Effect of surface treatment on the impact behaviour of fly-ash filled polymer composites

Kishore,* SM Kulkarni, D Sunil and S Sharathchandra
Polymer Composites Laboratory, Department of Metallurgy, Indian Institute of Science, Bangalore 560012, India

Abstract: The impact behaviour of epoxy specimens containing 10% by volume of fly-ash particles with their surface treated for improving or decreasing adhesion is studied. The resulting behavioural patterns are listed and compared to those of composites containing untreated fly-ash particles and unreinforced (ie neat) epoxy. It was noticed that samples involving adhesion-increasing (ie acetone and silane) treatments show greater absorption of energy and maximum load compared to untreated samples and those subjected to adhesion-reducing treatments. Ductility index, however, showed a reversed trend with adhesion-reducing treatment yielding the highest value. In contrast, the energy absorbed was highest for neat resin and lowest for oil surface bearing ash particulate composites. Scanning electron microscope examination of the failed samples was carried out to obtain information on the fracture features with the aim of correlating microstructure to impact response. Thus, the higher ductility indices cases are shown to be distinct and different from composites containing other surface treatments for fillers.
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Keywords: epoxy; fly ash; filler; impact; ductility index

INTRODUCTION

Among newer materials, particulate filled polymer composites are gaining growing acceptance from industry owing to their meeting specific properties for innumerable combinations of systems. Thus the use of such particulate filled composites has spread to the automotive, chemical and furniture manufacturing industries. Low cost and attractive properties such as light weight, high strength, corrosion resistance, elevated temperature applicability and ability to be tailored to specific engineering applications are responsible for the dramatic surge in the use of filled composite products. The order of the day is to look for more attractive low cost fillers and, where possible, meet recycling requirements. To this end, fly ash that finds many applications in civil engineering[1,2] is used as filler in composites.[3,4] Composites involving low cost fillers of fly ash,[5–8] considered to be an industrial waste product and pollutant, are among the newer entrants to the family of particulate filled polymer composites. The use of fly ash as a reinforcement in polymer matrices gets strong support from a discipline such as civil engineering. In this area, the utility of an abrasion, wear and tear resistant material to be mixed with other ingredients such as sand and cement is attractive. Whether such a realization is also possible for less demanding applications was the motivating factor leading to the present work.

In all particulate filled systems, the adhesion between the matrix and the filler.[9] plays a significant role in determining key properties such as strength and toughness. The size of the interface is generally dependent on the specific surface area of the filler. Modification of surface properties of the fillers can yield significant changes in strength. This can be done in a wide variety of ways such as cleaning the particles, or coating them with special materials. In this paper we show how the chemical treatment of the surface of filler particle will influence a dynamic property such as impact fly-ash filled epoxy based systems. Silane- and nonsilane-based[10,11] chemicals have been used as surface modifiers in the present study.

EXPERIMENTAL

Materials

The matrix system consists of a medium viscosity diglycidyl ether of bisphenol A (DGEBA) epoxy resin (LAPOX L-12) and a room temperature curing hardener containing a tetra-amine functional group (K-6) supplied by ATUL India Ltd (Gujarat, India). The density of cured neat resin was found to be $1120 \, \text{kg m}^{-3}$. The filler used, ie fly ash, was obtained from Neyveli Lignite Corp Ltd, Neyveli, India. This ASTM class 'C' fly ash with bulk density of about $900 \, \text{kg m}^{-3}$ was found to consist of a mixture of a solid and hollow spheres of assorted sizes (Fig 1). Particle size distribution of this fly ash as determined by the Malvern (Southborough, MA, USA) laser light particle size analyser (Fig 2) consists of two distinct

* Correspondence to: Kishore, Polymer Composites Laboratory, Department of Metallurgy, Indian Institute of Science, Bangalore 560012, India
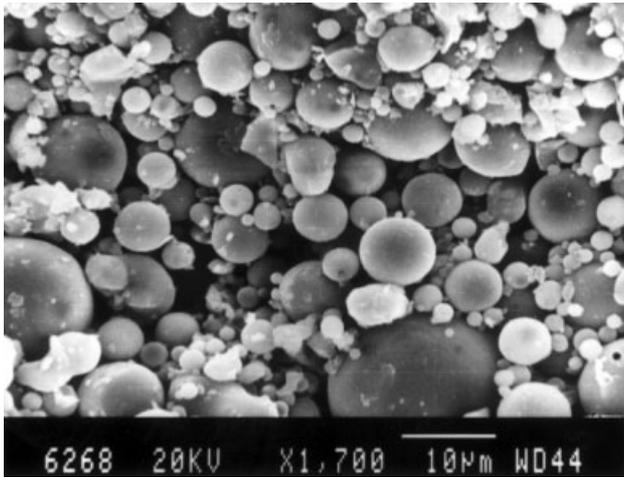
Figure 1. Scanning electron micrograph showing particles of fly ash.

clusters, emphasizing a gross bimodal nature.[12] Energy dispersive spectroscopy of the fly-ash sample revealed the main constituents to be silica and alumina of about 63% and 26%, respectively, while traces of other oxides (chiefly 7% Fe_2O_3 and 2.5% TiO_2) were also noticed. 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. Silane coupling agent used on the filler was 3-(triethoxysilyl)-propylamine supplied by Merck (Mumbai, India) (art 821619) (equivalent of 3-aminopropyltriethoxysilane).

Processing

Three treatments were attempted on the surface of the filler with the aim of modifying its characteristics of adhesion to the epoxy matrix system. For the first batch, a simple procedure of cleaning the filler surface with acetone to remove any dirt/foreign objects was adopted: this was designated FAAC. For the second batch, following acetone cleaning and drying, the fly-ash particles were coated with a silane-bearing system: this was designated FASC. Thus, both FAAC and FASC were designed to enhance the adhesion at the interface. For the third batch, the fly ash particles, after acetone cleaning and drying, were exposed to a process where for 35 min paraffin oil was condensed uniformly onto the surface of the filler: this was abbreviated as FAPC in this work.

The procedure followed to coat the filler with the silane coupling agent involved the preparation of 10% (of the weight of filler) coupling agent solution in 50 ml dry toluene. The filler, previously 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 FTIR spectroscopy for the amine functional groups (Fig 3) of the coupling agent involved in the curing process employing an amine-based hardener.

To prepare the composites, a measured quantity of epoxy resin was mixed with a preweighed amount of fly ash (10% by volume in all cases) and the hardener, in the ratio of 100:10 by volume of resin as recommended by the supplier, was added to this mixture with gentle stirring to minimize the formation of air bubbles. The mould into which the resin was slowly poured was of dimensions 320 mm × 170 mm × 3 mm, and was completely covered on all sides with Teflon sheeting with a coating of silicone-releasing agent for easy removal of the cast specimen after curing. The mixture was left to cure at room temperature for about 24–26 h. Subsequently, post-curing was done at a temperature of 75 °C for about 1 1/2 h. The cured rigid plate sample was withdrawn from the mould and its
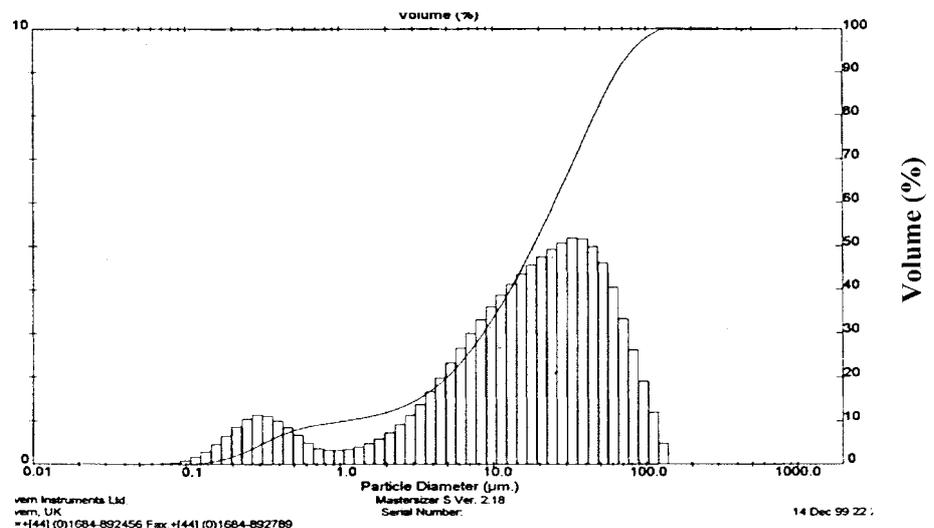

Figure 2. Particle size distribution of fly ash.
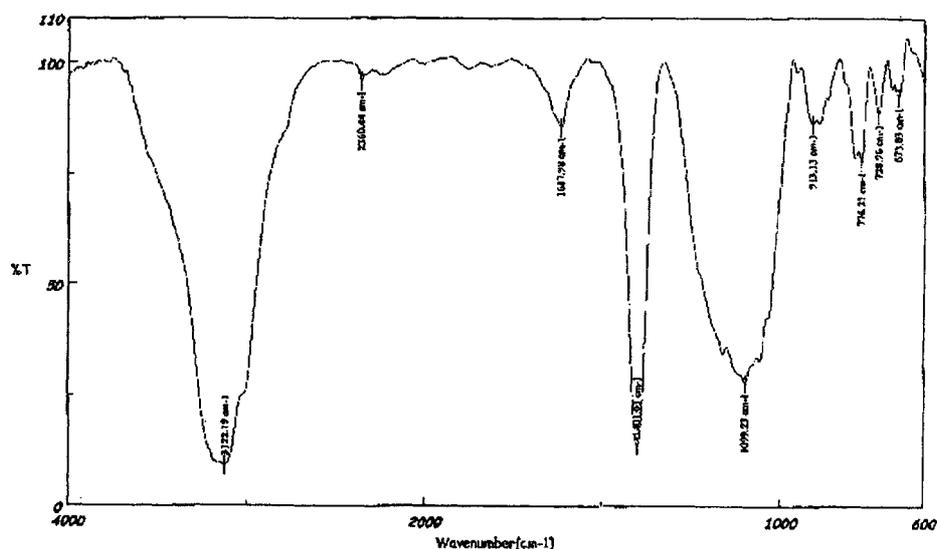
Particle Diameter (μm)

Figure 3. FTIR spectrum of silane-treated fly-ash filler.

edges were trimmed. In this way epoxy based systems were cast having fillers bearing various surface treatments, and also systems without reinforcement. Data are listed in Table 1.

Impact testing

The unnotched impact test samples of dimensions $50\,mm \times 10\,mm \times 3\,mm$ were cut from trimmed cast specimens using a diamond-tipped cutting machine to produce a smooth surface finish. The impact tests were carried out on slices having the geometry specified above which did not conform to ASTM specifications, to provide relative comparisons of performance. They were conducted using a Tinius Olsen (Willow Grove, PA, USA) pendulum type model 84 universal impact tester on test samples which resembled the Charpy type placement. Impacts were done on one face of the thickness with the width face resting on the flat end supports provided in the test set-up. The pendulum of mass $27\,kg$, when positioned at an angle of 15 degrees and released, could provide a maximum energy of 8.2 joules at a maximum velocity of $0.8\,m\,s^{-1}$. The test results provided by the system were in the form of plots of load and energy *versus* time. In each category, a minimum of four samples were tested and the average value was used for analysis. In this work, as stated earlier, because comparative evaluation is involved, the data obtained are often normalized/compared with respect to those derived on an untreated fly ash (FA10) system. Also included are the data on unreinforced (ie neat) epoxy resin.

Fractured surface features

The fractured specimens were scanned using an optical scanner and magnified on a computer screen for further analysis. The scanned image edges were obtained from Adobe (San Jose, CA, USA) photo deluxe software and later imported to AutoCAD (San Rafael, CA, USA) 14 for further investigations. From such macro features of the failed samples, the total curvilinear crack length and crack shift p are tabulated in Table 1.

Microscopic characterization

Samples subjected to impact were examined with a JEOL (Tokyo, Japan) JSM 840A scanning electron microscope. The samples were gold coated in an ion sputtering unit beforehand to make them conducting. Although the fractography features of various stages of crack development (from initiation to propagation and then its emergence on the other side of the test slice following impact) are studied, in this work particular importance is given to the propagation phase of the crack and hence this is discussed in a later section.

RESULTS AND DISCUSSION

Figures 4 and 5 show, respectively, the variation in energy absorbed per unit area and maximum load *versus* composition. Although the scatter bands seem to overlap, the significance tests (t-tests) on the data showed an increase in the total energy absorbed and the maximum load borne by the specimen for the acetone cleaned, FAAC fly-ash case and the silane-treated FASC filler case compared to that obtained on

Parameter	NE	FASC	FAAC	FA10	FAPC
Fly ash vol (%)	Nil	10	10	10	10
Total curvilinear crack length (mm)	17.2	11.9	16.5	14.4	10.7
Shift of crack p[a] (mm)	10.9	3.9	10.3	6.3	1.9

Table 1. Total crack length and the shift of crack for different samples

[a] Defined schematically in Fig 8.
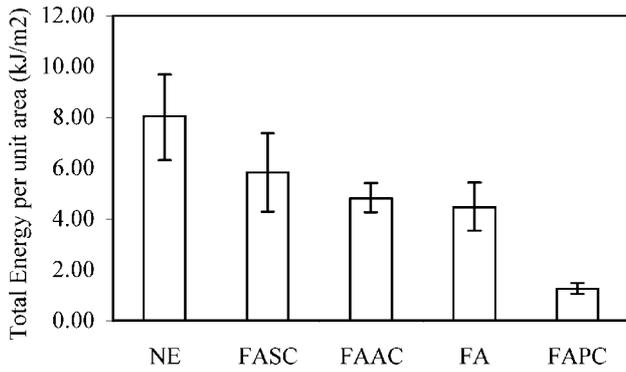
Figure 4. Variation in total energy absorbed per unit area for different samples.

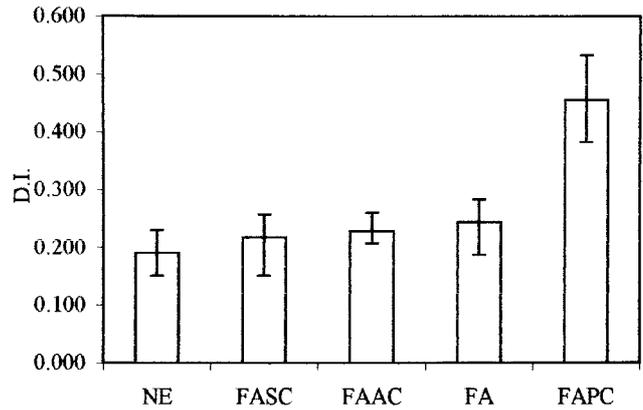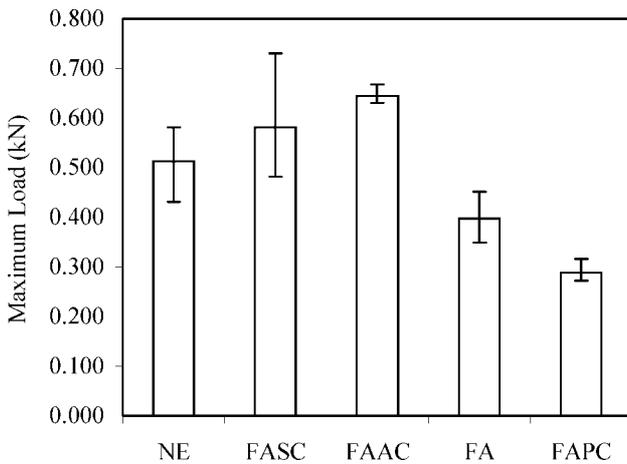**Figure 5.** Maximum load recorded during impact for all samples.

untreated FA10 fly-ash samples. Much less energy is absorbed by the paraffin treated specimen, however, than by the FA10 specimen. The time to maximum load shows a similar trend (Fig 6).

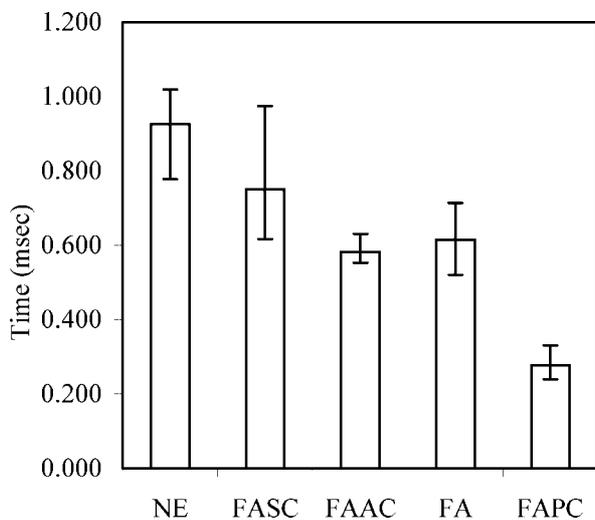The ductility index (DI)[13,14] results in Fig 7 show an increase for the paraffin treatment while a general

Figure 6. Time required to record the maximum load for different compositions.

Figure 7. Ductility indices for epoxy resin without and with fly ash in the as-received and treated samples.

decrease is observed in the *t*-tests for the silane-treated and the acetone-cleaned samples, compared to the untreated filler case. The DI is given by the expression

$$\mathrm{DI} = E_\mathrm{p}/E_\mathrm{i}$$

where E_p and E_i represent the energies for propagation and initiation, and correspond to energies absorbed after and before the maximum load (in the load/energy *versus* deflection data given by the instrumented impact set-up), respectively.

Figure 8 shows schematically the crack path from initiation on face 2 to its final emergence at face 1 (the impact side) of the test slice. The actual situations prevailing in various test samples are presented in Fig 9 from which it may be seen that a curvilinear tendency for crack progression is seen for adhesion-improving treatments, while this path straightens up considerably for paraffin-coated ones, thus revealing the differences in response among the various samples. Thus the total crack length (Table 1) is greatest for the acetone-treated case and is smallest for paraffin-oil-treated specimens. With the help of the macrofeatures presented in Fig 9 the crack shift *p*, illustrated schematically in Fig 8, is calculated. The results in Table 1 show the smallest value for the paraffin-treated case, while samples which had received treatments favouring adhesion (ie FAAC and FASC) show higher values than that for FAPC. An explanation of why these shift of crack and curvilinear paths
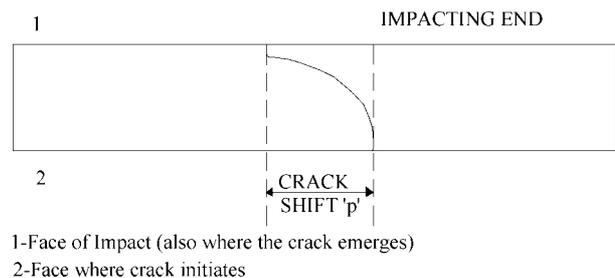

1-Face of Impact (also where the crack emerges)
2-Face where crack initiates

Figure 8. Diagram of the face receiving the impact and the total shift noticed between crack initiation and crack-emergence for the sample.
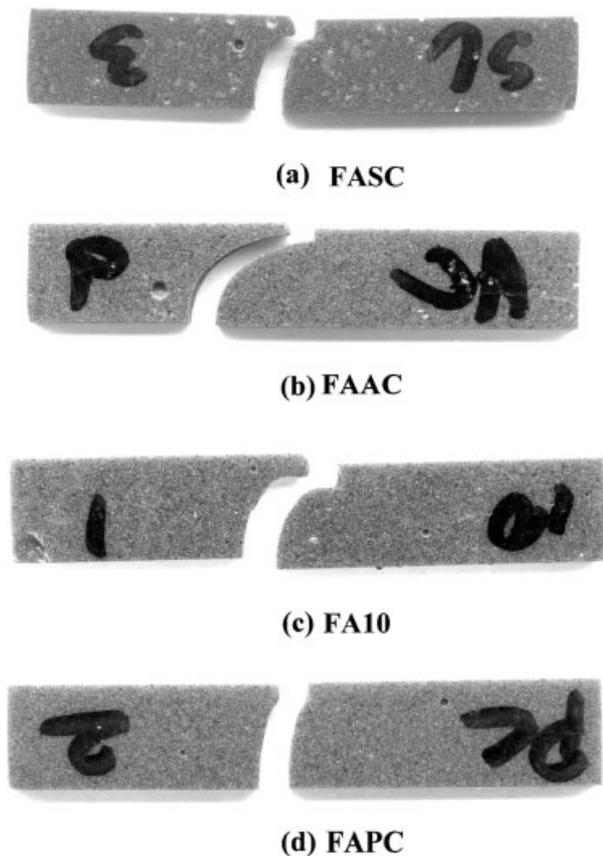
(a) FASC

(b) FAAC

(c) FA10

(d) FAPC

Figure 9. Macroscopic view of crack progression in the untreated (c), adhesion-improving (a,b) and adhesion-decreasing (d) surface-treated fly-ash bearing composites.

decrease with treatment involving decreasing adhesion of the filler to the matrix, together with the fact that FAPC shows the highest DI recourse to fractography, is given below.

The features for FA10 shown in Fig 10 suggest that the crack emanates from the lower left of the micrograph in which the matrix features are clearly seen. The corresponding situation in FAAC is shown
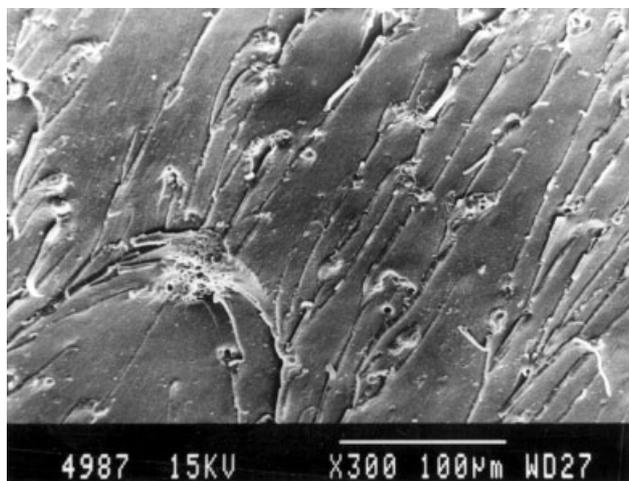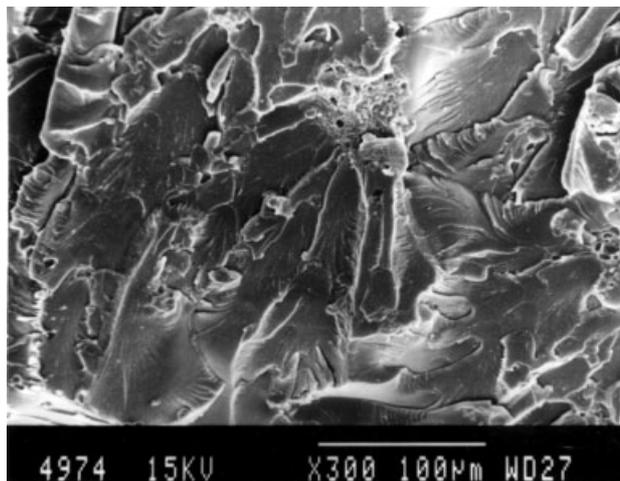

Figure 11. FAAC sample showing recognizable patterns of cleavage.

in Fig 11. Compared to FA10 (ie Fig 10) the FAAC (ie Fig 11) shows fewer straight running impressions on the resin matrix and an increased presence of cleavage features. Thus, the distinguishing features of treated (FAAC) over untreated (FA10) fly-ash epoxy systems are revealed in this work. As regards FASC (Fig 12), it shows cleavage features that are better depicted than those seen for FAAC (Fig 11). Thus, the work unambiguously demonstrates that as adhesion factor improves due to surface treatment, the cleavage patterns appear in a better and recognizable way in fly-ash-filled epoxy systems. Coming to the last category, FAPC shows a feature where the lines emanating on either side of the particles tend to follow a downward path with some traversing the two wings and appearing to join together (Fig 13; for instance at the point marked X).

Thus, those treatments that improve adhesion between matrix and filler (ie FAAC and FASC compared to FA10) lead to brittle cleavage features and particles well embedded in the matrix which resists deformation, and outward radial-like lines
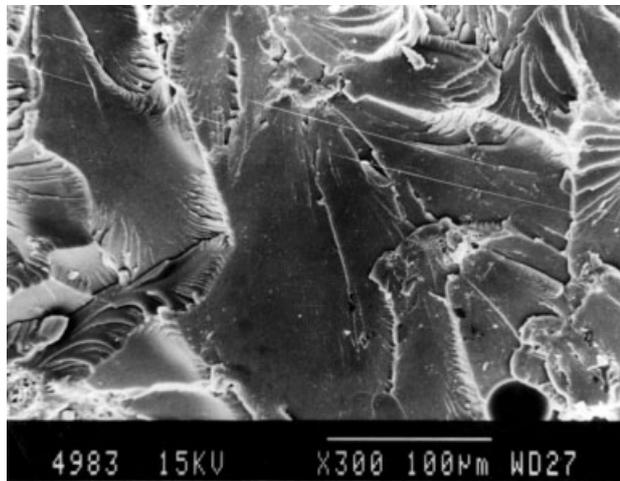

Figure 10. FA10 sample showing matrix features and flow patterns following impact.

Figure 12. FASC sample showing clear and distinguishable cleavage facets with river patterns.
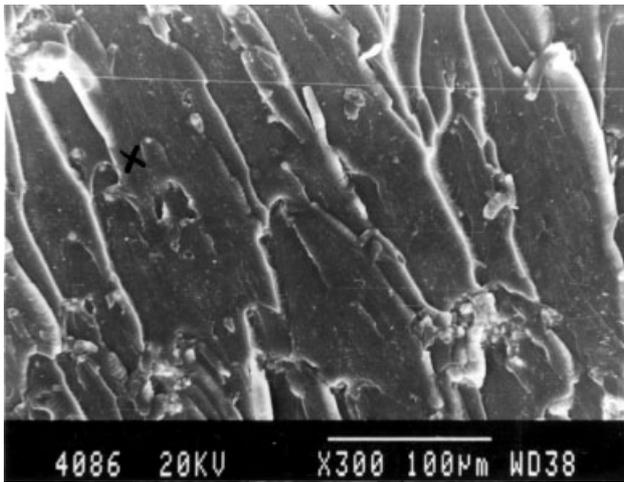
Figure 13. FAPC sample displaying features such as matrix flow, and two arms around a particle drooping down with a tendency to join later.
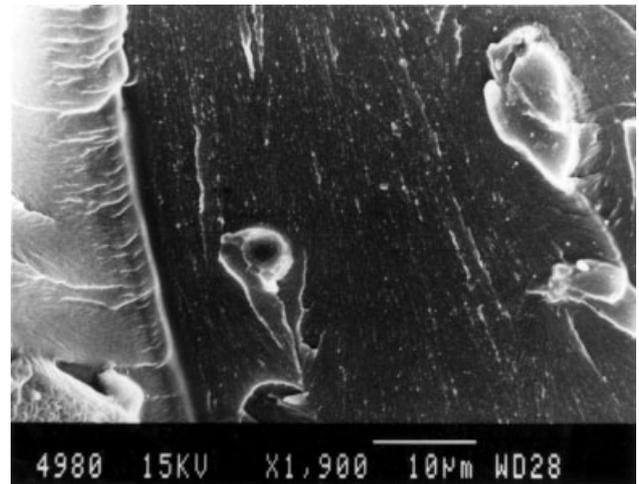

Figure 15. Arms branching out around the centrally positioned FAPC particle and joining later on can be seen.

indicating the origin of crack initiation during impact. The higher adhesion ensures greater strength, longer time to peak, etc, while the faster fracture (ie cleavage features) in such samples (FAAC and FASC) results in a lower E_p and hence lower DI. FAPC, however, shows both matrix deformation and particles that are displaced from the matrix. Therefore, FAPC shows lower load, and the plastic nature of matrix deformation increases E_p, thereby increasing DI. Thus, fractography can aid the analysis and interpretation of mechanical data.

Concentrating on the region around the ash particles, FASC shows the least debonding (ie the best adhesion) of all treatments, as is evident from Fig 14. The fact that the ash particle (being hollow) shows two noticeable punctures following impact can be clearly seen in this fractograph. Also, some kind of void-like features can be seen immediately surrounding the interfacial region, a phenomenon not recorded for any other set discussed earlier. However, FAPC
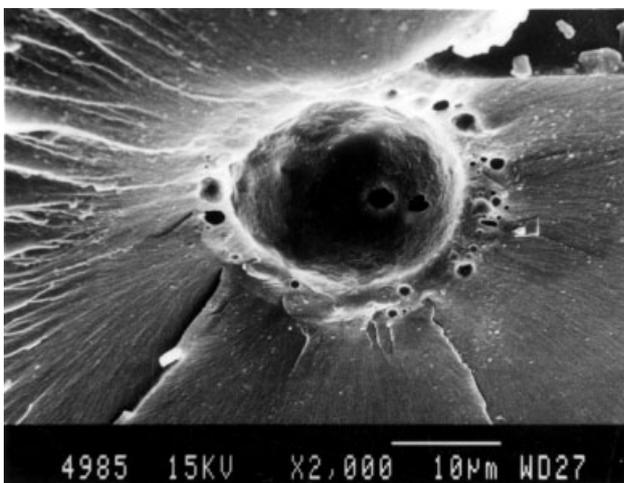

Figure 14. Fractograph showing termination of a large crack at the top right corner in the matrix present in the vicinity of a particle. The unique interfacial feature constituted by the particle and the matrix and the punctured face of the particle in the FASC sample can also be seen.

shows (Fig 15) the two flow wings (as discussed earlier) of the deformation bands around the central ash particle joining in towards the centre bottom of the micrograph where the ash particle is displaced due to the impact and leaves a crater. Figure 15 also reveals matrix flow lines running from the top to the bottom on the left of the micrograph. Thus, features in adhesion-improved conditions are different both within the matrix and at the regions where ash particles encounter the epoxy material compared to those for FAPC sample where the oil film favours less bonding between the two constituent materials comprising this composite system. Together, these differing features within the matrix and at the filler/matrix interface contribute to the varying response of the system.

CONCLUSIONS

Treatment of particulate fillers to improve their adhesion characteristics to the matrix improves the overall properties of the system, especially strength and load bearing capacities. Among the various treatments, the silane treatment was found to be quite effective. Acetone-cleaned fly-ash particulate also yielded comparable results. Treatment with paraffin oil reduced the adhesion and thus also the energy and load-bearing capacities during impact. Microscopic examination showed cleavage patterns in FA10, FAAC and FASC (improving in that order). Deformation of matrix features and some dislodged ash particles resulting from impact are seen in FAPC, which displays the highest ductility index.

ACKNOWLEDGEMENTS

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