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Effects of surface treatments and size of fly ash particles on the compressive properties of epoxy based particulate composites

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Particulate reinforcements for polymers are selected with dual objective of improving composite properties and save on the total cost of the system. In the present study fly ash, an industrial waste with good properties is used as filler in epoxy and the compressive properties of such composites are studied. Particle surfaces are treated chemically using a silane-coupling agent to improve the compatibility with the matrix. The compressive properties of these are compared with those made of untreated fly ash particulates. Furthermore properties of fly ash composites with two different average particle sizes are first compared between themselves and then with those made using the as-received bimodal nature of particle size distribution. Microscopic observations of compression tested samples revealed a better adherence of the particles with the matrix in case of treated particles and regards the size effect the composites with lower average particle size showed improved strength at higher filler contents. Experimental values of strengths and modulii are compared with some of the theoretical models for composite properties.

1. Introduction

It is a common feature to fill the polymers with rigid particulate materials like metal powders [1] and inorganic oxides [2–4] to improve the mechanical, electrical or rheological properties. Abundantly available cheaper materials like 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 the thermal power plants, possesses very good mechanical properties on account of the constituent phases contained in it like silica and alumina. 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 display particles of assorted sizes. These characteristics of fly ash qualify it as one of the good alternatives for use as filler in polymers especially in epoxy, which by virtue of its good mechanical properties and excellent corrosion resistance 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 less attention was focused on the mechanical properties in general and compressive properties in particular involving the system of epoxy and fly ash.

Mechanical properties of these particulate composite systems depend on the matrix properties, filler characteristics and polymer/filler interface properties. Filler nature or its constituents, size, shape and size distributions greatly influence the properties of composites. As the role of the matrix is to transfer the load to the filler, the interface between the filler and the matrix influences to a significant extent, the properties of the composites. The attributes of the interface such as size and the strength of the bond influence the strength of the composite. The size of the interface is generally dependent on the size of the filler or more specifically its specific surface area. Previous studies dealing with this aspect generally have lead to the inference that smaller the filler or larger the specific filler surface the larger the chances of ensuring better interface structure and hence improved properties [6, 14]. As regards interface 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 properties of wide variety of

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metal powders and inorganic oxides [15, 16], mica [17] and a low cost organic natural filler [18] into a number of polymer matrix systems was observed in earlier studies. Hence the present investigation looks at this aspect of study on the compressive properties of epoxy resin containing fly ash additions in varying contents with particle surfaces treated with silane agent. The study also includes a comparison of compressive properties of composites containing varying amounts of ash with two different average particle sizes first among themselves and thereafter with that recorded for composites having ash particles in the as received condition and displaying a bimodal distribution for the filler sizes. Fracture features of samples subjected to compression are observed by examining surfaces under the Scanning Electron Microscope (SEM).

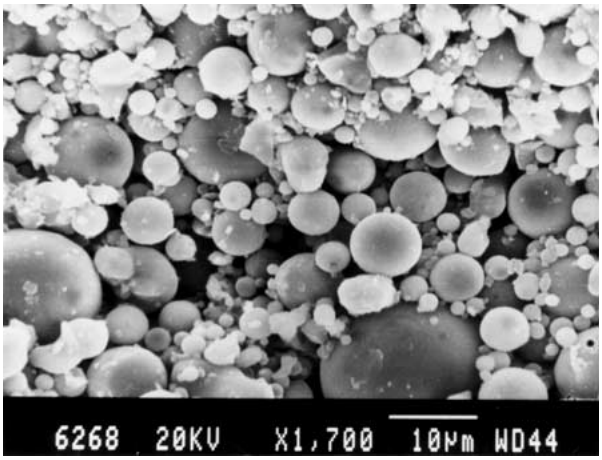

Figure 1 SEM picture showing assorted sizes of fly ash particles.

2. Experimental

2.1. Materials

The matrix system consists of a medium viscosity epoxy resin Diglycidyl Ether of Bisphenol – A (DGEBA) (Trade Name: LAPOX L-12) and a room temperature curing hardener Triethylene Tetra-amine (TETA) (Trade Name: K-6) supplied by ATUL India Ltd. The density of cured neat resin was found to be 1120 kg/m^3. 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 900 kg/m^3 was found to consist of mixture of solid and hollow spheres of different sizes (Fig. 1). Particle size analysis using Malvern laser particle size analyzer shows grossly bimodal distribution (Fig. 2) with about 77% larger-sized particles and 23% of smaller-sized ones. As regards the compositional aspect, the energy dispersive spectroscopy of the fly ash sample revealed the main constituents to be silica and alumina of about 63% and 26% respectively by weight. Chief among other oxides present were Fe_2O_3-6.7% and TiO_2-2.5%. Silane coupling agent used for the treatment of surface of particles was 3-(Triethoxysilyl)-propylamine (3 TESPA) supplied by Merck (Art. 821619) (equivalent of (3-aminopropyltriethoxysilane).

2.2. Fabrication procedure

Fly ash in the required amount was mixed into a measured quantity of epoxy resin plus hardener with gentle stirring in order to reduce the formation of air bubbles. The mixture was then slowly decanted into a mould of size 320 mm × 170 mm × 3 mm coated before hand with uniform film of silicone releasing agent to fill

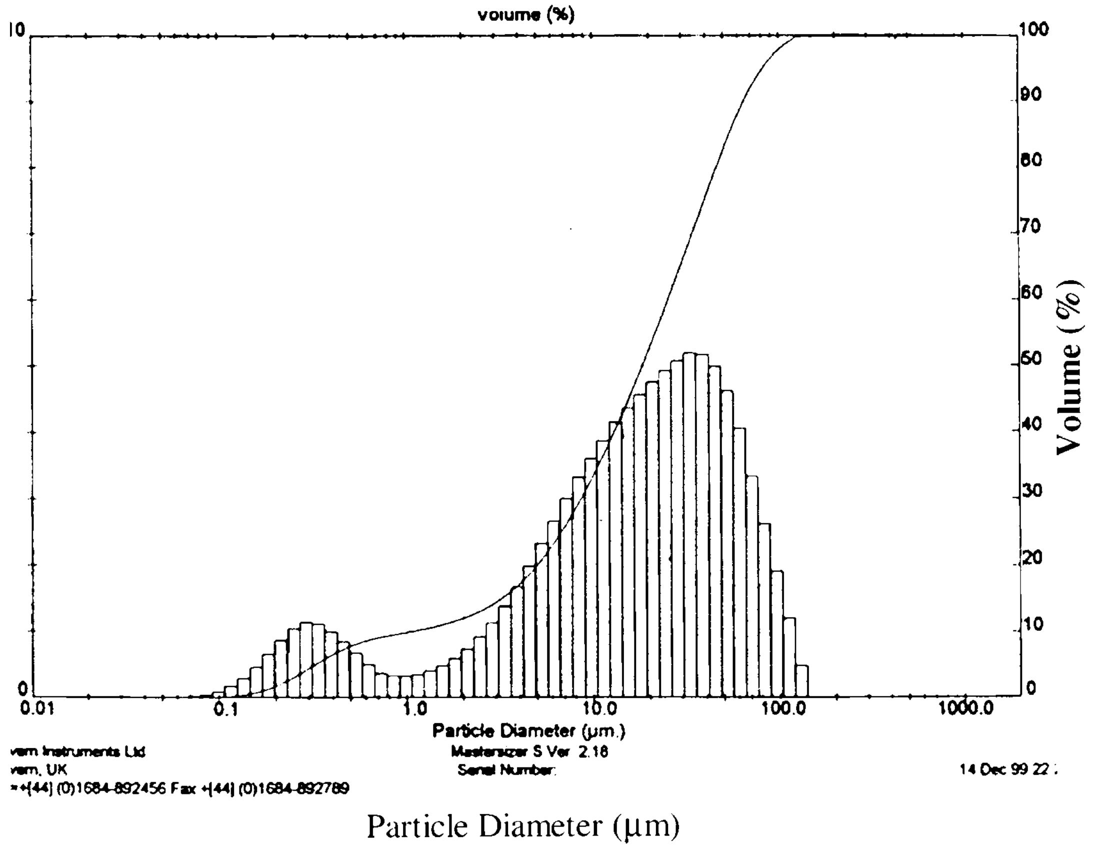

Figure 2 Particle size distribution of as received fly ash.

the entire mould. It was then left to cure at room temperature for about 24–26 h. 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 were then subjected to C-scan non-destructive test to map out the regions of uniform material distribution from where the compression test coupons of required size were sectioned from the cast slabs.

A set of composites with different volume fractions of fly ash in as received condition was made with the procedure described above. This as received fly ash had an average particle size of 18 μm (specific surface are 2.69 m^2/g). In order to study the effect of particle size on strength, the filler which consisted of bimodal nature was sieved to two fractions one bearing particles smaller than 500 mesh and other containing particles larger than 500 mesh. The average particle sizes for these categories were 11 μm (specific surface area 0.7852 m^2/g) and 34 μm (specific surface area 0.4267 m^2/g) respectively. Slabs with discretely chosen but varying volume fractions of fly ash containing the smaller sized (coded FASZ) and larger sized (abbreviated FALZ) respectively were made.

A treatment to the surface of the filler with a view to modify its characteristics of adhesion to epoxy matrix system was attempted in this study. A silane bearing system was made to envelop the ash particles that had a bimodal distribution in the as received condition and which did not have a sieving (to size particles) treatment. The resulting surface is expected to show greater compatibility with the epoxy matrix material because of the ability of the silane agent to form primary Si—O—Si bonds with the filler surface and with its free amine functional groups involving in the curing reaction with the hardener in order to bind to the epoxy matrix as well.

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 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 amine functional groups of the coupling agent that are to be involved in curing process with amine-based hardener. Cast slabs of epoxy were thus prepared incorporating the different volume fractions of treated filler available in free (individual) particulates for dispersion into epoxy resin. These were designated FASC.

2.3. Testing

Compression testing was done in DARTEC 9500, a servo-hydraulic microprocessor based computer controlled testing machine. Test coupons of size 12.5 mm × 12.5 mm × 3 mm, conforming to ASTM specification, were used. The loading direction was perpendicular to the 12.5 mm × 3 mm cross-section of the sample. The machine crosshead, owing to the built in software, was programmed to apply the compression load at constant strain rate of 0.01 s^{-1} through the entire duration of the test. The test was automatically terminated in the event of sample fracturing or reaching the 50% strain, which ever occurred earlier. Samples generally fractured in compression. From the load-stroke history, the compressive modulii and strength were determined. Minimum of five samples were tested in each category and average strengths and modulii were noted. Modulus was calculated for a strain about midway between the start and the strain corresponding to maximum load.

2.4. Microscopy

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

3. Results and discussion

Fig. 3 shows the strengths and modulii of composites made out of fly ash both in the untreated and silane treated conditions. It can be observed from the plot showing variation of strength (Fig. 3a) that for initial volume additions of fly ash the strength increases and for larger volume fractions it shows a decreasing trend. With the microscopic observation of these samples with untreated fly ash, it was observed that larger sized particles showed crescent-shaped debonds (Fig. 4) around them. That their formation in assorted-sized and untreated ash particles could be due to the effect of particle size on the dewetting stresses (Vollenberg *et al.* [6])

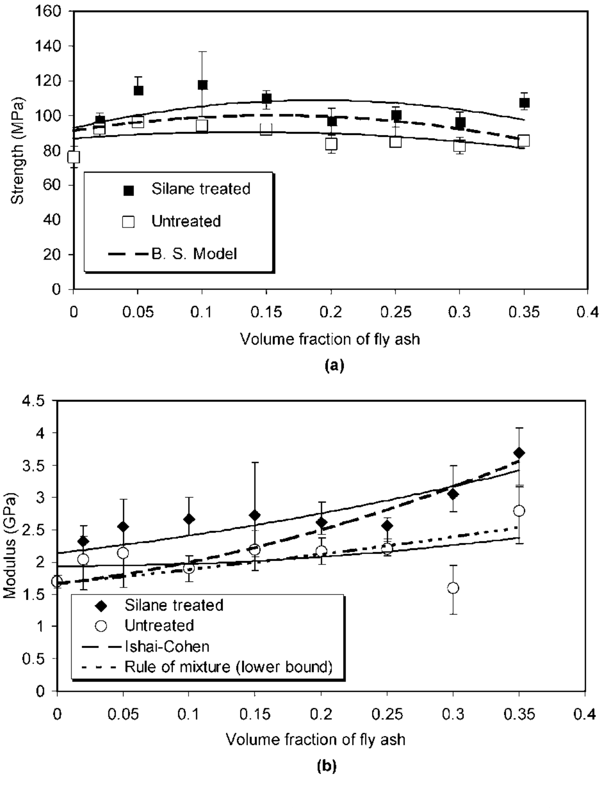

Figure 3 Strengths and modulii of silane treated and untreated fly ash composites.

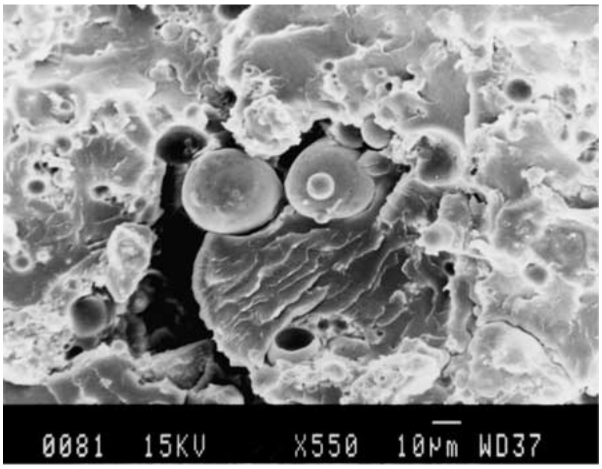

Figure 4 SEM micrograph showing debonds around larger of the fly ash particles.

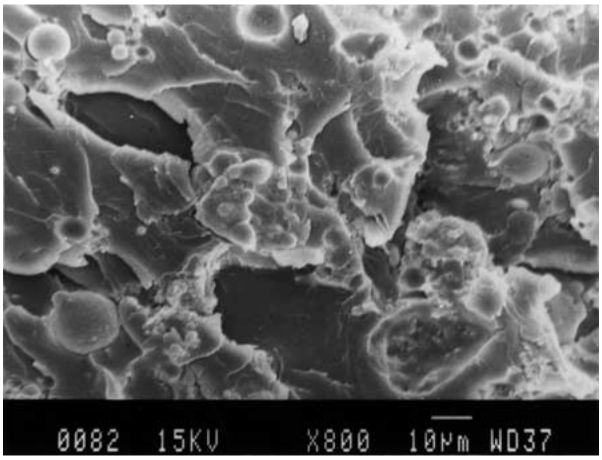

Figure 5 SEM micrograph showing less of debonds about the surfaces of fly ash particles including the larger-sized ones.

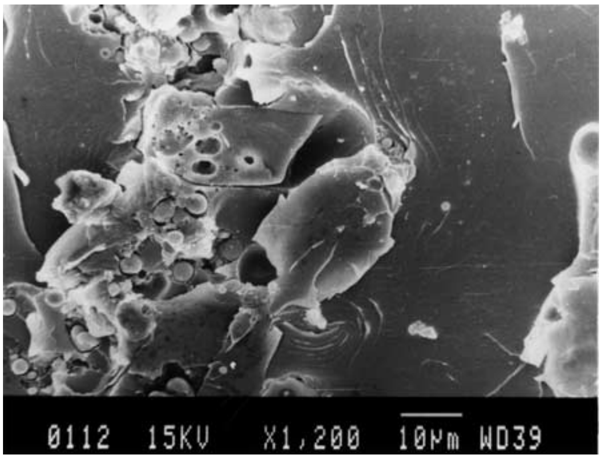

Figure 6 SEM micrograph displaying in a matrix region the occurrence of cluster of untreated fly ash particles.

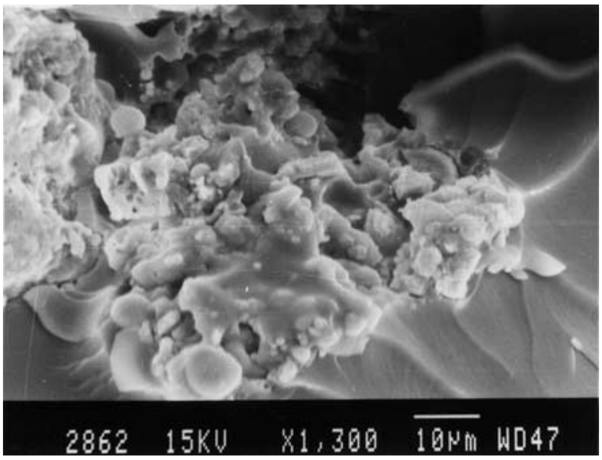

Figure 7 SEM micrograph illustrating the feature where a cluster of treated fly ash particles occur.

formed the subject of earlier investigations [19, 20]. To improve the adhesion characteristics at the interface and hence reduce the formation of debonds a silane treatment on the fly ash filler was attempted in this work. The strengths and modulii for composites with silane treated fly ash (Fig. 3a and b) show an improvement over the untreated filler composites. An increase of strength of about 26% (maximum) was observed from such an exercise (Fig. 3a). The microscopy revealed improved interface compatibility between treated particles and the epoxy matrix. Thus, Fig. 5 shows a SEM micrograph of composite with treated fly ash particles showing less of debonds compared to that seen in Fig. 4. A marginal decline in the strength at higher volume fractions compared to lower has been attributed to the tendency of the particles to form a network or clusters [20] that will make the resin to spread uniformly over the surfaces of closely-spaced untreated particles (Fig. 6) difficult [20]. Though this tendency for particles to cluster together is seen in treated ash composites as well, the particles still tend to display what may be termed ‘a better smearing of resin’ on its surface unlike in the case of untreated ash composites. Thus, SEM micrograph presented in Fig. 7 shows cluster of particles with better cohesion with the matrix compared to that seen for untreated case (Fig. 6). This difference in the situation prevailing at the interface of ash/epoxy can be invoked to explain the higher strengths seen (Fig. 3a) in treated even at larger volume levels of ash in the composites. Thus the surface treatment involving silane agent brings about improvement in compressive properties. The experimental values of strengths and modulii are compared with (Fig. 3) theoretical values of a few models for composite properties [21]. The trend in the variation in the strength values best matches with breaking strength model proposed by Gao and Tsou [22]. Experimental values of modulii find close proximity with the lower bound rule of mixtures in untreated ash case and Ishai-Cohen [5, 21] equation in treated case especially for larger content of filler suggesting the improvement in properties of the filler-matrix interface in the latter.

As stated earlier, the effect of particle size on the strength value is also looked into in the present work. Fig. 8 illustrates the strengths and modulii for composites with different volume fractions of ash. The as received ash possessing a bimodal distribution (Fig. 2) of the particles shows lower strengths and modulii. Formation of debonds at the larger particles, which form a greater portion of the bimodal distribution (Fig. 2), and these acting as stress raisers can cause a reduction in strength. To support this view of debonds acting as stress raisers and promoting lowering of the strengths,

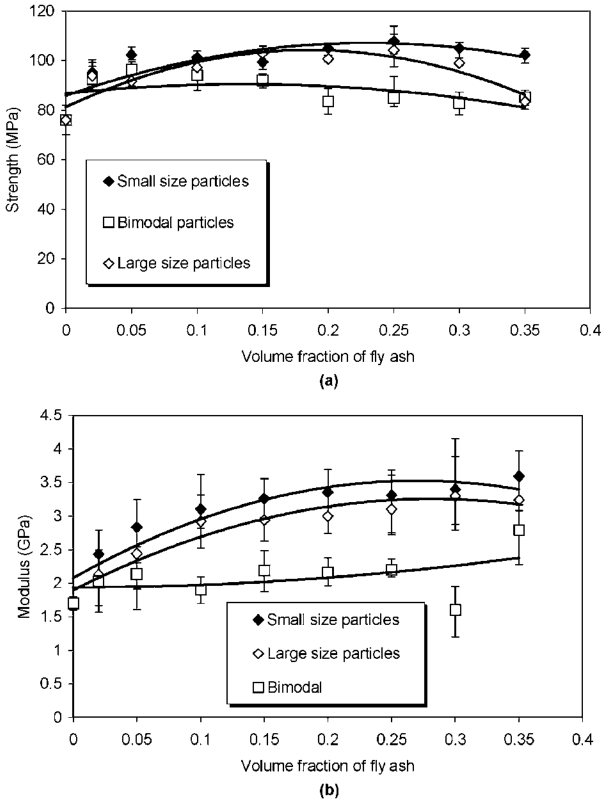

Figure 8 Strengths and modulii of fly ash composites with different average particle sizes.

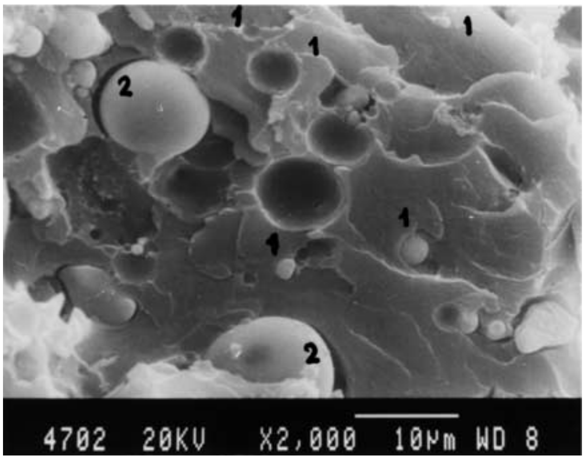

Figure 9 SEM micrograph showing less of debonds at smaller particles in FASZ sample.

in this work strengths and modulii of composites containing ash particles with lower average particle size (FASZ) has also been catalogued (Fig. 8). The FASZ variety shows improvement over that of composites with bimodal fly ash. These FASZ samples besides showing lesser debonds, displayed a better adherence to matrix. Thus in the SEM micrograph presented in Fig. 9 the smaller particles marked '1' and displaying less debonds compared to the relatively bigger ones (marked '2') can be seen. This aspect also gets support from the higher stress required for the formation of debond as given by the expression $\sigma_{\text{dewetting}} = A_r^{-2}$ where r is the particle size [6]. For composites containing ash with larger average sized particles (FALZ), it can be seen that the strengths are almost the same as those of FASZ for lower volume fractions of ash content but drop (Fig. 8a) at higher volume fractions of filler. This behavioral change may be traced to the clustering of particles and the debonds around such clusters (marked by arrows) which are generally seen at larger particles (Fig. 10). As regards modulus though there is an improvement observed in the modulus of FASZ and FALZ composites over those containing the as received bimodally distributed fly ash, between themselves the two varieties FASZ and FALZ do not display any significant variation in pattern (Fig. 8b).

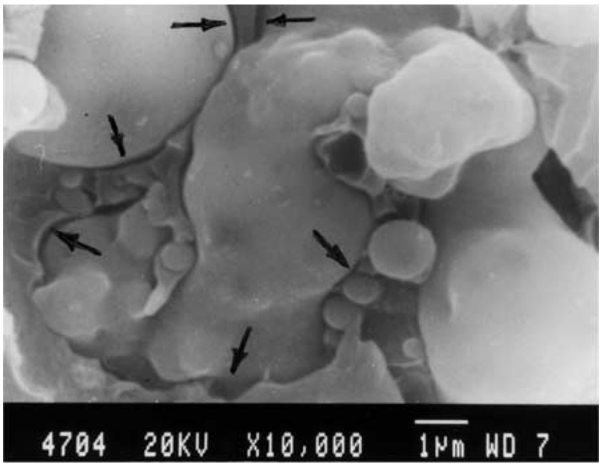

Figure 10 SEM picture illustrating a cluster containing large particles with debonds.

4. Conclusion

Fly ash composites containing treated filler particles displayed improvement in strength and modulus for all volume fractions of the filler. The better compatibility with the matrix responsible for the improvement in properties was observed in the microscopic examination of the compression-failed sample. Though the composites with smaller and larger average particles registered improvement over the fly ash used in the as received bimodally particle distributed condition, amongst themselves they had differing values only at higher volume fractions, the smaller average values showing improvement in strength. The microscopic observation of these samples revealed lesser debonds at the interface of epoxy and the smaller particles compared to that witnessed for corresponding positions in composites containing the larger-sized ones. Composites with different average particles sizes did not show much variation in the values for modulus. The experimentally determined values were found to tally with those got by breaking strength model in the case of strength where as for modulus those involving the lower bound equation from rule of mixtures and Ishai-Cohen equation were found to explain better the values for untreated and treated ash cases especially at the larger filler levels respectively.

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