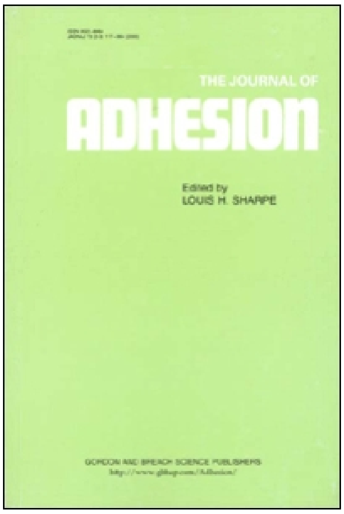

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Mechanical Properties of Modified Epoxies as Related to Free Volume Parameters

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Epoxy resins need modifications by rubbery additives, fillers, etc. for enhancement of their usage in various applications. This study aims to determine the mechanical properties of silicone (i.e., amine-containing poly dimethyl siloxane)-modified resins in combinations with fly ash. The mechanical properties, especially tensile/flexural strength and moduli, were determined. Amine-containing silicone (ACS) was found to weaken the epoxy resin. However, ACS-modified epoxy resin was found to tolerate the addition of a small amount of fly ash filler as it had better tensile and flexural strengths compared with the unfilled, modified resin. In contrast to this, the unmodified resin was found to have its tensile and flexural strengths deteriorated by the filler. The reason for this behaviour was speculated to be due to the ACS acting as an additional coupling agent between the resin and the filler. These properties were sought to be correlated with free volume parameters measured from Positron Annihilation Lifetime Spectroscopy. Free volume measurements appear to indicate enhanced epoxy-fly ash interactions by ACS. Scanning Electron Microscopy indicates better filler distribution in the ACS-modified resin compared with the unmodified resin.

Keywords: Amine-containing silicone polymer; Epoxy resin; Fly ash-filled epoxy resin; Free volume measurements; Positron annihilation lifetime spectroscopy; Silicone-modified epoxy resin

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1. INTRODUCTION

Epoxy resins show a few outstanding characteristics such as high strength and stiffness, good chemical and electrical resistance, and also very good adhesion to fibres and inorganic substrates [1–3]. Because of these properties, epoxies have a wide range of applications in industries such as paints, surface coatings, adhesives, and electrical accessories. Despite the above outstanding properties, epoxies have a major drawback in the form of poor resistance to crack initiation and its growth [2] and additionally low impact strength. Therefore, in the last few decades, toughening of epoxies has received, and continues to receive, attention by researchers [4]. Adding inorganic fillers alters other properties—*e.g.*, metal powders increase electrical conductivity, alumina improves thermal conductivity, and micro spheres of glass help to improve compressive modulus, etc. [5].

Toughening of epoxies is done in two ways. One is by reducing the crosslink density and the other is by modifying the epoxy matrix using rubbery or rigid particulate additives (functionalized engineering plastics or ceramics) which would contribute to improving the fracture properties of the system [3,4]. The modification using different functionalized liquid rubbers is a widely used technique to improve the toughness of the epoxy system [3]. Though improvement in toughness is seen, deterioration of other properties, such as reduced glass transition temperature (T_g) and stiffness, is a common side effect of this approach.

The commonly used rubber for toughening epoxies is Carboxyl Terminated Butadiene Acrylonitrile copolymer (CTBN). In this modifier, the acrylonitrile content is maintained at a low percentage so as to give some polarity and hence, minimal compatibility with the epoxy resin at the time of mixing. This modifying polymer will precipitate as spherical, rubbery particles during cure. This should help in toughening with minimal loss of stiffness and small shift in T_g. However, CTBN has a few disadvantages; *e.g.*, it may reduce heat and weather resistance due to its butadiene units and it also may not improve the low temperature properties. Silicones may be considered as another modifier—they have poor compatibility with epoxies but, if compatibilised, they can improve moisture resistance and low temperature resistance [6–9].

Adding inorganic fillers to epoxy resin often leads to agglomeration of the filler particles which reduces their tensile and flexural strength. Treatment with a silane coupling agent may neutralize this effect to some extent.

Poly dimethyl siloxanes (silicones) containing reactive groups can also be good rubbery modifiers for epoxies, especially for electronic applications [6–8]. Compositions used in this application contain silica filler and these filled resins are reported to be toughened by the silicone polymer with a marginal increase in flexural strength [6,7]. We have observed that this concept can be extended to glass fibre-epoxy composites, where the presence of amine-containing silicones not only toughens the composite but also slightly increases tensile and flexural strength and improves resistance to deterioration by water at higher temperatures [3].

In a rubber-modified epoxy resin, toughness is improved mainly by shear yielding between the holes formed by the cavitated rubber particles. Shear yielding is caused by the increased dilatational deformation of the epoxy resin, at the resin-rubber particle. For this to occur, good bonding between the resin and the rubber particle is a must. Cavitation at the rubber particle and the rubber-resin interface further enhances plastic deformation and leads to toughening. Rigid particles, also, can help in toughening epoxy resin—*e.g.*, alumina or silica or engineering thermoplastics—again provided that good bonding between the resin and the particle is achieved, which calls for surface treatments of these particles. In the case of the rigid particles, crack pinning at the particle leads to toughening. These are discussed in [10].

Addition of inorganic fillers to epoxy resins also seems to enhance properties such as electrical conductivity and thermal conductivity, and microspheres of glass help in drastically improving the compressive modulus, etc. [9]. Fly ash, a waste product from thermal power plants, has recently gained importance as a filler in epoxy resins due to their low density, low cost, easy processability, etc. Additionally, fly ash, though not environment-friendly, can be used to generate environment-friendly products. Researchers are now exploring their possible use in composites to produce good materials for a wide range of applications.

In the present work, the effect of amine-containing poly dimethyl siloxanes (ACS) on diglycidyl ether of bisphenol A (DGEBA) resin as modifiers are studied by mechanical property measurements. Further, the effect of ACS on epoxy composites with fly ash, which is a waste material (containing aluminum silicate) from thermal power plants, are studied. To understand the microstructure and its influence on the mechanical properties, free volume measurements have been carried out using Positron Annihilation Lifetime Spectroscopy, a sophisticated tool used for direct measurement of the nanometer-sized free volume holes and their relative number densities in polymers and polymer blends.

2. EXPERIMENTAL DETAILS

2.1. Materials

The epoxy resin used was LY 556 of Huntsmann Advanced Materials (Mumbai, India), with an epoxy equivalent of 170 g/mol. The hardener used was an aliphatic amine (mainly triethylene tetramine), HY 951 from Huntsmann Advanced Materials. The silicone used was grade AN 102 of molecular weight of 5000 g/mol, supplied by Resil Chemicals Ltd., (Bangalore, India). It has the structure shown in Fig. 1.

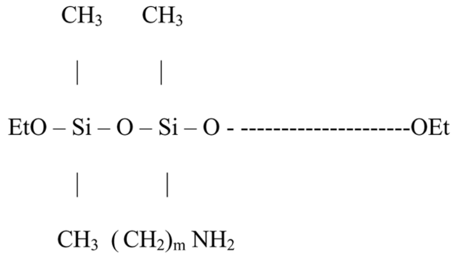
Fly ash was obtained from a thermal power plant near Chennai, India. It was of the Type C (ASTM C- 618). It contains 20% CaO, 15–45% silica, 20–25% alumina, and about 5% of Fe_2O_3. The fly ash particles are spherical with a diameter of about 27 microns. In between the spherical particles, unburnt carbon was present. Functional groups present in the unburnt carbon may help in adhesion to organic polymers.

2.2. Preparation of Test Specimens

The ACS-modified epoxy resin was prepared by heating the resin with ACS at the desired proportions at 50°C for about 30 min when a creamy liquid forms. This was cooled and then the filler and hardener (resin: hardener weight ratio 10:1) were added with stirring. The mixture was cast into slabs using aluminium moulds at room temperature. Demoulding of these slabs was done after 24 h. Test specimens were cut from these slabs.

2.3. Mechanical Property Measurements

Mechanical properties, namely tensile strength, tensile modulus, elongation at break (%), flexural strength, and flexural modulus, of



$$EtO-\underset{CH_3}{\overset{CH_3}{Si}}-O-\underset{(CH_2)_m\,NH_2}{\overset{CH_3}{Si}}-O-\text{---------------------}OEt$$

(about 1 amine group for 7-8 dimethyl siloxane units)

FIGURE 1 Chemical Structure of ACS.

the different compositions were measured at room temperature (26°C) according to ASTM D 638 and ASTM D 790, respectively, using the universal testing machine, Autograph, AGS 2000 G (Shimatzu, Kyoto, Japan). Test specimens were rectangular bars with a width of about 10–12 mm and a thickness of 2.5 mm for tensile tests and 80 × 25 × 2.5 mm for flexural tests. The testing rate was 1 mm/min for tension tests and 3 mm/min for flexural tests. Five specimens were tested in each class to report the average values of the properties.

2.4. Scanning Electron Microscopy (SEM)

Morphological studies were performed on the tensile fractured surfaces of cured neat epoxy, ACS-modified epoxy, and fly ash-filled composite systems using a JEOL (JSM-5800) Scanning Electron Microscope (JEOL, Tokyo, Japan).

2.5. Positron Annihilation Lifetime Studies (PALS)

To evaluate free volume cavity size and their content in the epoxy and modified epoxies, positron lifetime spectrometry was used. A brief description of the basis of the technique is given here. For more details, one can refer to our earlier published work [11–13]. A brief description of the technique is given as follows.

When an energetic positron from a radioactive source like ^{22}Na enters a condensed medium like a polymeric material, it thermalizes quickly and, thereafter, annihilates with the electrons of the medium *via* free annihilation or from a localized state (trapped state) or forms a bound state with an electron called Positronium (Ps) atom. The free annihilation is the one in which the positron annihilates with an electron of the medium, without getting trapped into defects of the medium and this is faster. Free annihilation lifetime is of the order of 200 ps. Secondly, some of the positrons may get trapped into defects like smaller voids and annihilate in a time ranging from 200 to 500 ps. The bound state of Ps can exist in two spin states. The *para* state (*p*-Ps) (particle spins anti-parallel) annihilates with a lifetime of 125 ps. The *ortho* state (*o*-Ps) (particle spins parallel) annihilates with a lifetime of 140 ns. In condensed matter, o-Ps annihilates mainly into two photons by a pick-off mechanism in which the positron of o-Ps annihilates with an electron of opposite spin from the surrounding molecules; thereby, its lifetime is reduced to a few nanoseconds. The lifetime of o-Ps depends on the overlap of the Ps wave function with the electron wave function of the free-volume cavity. Hence, the larger is the hole size, the smaller is the overlap and, hence, the longer the lifetime. So, the o-Ps pick-off lifetime (τ_3) and its intensity (I_3) are a measure of the free-volume size and their relative number density in a condensed medium [14,15].

Positron lifetime measurements were carried out using a standard fast–fast coincidence system with conically shaped BaF_2 scintillators, coupled to photomultiplier tubes of type XP2020/Q with quartz window as detectors. The equipment used was an assembled system with components from EG&G ORTEC, (Oak Ridge, TN, USA).

The coincidence lifetime spectrometer had a time resolution of 220 ps. All measurements were made at room conditions. The source-sample sandwich geometry was used for positron lifetime measurements. A 17 μCi Na^{22} positron source deposited at the centre of a square Kapton® foil 0.0127 mm thick was used. The experimental and procedural details of this technique can be found in References [11–13]. Typical spectrum accumulation times were around 2 h with nearly 10^6 counts under each spectrum. The instrumental time resolution and source correction terms were obtained from the lifetime spectrum of a well-annealed aluminum, using the program RESOLUTION [16]. The lifetime spectra so acquired were analyzed using the PATFIT-88 (RISO Group, Roskilde, Denmark) computer program [16], with 14% of source correction as the positron fraction annihilating in the Kapton foil 12.7 micron thick.

Three lifetime component analyses resulted in better χ^2 values and standard deviations and these are used in the present case. The reproducibility of the results was found to be satisfactory and was within the measured error limits.

3. RESULTS AND DISCUSSIONS

Table 1 shows the mechanical properties measured for the filled and unfilled particulate composites.

3.1. Mechanical Properties

The measured mechanical properties of the neat and the modified epoxies, with and without filler additions up to 15 phr levels, and the corresponding free volume measurements are shown in Tables 1 and 2, respectively, and graphs (Figs. 2 and 3).

1. Silicone (ACS) is known for high compatibility with epoxy resin, though to a much lesser degree than CTBN. The Tg values of the neat and the ACS-modified epoxies were 106 and 102°C,

TABLE 1 Mechanical Properties of Silicone (ACS)-Modified Epoxies Filled by Fly Ash

S. No.	ACS (Phr)	Filler (fly ash) (Phr)	TS (MPa)	Tensile modulus (GPa)	EB (%)	FS (MPa)	FM (GPa)	Flexural strain to failure (%)
1	0	No filler	61	1.5	3.4	98	3.5	2.5
2	5	No filler	43	1.3	3.5	75	2.4	2.8
3	0	5	45	1.0	3.8	62	4.5	1.7
4	0	10	40	1.0	4.1	60	5.4	1.5
5	0	15	38	0.8	5.4	58	3.5	1.3
6	5	5	47	0.9	7.0	85	3.9	2.7
7	5	10	40	0.7	3.5	66	3.7	1.6
8	5	15	21	0.6	3.0	63	3.4	1.4

(TS-tensile strength, FS-Flexural Strength, FM-Flexural modulus, EB-Elongation at break).

respectively, as measured using our Differential Scanning Calorimeter of TA Instruments (New Castle, DE, USA) at 10°C per min heating rate. This shows limited compatibility between the resin and ACS. Silicone polymers are known to have very high free volume spaces between the chains [17]—this property seems to be reflected in the blend of ACS with epoxy resin. Another reason for reduction in Tg may be the high flexibility of the additional crosslinks which may form between ACS and the epoxy resin [18]. The ACS polymer has many amine groups per chain, *i.e.*, one amine for each seven or eight Si-O links in the chain, and this can cause additional crosslinking between epoxy chains by the ACS in addition to those by the hardener. The tensile elongation at breaks does not show much improvement by the addition of ACS (S. No. 1 and 2 in Table 1) in the

TABLE 2 Positron Lifetime Results (Free Volume Parameters) of Epoxy + ACS + Fillers

Sl. No.	Filler (fly ash) (phr)	ACS (phr)	$I_3 \pm 0.1$ (%)	$V_f \pm 0.6$ ($\mathring{A}^3$)	F_{vR} (%)
1	No filler	0	14.6	66.7	9.74
2	No filler	5	17.0	85.0	14.45
3	5	0	14.6	67.2	9.81
4	10	0	14.7	61.5	9.04
5	15	0	13.9	70.6	9.81
6	5	5	13.2	80.4	10.61
7	10	5	14.6	76.1	11.11
8	15	5	12.7	73.6	9.35

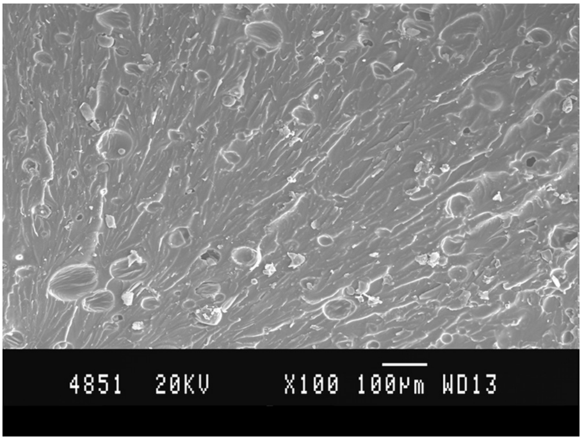
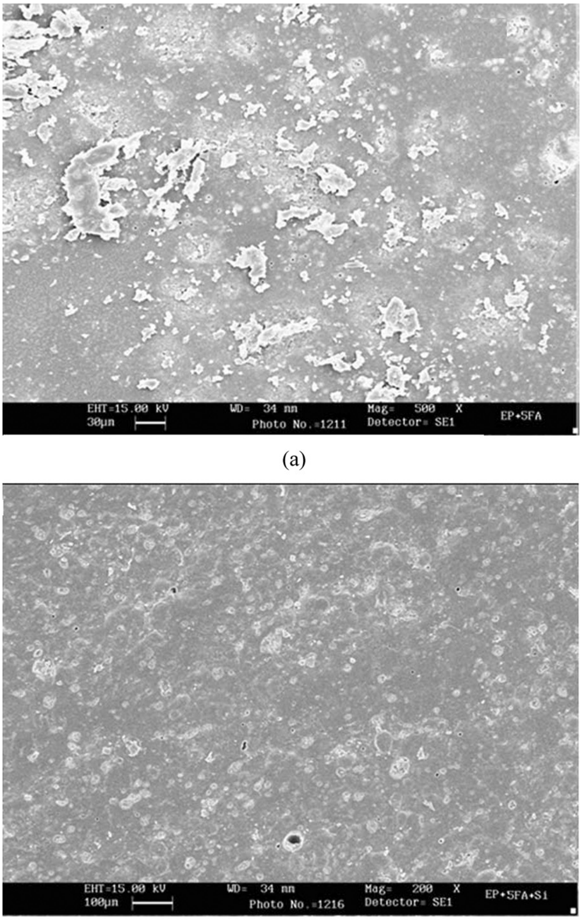


FIGURE 2 Plot of free volume hole size, V_f against (a) Tensile Strength, (b) Tensile modulus, and (c) Elongation at break for fly ash-filled epoxy resin. NOTE: The errors on TS, TM, and EB are within the dimensions of the points shown.

unfilled resin. This may be due to crosslinking of the resin by ACS. Ideally, amine groups should be present only in the chain ends of the rubbery modifier, but the ACS used in this study contains seven to eight amine groups per polymer chain, which may lead to crosslinking.

2. The lack of improvement of mechanical properties by the added ACS modifier, in the unfilled resins, can be seen by the reduction in tensile modulus and elongation at break (S. No. 1 and 2 Table 1). The lesser compatibility of ACS with epoxy resin is seen by the large particles of the dispersed phase in the SEM studies—20 micron level (Fig. 4). It can be concluded that this modifier (ACS) is not an ideal toughener for epoxy resin. The decrease in Tg at 5 phr level addition of ACS is about 4°C. The silicone modifier is precipitated as discrete particles. ACS particle detachment is not seen (Fig. 4) in this micrograph which shows good bonding between ACS particles and the epoxy resin.
3. From Table 1 it can be seen that the presence of ACS weakens the resin—tensile and flexural strength and flexural modulus decrease by the addition of ACS to the resin (S. No. 1 and 2 of Table 1). However, in the fly ash-filled resin, mostly tensile and flexural strength increases, in relation to the unfilled, ACS-modified, epoxy resin. This may be because ACS acts as an additional coupling agent between the filler and the resin. Similar



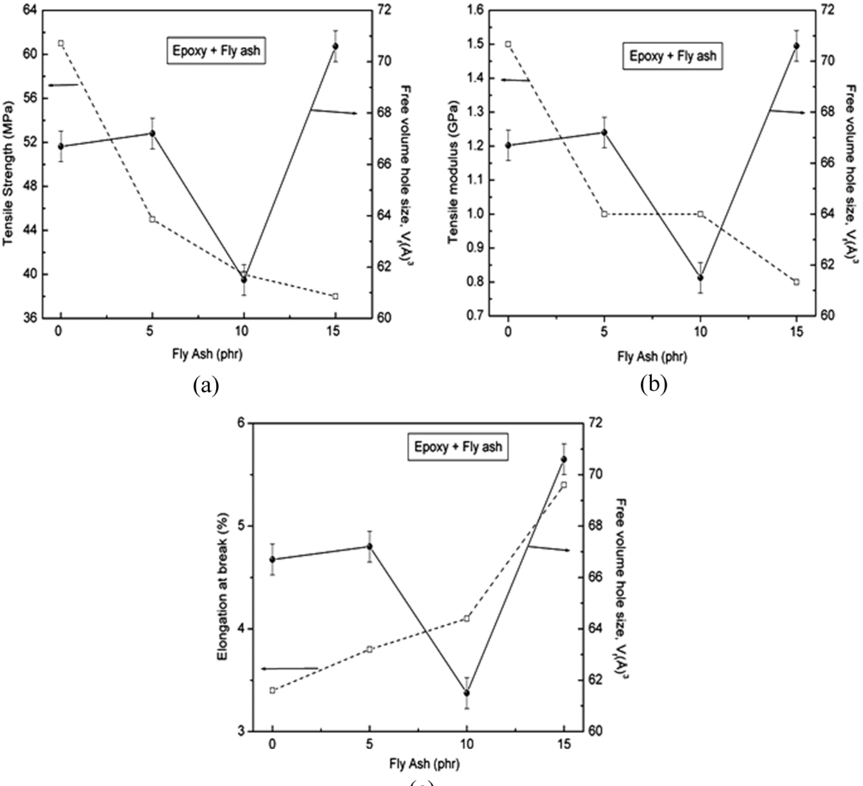
(a)

(b)

FIGURE 3 Plot of free volume hole size, V_f against (a) Tensile strength, (b) Tensile modulus, and (c) Elongation at break for ACS-modified fly ash-filled epoxy resin.

observations and inferences were made by Takahashi *et al.* [6] and Lin *et al.* [7], when they studied the effect of amine-terminated silicone polymer on epoxy particulate composites containing silica filler.

4. The variation of mechanical properties of epoxy resin by fly ash is in line with observations made by others. For instance, Ramos *et al.* [19] reported a drastic decrease in impact strength on addition of 8 phr of fly ash which, to some extent, is improved by adding



(a) (b)

(c)

FIGURE 4 SEM photograph of ACS (5 phr)-modified epoxy.

CTBN. It is to be noted that even after modification of the resin by CTBN, the reduction of impact strength was severe compared with the neat resin, with and without CTBN modification. This may be because fly ash may cause stress concentration at the resin-filler interface. Similarly, Chaowasakoo *et al.* [20] reported a reduction of tensile and flexural strength of epoxy resin due to addition of fly ash. On treatment of fly ash with a silane coupling agent, flexural strength was found to come close to that of epoxy resin. These results indicate that fly ash particles, like those of any other inorganic filler, tend to agglomerate when added to epoxy resin and deteriorate the mechanical properties (except, perhaps, tensile and flexural modulus) of the resin. Treatment with a silane coupling agent has probably prevented this agglomeration.

ACS seems to act in a similar way by improving the wetting of the fly ash by the resin. This prevents agglomeration and thus, ACS probably acts as a coupling agent between epoxy resin and fly ash. This may explain why in the presence of ACS the resin is able to tolerate fly ash filler up to 5 phr level without loss of flexural and tensile strength (in relation to the unfilled, ACS-modified resin).

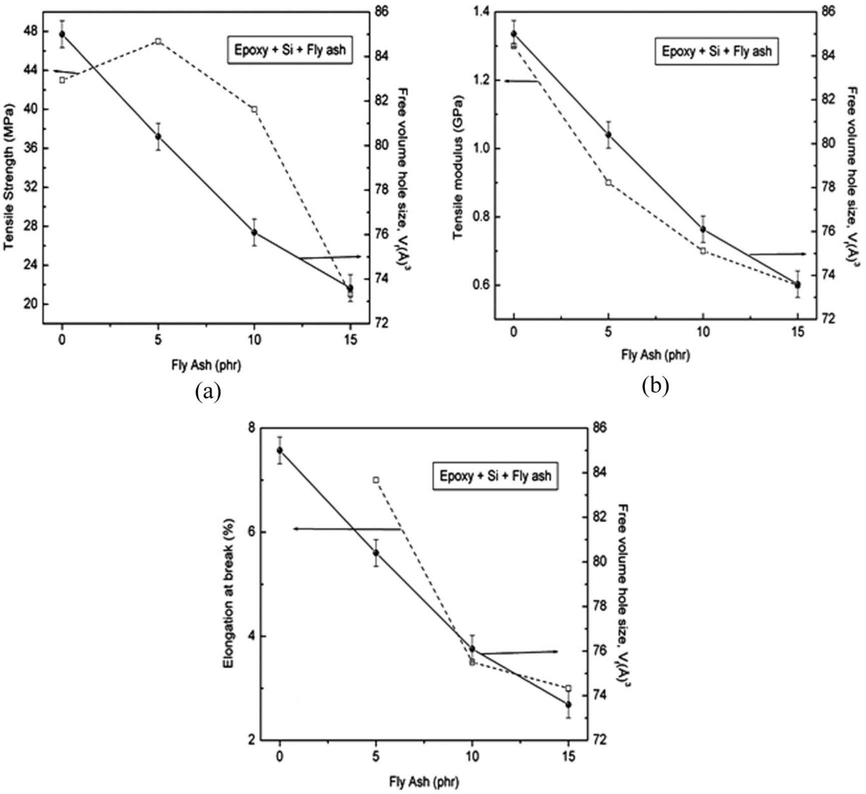
5. In our earlier unpublished work, we have observed that when a cure was attempted at high temperature (here the resin viscosity will be very low before gelation) using aromatic amine hardener, a similar filler (*i.e.*, glass spheres) tended to settle down before gelation, leading to uneven mechanical properties along the casting. When we used ACS-modified resin this problem was not seen. The filler appeared to be distributed uniformly, leading to better and more consistency in mechanical properties throughout the cast sheet. This can indicate that ACS helps in wetting of the filler by the epoxy resin.

Further, SEM photographs on the filled composites (Figs. 5a and 5b) show that in presence of ACS fly ash seems to be distributed more finely in the resin while in the compositions without ACS, fly ash particles agglomerate. This shows better epoxy—fly ash interaction in the presence of ACS.

3.2. Correlation of Mechanical Properties with Free Volume Measurements

The measured o-Ps lifetime and its intensity using the PALS were used to calculate the radius of the free volume hole and the density of the free volume holes in the samples of this study. The acquired positron lifetime spectra were resolved into three life time components τ_1, τ_2, and τ_3, with intensities I_1, I_2, and I_3, respectively. The general interpretation of these lifetime components is as follows. The shortest life time component, τ_1, with intensity, I_1, is attributed to p-Ps and free positron annihilations. τ_2 is the intermediate lifetime and it is not considered in this study. This is mainly due to annihilation of positrons trapped at defects present in the crystalline regions or at crystalline-amorphous interface regions. τ_3 has the longest lifetime due to pick-off annihilation of o-Ps from the free volume sites in the amorphous regions of the polymer [21]. From τ_3, the radius of the free volume hole or cavity (R) can be calculated using the following relation, developed by Nakanishi *et al.* [22]:

$$(\tau_3)^{-1} = 2\left[1 - \frac{R}{R_o} + \frac{1}{2\pi}\sin\left(\frac{2\pi R}{R_o}\right)\right]\mathrm{ns}^{-1}, \tag{1}$$



(a) (b)

(c)

FIGURE 5 (a) SEM photographs of epoxy-fly ash composite. Scale Marker = 30 μm; (b) SEM photograph of epoxy-ACS-fly ash composite. Scale Marker = 100 μm.

where $R_o = R + (R$ and δR is an adjustable parameter. By fitting Eq. (1) with τ_3 values for known hole sizes in porous materials like zeolites, a value of $\delta R = 0.166\,\text{nm}$ was obtained. We also verified that the same value of δR is valid for the present system investigated in this work [23]. Using this value of δR, the free volume radius, R, has been evaluated using Eq. (1) and the average size of the free volume holes, V_f, is calculated as $V_f = (4/3)\pi R^3$. The relative fractional free volume or the free volume content (F_{vR}) of the system, can then be estimated as

$$F_{vR} = V_f * I_3, \tag{2}$$

where V_f is the free volume hole size and I_3 is the o-Ps intensity. The positron results are tabulated in Table 2. Figures 2 and 3 show the variation of tensile strength, tensile modulus, and elongation at break with fly ash content in unmodified and ACS-modified composites, respectively.

It has been well established that, in polymeric systems, macroscopic properties such as elongation at break and toughness depend on the microstructure properties such as free volume cavities and their concentration [11,24–26]. These properties depend on the chain morphology of the system: they depend on the ease with which the chains can slide past each other under the influence of an external force. Therefore, an increase in V_f is certainly expected to provide more space for the chain movement and, hence, elongation at break is also expected to increase. It is difficult to correlate V_f with elongation at break values from Tables 1 and 2 as there are uncertainties in the values of elongation at break in this study.

The variation of tensile strength (TS) and free volume hole size, V_f, in epoxy/fly ash composites as a function of fly ash content is shown Fig. 2a. As can be seen, the correlation between V_f and TS is more or less opposite to what is the expected behaviour. When 5 phr of FA was added, a small increase in V_f was observed that may be due to the poor interaction between filler and matrix, which results in generation of additional free volume holes leading to effective reduction in the strength of the composite. At 10 phr fly ash content, a decrease in free volume size is observed which may be due to uniform loading of the fly ash in the epoxy matrix and, at 15 phr, we observe an abrupt increase in free volume size suggesting weak particle/matrix interaction at high fly ash content. From the above observation, since 5 phr of fly ash seems to produce moderate values for these two parameters, it could be taken as the optimum fly ash content. A similar observation applies in the case of variation of V_f and tensile modulus with fly ash content as can be seen from Fig. 3b. In the case of V_f against percent elongation at break (EB) (Fig. 2c), we see a continuous increase in EB with fly ash content that is difficult to explain due to uncertainties in the values of elongation at break, as mentioned earlier. Except at 10 phr, the variation of both the parameters V_f and EB appears to be similar, which is the expected correlation.

Figure 3a shows the variation of V_f and TS with fly ash content in ACS-modified epoxy resin. We can observe that at 5 phr of fly ash, a slight increase in tensile strength and a decrease in free volume hole size is observed. This shows that silicone has, to some extent, improved the adhesion between epoxy and fly ash, which resulted in increased strength and reduction in free volume. Beyond 5 phr of fly ash, we observe that both TS and V_f decrease with increasing fly ash content. This can be due to the presence of flexible silicone linkages and free rotation of the –Si–O–Si– bond which leads to weak intermolecular attraction of pendant methyl groups present in the silicone molecule which results in a weak interface between silicone and epoxy matrix [18,24].

From Fig. 3b, we observe a decrease in both the free volume hole size and tensile modulus with increasing fly ash content. The decrease in modulus may be due to the entanglement of flexible silicone chains with the epoxy matrix, which resulted in a larger interphase region, which also seems to be the reason for the reduction of V_f.

Figure 3c shows the plot of free volume hole size and variation in percent elongation at break as a function of fly ash content. The variation of both these parameters appear to be similar and continuously decreases with increasing fly ash content in the ACS-modified resin, which was the opposite of the case of unmodified epoxy composite (Fig. 3c). The decrease of elongation at break with increasing fly ash content would suggest embrittlement of the resin due to the filler (due to poor dispersion), which also agrees well with the observed decrease in free volume.

Flexural tests seem to show better correlation with free volume parameters. The increase in flexural strength in fly ash-filled composite at the 5 phr level by ACS modification (at 5 phr level) is more pronounced (compare S. No. 1 and 3 with 2 and 6 in Table 1). The flexural strain to failure values (in %) show a somewhat clearer trend than elongation at break values. The flexural strain to failure decreases drastically on addition of fly ash in modified (by ACS) and unmodified composites. The flexural strength and strain to failure values show that ACS modification can make the epoxy resin tolerate the addition of 5 phr of fly ash filler without loss of mechanical properties, with reference to the unfilled ACS-modified resin.

Based on the above observations, we can infer that 5 phr of fly ash content in the ACS-modified epoxy composite seems to be the optimum composition for obtaining moderate values of mechanical properties, and through this study the correlation between the microstructure and its influence on mechanical properties has been clearly demonstrated.

4. CONCLUSIONS

1. The addition of ACS to the epoxy resin resulted in the decrease of TS and TM but on incorporation of 5 phr fly ash these properties improved, indicating that ACS acted as a good coupling agent between the filler and the resin.

2. The SEM micrographs showed uniform dispersion of fly ash in the epoxy matrix in the presence of ACS compared with unmodified epoxy resin in which fly ash seems to have agglomerated due to poor interaction between the filler and resin.
3. The free volume hole size, V_{f4}, showed a decrease and the mechanical properties, namely, TS and TM, showed an increase at 5 phr fly ash content of ACS-modified epoxy composite. This clearly shows the correlation of mechanical properties with the free volume parameters (PLS).
4. Based on the above observations, it was concluded that 5 phr fly ash content in the ACS-modified epoxy resin can be considered as the optimum composition in achieving moderate mechanical properties for the composites.

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