylamine supplied by Merck (Art. 821619) (equivalent of 3-amino-propyltriethoxysilane).

Fabrication Procedure

Fly ash (10 vol.%) was mixed into the measured quantity of epoxy resin and hardener with gentle stirring in order to minimize formation of air bubbles. The mixture was then slowly decanted into a mould of size 320 mm × 170 mm × 3 mm (coated beforehand with a uniform film of silicone releasing agent) to fill the entire mould. It was then left to cure at room temperature for about 24–26 hrs. Subsequently, post-curing was done at a temperature of 75°C for $1\frac{1}{2}$–2 h. The cured rigid plate was withdrawn from the mould and the edges trimmed. Samples of these plates were then subjected to a C-scan non-destructive test to map out the regions of uniform material distribution from which the compression test coupons of required size were sectioned.

Three treatments to the surface of the filler with a view to modify its characteristics of adhesion to the epoxy matrix system were attempted in this study. For the first batch, a simple procedure of cleaning the filler surface with acetone to remove any dirt/foreign material was

adopted. These were designated as FAAC. For the second batch, following the cleaning with acetone and drying, the fly ash particles were exposed to a process where, for 35 minutes, condensation of paraffin oil uniformly on to the surface of the filler was attempted. These were designated as FAPC in this work. For the third batch, the ash particles were coated with a silane bearing system. The resulting surface is expected to show greater compatibility with the epoxy matrix material. These were designated FASC in this study.

The procedure followed to coat the filler with silane coupling agent involved the preparation of 10% (of the weight of filler) coupling agent solution in 50 ml dry toluene. The filler, earlier washed with acetone and dried, was added to the solution. The solution was agitated with reflux condensation of toluene for about 5 h at 110°C. Following this the slurry was washed with toluene and was vacuum filtered with a sintered funnel. The filler mass was then dried again in an oven to remove the excess toluene. The coated filler was characterized using FT-IR for the amine functional groups of the coupling agent that are to be involved in the curing process with the amine-based hardener. Cast slabs of epoxy were then prepared with 10% volume of filler incorporating each of the above three surface modifications.

Testing

Compression testing was done in a DARTEC 9500, a servo-hydraulic, computer controlled testing machine. Test coupons of size 12.5 mm × 12.5 mm × 3 mm, conforming to the ASTM-D695 M specification, were used. To reduce the chances of off-axial loading and the resulting slippage of the specimen, the coupons were held in a specially designed fixture. The machine crosshead was programmed to apply the compression load at constant strain rate of $0.01\,s^{-1}$ through the entire duration of the test. From the load-stroke history, the compressive moduli and strength were determined. A minimum of five samples was tested in each category and average strengths and moduli were noted. Inferences regarding the differences in averages were checked with null hypothesis significance (t-test) tests.

Microscopy

Samples subjected to compression and fracture were examined in a JEOL JSM 840A SEM. The samples were wrapped in silver foil and the fracture surface gold coated beforehand under vacuum with an ionizing current of 10 mA in an ion sputtering unit to make them conducting.

RESULTS AND DISCUSSION

Figure 3 depicts the strength and modulus values for epoxy castings filled with fly ash particles whose surfaces were subjected to differing

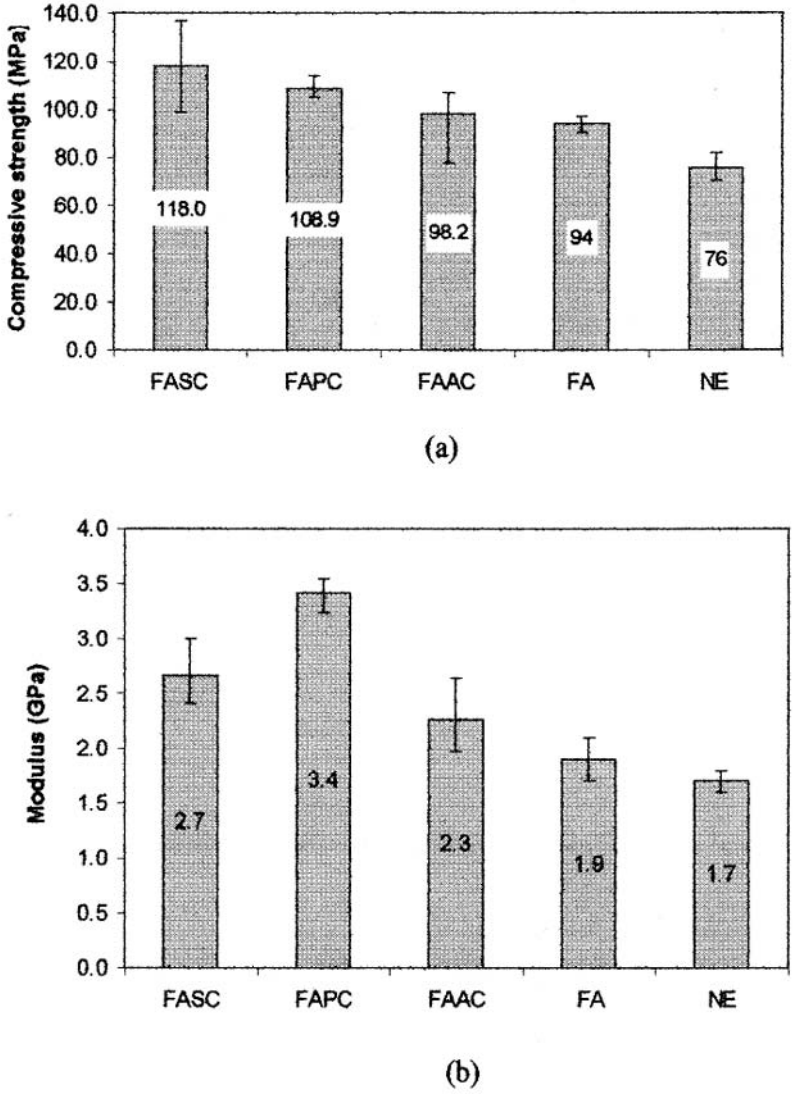

FIGURE 3 The variation in (a) Strength and (b) Moduli for neat epoxy and composites containing untreated and surface treated fly ash particles.

treatments. It can be noticed that strength increases with surface modification from simple cleaning with acetone (FAAC) to coating with a silane-coupling agent (FASC) with values for the case of modification by paraffin liquid (FAPC) falling in between. Also shown is the histogram pertaining to a case where fly ash in the as-received condition was used in making the casting (designated as FA). The strength for the system with fly ash treated by silane coupling agent (FASC) has increased by about 25% as compared with the system having plain fly ash (FA; Figure 3a). When the tests for significance (t-test) of strength values were done, they revealed a change of considerable magnitude between NE, FA and FASC. Between FA and FAAC on the one hand and FAPC and FASC on the other, however, the differences were not significant. It can be noticed in Figure 3b, where the modulus data are plotted for different treatments, that it increased marginally for FA as compared with neat epoxy (NE). Though the FAAC and FASC batches showed an increase in modulus, the highest modulus was recorded for the case of FAPC. In all the cases for modulus, the tests were positive for significant differences.

The presence of stronger and higher modulus filler particles (*vis-à-vis* the epoxy matrix) accounts for the higher strength of FA compared with NE. The moduli of the constituent materials, *viz.*, fly ash and epoxy, used in the work are 70 GPa [13] and 1.7 GPa, respectively. Based on the rule of mixture for particulate composites, at 10% volume fraction of filler the computed modulus is 1.88 GPa, which is very close to the experimentally-obtained value of 1.9 GPa. But the debonds due to dewetting present (Figure 4) around the particles are deemed to be responsible for minimizing the effective load transfer and, thereby, limiting the improvement in the strength. The fly ash consists of a bimodal distribution of particles (Figure 2) where smaller-sized ones, which occupy about 23% by vol. as stated earlier, are wetted uniformly by the matrix material and show better adherence. In the literature, there is reference to the fact that the stress required to form a debond due to dewetting at the interface is given by the expression $\sigma_{\text{dewetting}} = A_r - 2 \ldots\ldots\ldots (\textit{where } r = \textit{particle size})$ [6]. Based on this, larger particles are more susceptible to the formation of debonds around them. On the contrary, for smaller particles the stress required is higher and, hence, they are less prone to debond formation. Thus, from the micrograph, Figure 4, the fact that the adherence around smaller particles (for instance, A and B marked by arrows) is better than those for larger particles can be discerned.

Cleaning the filler with acetone displayed only a marginal, and not significant, increase in strength as compared with the case of plain fly ash (FA). The marginal increase with this type of treatment may be

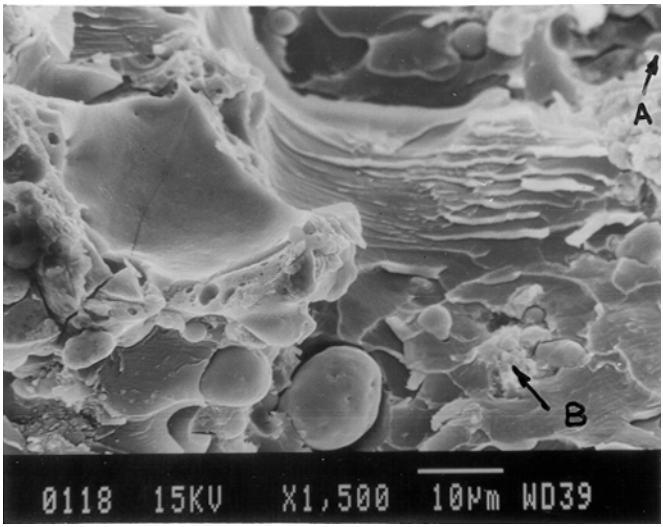

FIGURE 4 SEM picture showing debonds around large fly ash particles.

due to the elimination of extraneous biomaterial on the surface of the particle, thereby improving the surface energetics. But these samples still display debonds prevailing at the interfaces of larger particles (Figure 5). However, around some portions of the particle surface (shown by arrows), some adherence of the matrix to fillers can be seen, pointing to improved adhesion characteristics.

The strength showed a further increase in the case of FAPC (Figure 3a) while for this treatment the modulus recorded was the highest (Figure 3b). The possible cause for the higher modulus can be traced to the paraffin oil acting as a viscous lubricating medium facilitating greater load transfer over the entire (true) surface area. In other words, these surfaces with a film of oil assist in sustaining a higher load. In Figure 6, a large number of shear failure features [16], indicative of larger energy absorption, can be observed. This can be attributed to the plasticizing of the matrix in the vicinity of the filler/matrix interface. This could result in blunting of cracks, which generally originate at such interfaces. The fact that cracks do not propagate rapidly gives credence to the decrease in energy dissipated and, hence, higher absorbed energy. Plastic flow-like features, especially around the particles, can be observed in Figure 7.

But, in case of the filler coated with silane coupling agent, the larger improvement in strength can be traced to the good adhesion at the

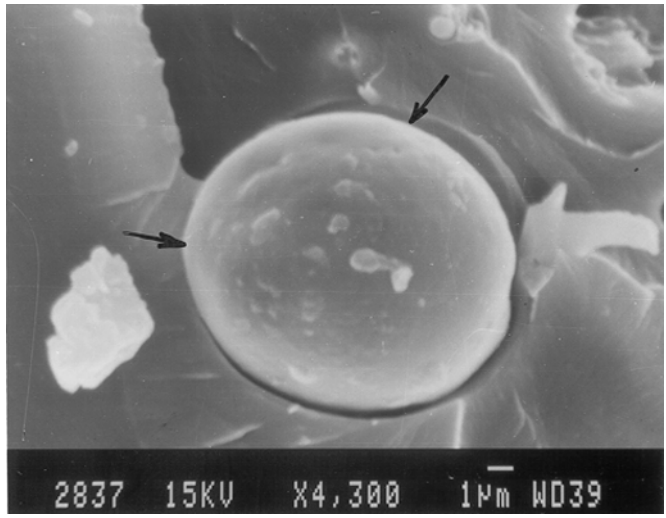

FIGURE 5 SEM micrograph showing partial adhesion of matrix to fly ash particle in case of FAAC.

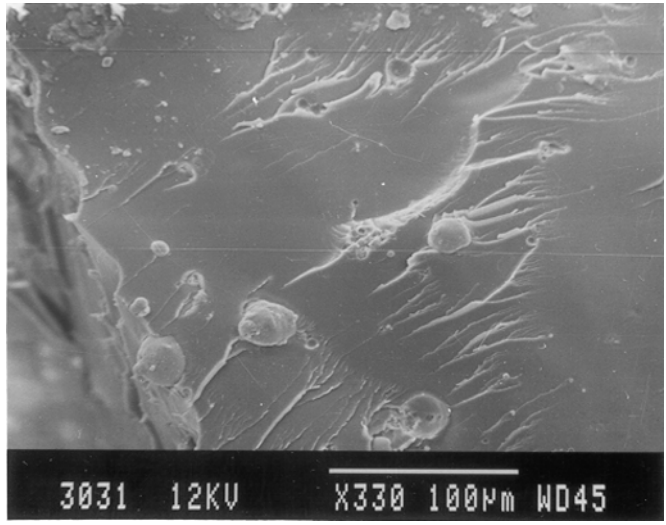

FIGURE 6 SEM micrograph showing marks of shear deformation bands (FAPC).

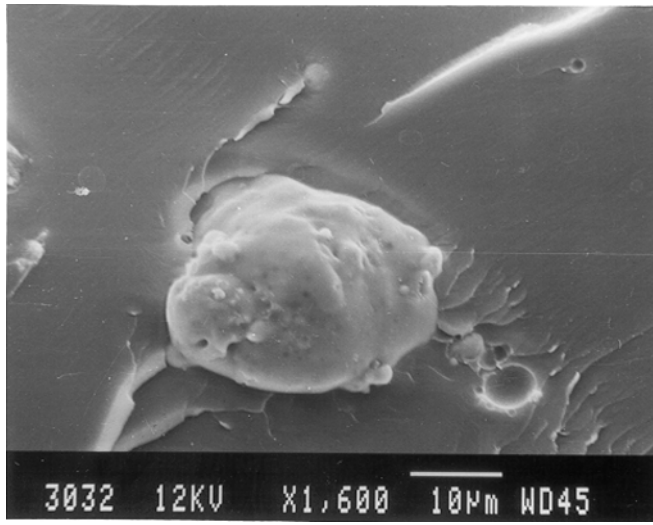

FIGURE 7 SEM picture showing a particle with plastic flow-like occurrence around it (FAPC).

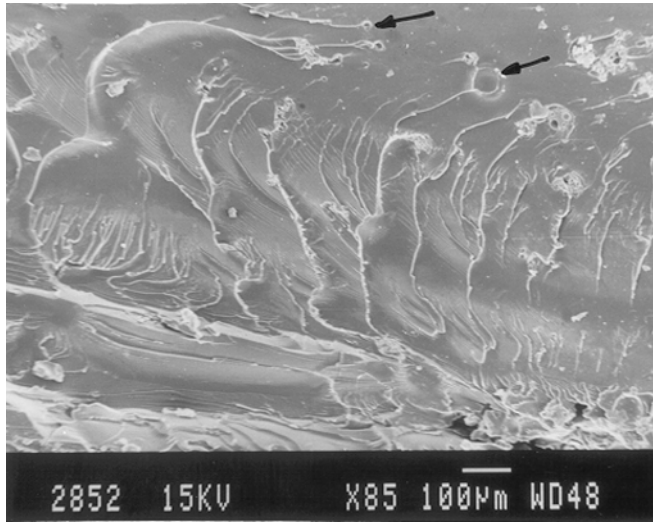

FIGURE 8 SEM micrograph showing extensive curvilinear shear bands (FASC).

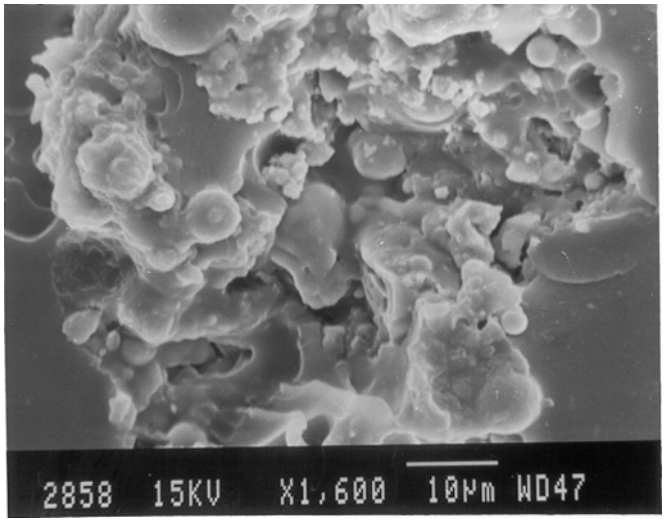

FIGURE 9 SEM fractograph showing better adherence of particles to matrix in the vicinity of a cluster (FASC).

interfaces brought about by this surface treatment. Consequently, a large number of shear deformation bands that are highly curvilinear in nature can be seen in this failed FASC sample (Figure 8). It can also be noted in the same figure that very few particles (shown by arrows) are seen on the fractured surface, which lends credence to the important role played by this surface treatment in deflecting the fracture path around the particles. This situation arises due to good adhesion by way of compatibilizing of the filler surface to bind with the organic matrix through the silane bond. This fact can be inferred from the SEM micrograph (Figure 9), where particles are seen to be wetted properly despite the tendency to exhibit agglomeration which, in the untreated case, can yield place to insufficient penetration of the interparticle space by the resin and its subsequent inadequate spreading and the attendant changes in strength.

CONCLUSIONS

The effect of three different modifications of the filler surfaces on the properties of a fly ash filled epoxy resin was studied. The increased adhesion of the filler surface by coating with a silane coupling agent was found to yield the highest strength. The case with filler cleaned using acetone showed a marginal increase over that involving epoxy

and as-received fly ash. The composite with filler coated using paraffin oil displayed the highest modulus coupled with slight improvement in strength. This situation may have been due to the viscous interface spreading along the entire true surface area of the particles making the contact a much-improved one.

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