

# Positron Lifetime Spectroscopy and Differential Scanning Calorimetric Study of Polystyrene-Based Composites with Fly Ash, Cenospheres, and Calcium Aluminosilicate as Fillers

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**ABSTRACT:** Polystyrene-based composites with Fly ash, Cenospheres, and Calcium aluminosilicate as fillers have been examined for their mechanical and microstructure properties. Free volume measurements have been carried out using Positron Lifetime Spectroscopy to probe the microstructural features of the composites. Incorporation of fly ash, cenospheres, and calcium aluminosilicate improved the thermal properties of the composites due to increased  $T_g$  of the composites as revealed by the DSC data. Also, it was observed that the mechanical properties

of calcium aluminosilicate filled composites improved more compared to fly ash and cenospheres filled composites. We attribute these favorable changes to the higher silica content of calcium aluminosilicate on account of possible interactions between the polymer matrix and silica and to some extent from particulate size. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 3087–3094, 2010

**Key words:** composites; polystyrene; fillers; mechanical properties; free volume; glass transition

## INTRODUCTION

During the past few decades there has been an immense activity in metallurgy and materials science in the synthesis and characterization of polymer-matrix, ceramic-matrix, and metal-matrix composites for variety of applications. Out of these, the polymer-matrix composites<sup>1–4</sup> are very important as they are widely used in large number of applications due to their lightweight, ease of fabrication, and variety of other properties. With increasing demands of high technology areas, such as airframe, jet engines, space shuttles, deep-sea submersibles, and atomic energy field, there is a need to develop materials with improved performance capabilities. The composite concept allows us to produce stiffer, stronger, and tough materials with improved elevated temperature capability.<sup>1</sup> Polymers have low strength and stiffness and are ductile. Ceramics and glasses are stiff and strong, but are highly prone to brittle failure. In polymer matrix composites, we exploit the great strength of the ceramics and also avoid catastrophic brittle failure of the fillers.

Composites of polymers with particulate fillers have generated considerable interest owing to desirable improvement in certain properties for various applications.<sup>5–10</sup> In recent times, researchers are exploring the possible use of waste materials like fly ash (FA) and cenospheres (CS) in composites to produce good materials for a wide range of applications.<sup>11–14</sup> Coal fly ash can replace clay, sand, limestone, and gravel, and save the energy costs of mining such materials. The class 'C' fly ash and cenospheres are hollow silica–alumina microspheres, with similar components but varying composition. The incorporation of these low density (0.6–0.9 g/cc) and low-cost particulates into polymer matrix reduces the consumption of the resin material and improves the bulk properties of composites.<sup>15</sup>

There are only few investigations on the mechanical properties of fly ash filled polymer composites reported so far. Use of cenospheres, fly ash, and calcium aluminosilicate (CAS) as fillers in the making of polystyrene matrix composites can reduce the density of composite material while maintaining or increasing their strength, making these light-weight composites very desirable for the automotive, aircraft/aerospace industries.

Keeping this aspect in mind, we report in this article, a study on the mechanical and microstructural properties of polystyrene - fly ash/cenospheres/calcium aluminosilicate composites using Positron

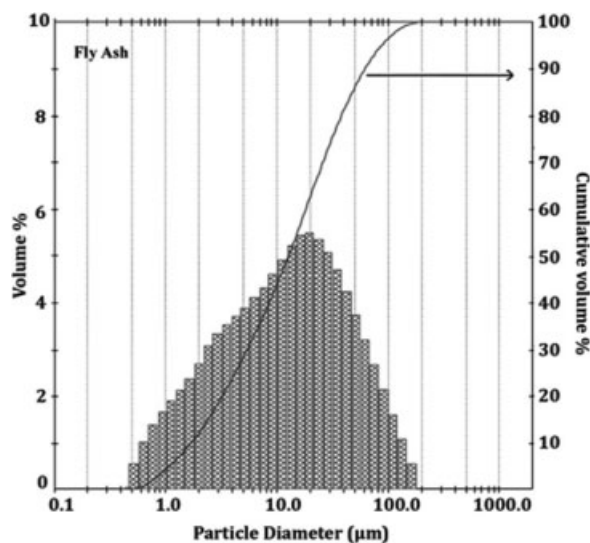
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Lifetime Spectroscopy (PLS) and Differential Scanning Calorimetry (DSC). Tensile modulus (TM), tensile strength (TS), elongation at break (EB) data have been analyzed as a function of filler loading, particulate size and the possible interactions between matrix and fillers. For this particle filled composite materials, it is important to clarify the reinforcement effect of fillers. A variety of theoretical and experimental studies have been reported on the reinforcement effect in terms of macroscopic mechanical properties.<sup>16</sup> But, the fundamental mechanisms for mechanical property improvement are not yet completely understood.<sup>17</sup> Importantly, the influence of composite microstructure on its mechanical properties need to be well established. Free volume is an important microstructural property that involves localized regions of holes, defects, and molecular segments that rearrange cooperatively for plastic flow to occur,<sup>17</sup> thereby influencing a number of physicochemical behaviors of polymeric materials. Therefore, it is interesting to correlate the free volume with mechanical properties of polymer composites an attempt not being done often. This, we accomplish by employing PLS, a sophisticated tool used for direct measurement of the nanometer sized free volume holes and their relative number density popularly used in the field of polymers and polymer blends.<sup>18,19,20</sup> DSC studies have been carried out to assess the thermal stability of the composites influenced by different fillers.

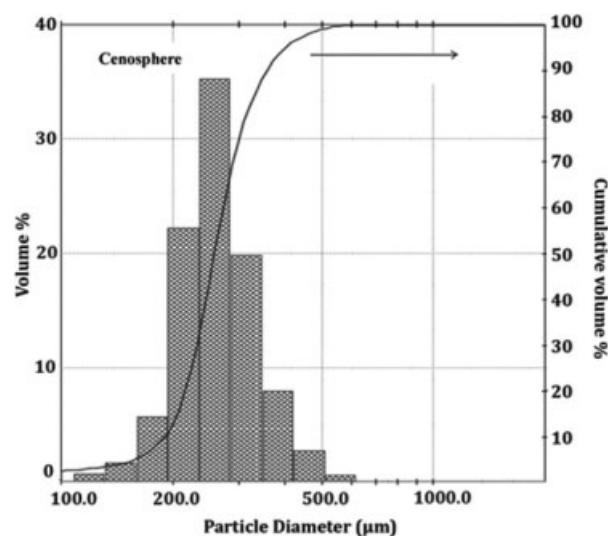
## EXPERIMENTAL

### Materials

Materials used in the preparation of samples were procured from the following suppliers: Polystyrene

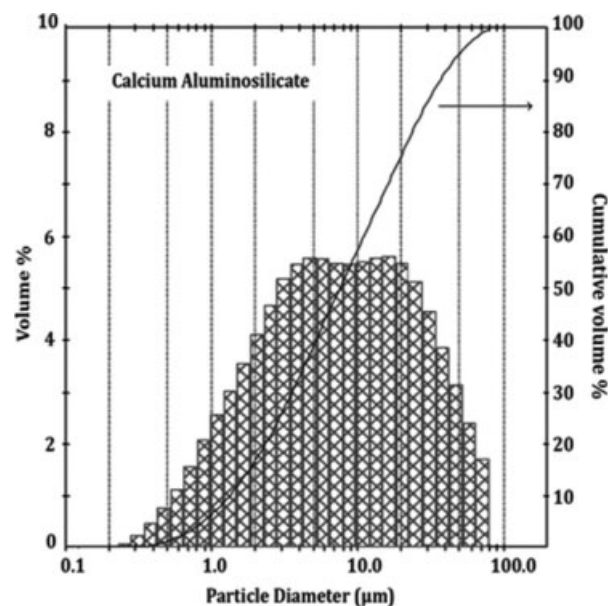


**Figure 1** Particle size distribution (PSD) of fly ash filler particulates.



**Figure 2** Particle size distribution (PSD) of cenospheres filler particulates.

was procured from M/s Sigma-Aldrich Chemicals. Its weight average molecular weight was determined to be 190,000 g/mol and density 1.04 g/cc. The fly ash and cenospheres samples were collected from Ramagundam super thermal power plant, India. Calcium aluminosilicate was obtained from commercial sources. The average particle size of FA, CS, and CAS particulates used in this study was determined by performing the particle size distribution (PSD) measurement (Figs. 1–3). The fly ash was found to have an average particle diameter of 19.00  $\mu\text{m}$  with specific surface area 1.5957  $\text{m}^2/\text{g}$ , cenospheres are of average diameter 256.30  $\mu\text{m}$  with specific surface area 0.0564  $\text{m}^2/\text{g}$  and calcium aluminosilicate



**Figure 3** Particle size distribution (PSD) of calcium aluminosilicate filler particulates.

particles are of average diameter 4.82  $\mu\text{m}$  with specific surface area 1.7738  $\text{m}^2/\text{gm}$ . The density for fly ash, cenospheres, and CAS was respectively 0.90 g/cc, 0.60 g/cc, and 2.46 g/cc. From the figures it is evident that both FA and CS particles come with almost unimodal size distribution. However, CAS seems to have unimodal but a wide range of sizes.

### Preparation of the Samples

Polystyrene (PS) matrix: The weighed fractions of PS were dissolved in methyl ethyl ketone (solvent) and heated at 60°C with continuous stirring for 2 h when a homogenous transparent liquid was obtained. Different percentages of additives (FA, CS, CAS) were weighed and mixed with dispersed PS, with continuous stirring for 1 h when a homogenous thick liquid was obtained and this was cast into a specially made glass mold coated with Vaseline release agent. The paste so obtained was left for 3 days at room temperature ( $25 \pm 2^\circ\text{C}$ ) to evaporate the solvent. The casted samples were removed and cured at the same temperature for 25 days. The cured samples were used in measurement of different properties.

### Mechanical property measurements

Mechanical properties namely tensile strength, tensile modulus, and elongation at break for different compositions of the composites were measured according to ASTM D 638 standard using universal testing machine (UTM), model 4302 H50 KM, 50KN, Hounsfield, UK. Three samples were tested for each composition and the average value has been reported.

### Differential scanning calorimetry measurements

The glass transition temperatures ( $T_g$ ) of the pure polystyrene and composites with fly ash, cenospheres, and calcium aluminosilicate were measured using a Mettler FP90 DSC instrument. Samples of approximately 5 mg weight were heated from 40 to 160°C at a heating rate of 20°C/min.

### Positron annihilation lifetime (PAL) studies

Free volume cavity size and their content in Polystyrene and its composites with fly ash, cenosphere, and calcium aluminosilicate as fillers have been experimentally determined by using Positron Lifetime Spectrometer. A brief description of the basis of the technique is given here. For more details one can refer to our earlier published work.<sup>19–22</sup> In brief, the positron lifetime method can be explained as follows: When an energetic positron enters a condensed medium like a polymer or a polymeric system, it ther-

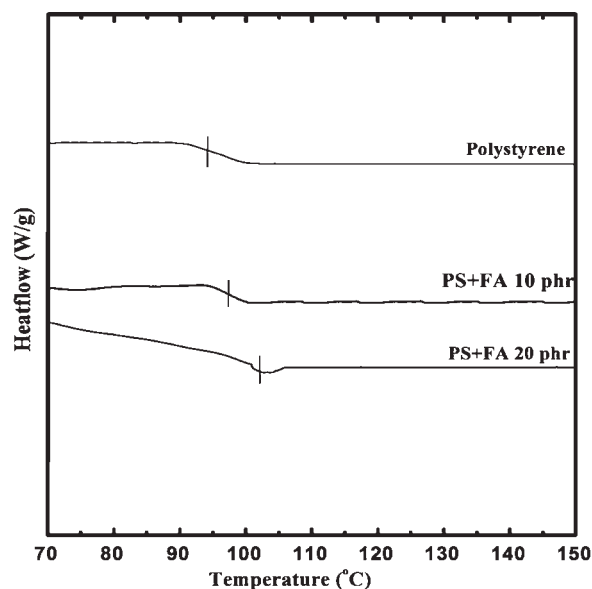
malizes quickly and thereafter annihilates with the electrons of the medium via free annihilation or from a localized state (trapped state) or forms a bound state with an electron of the medium called Positronium (Ps) atom. The free annihilation is the one, in which positron annihilates with an electron of the medium, without getting trapped into defects of the medium. Free annihilation lifetime is of the order of 200 ps. Secondly, some of the positrons may get trapped into defects like 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 antiparallel) annihilates with a lifetime of 125 ps. The *ortho* state (*o*-Ps) (particle spins parallel) annihilates with a lifetime of 140 ns in free space. 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 gets reduced to few nanoseconds. The *o*-Ps predominantly annihilates from the free volume cavities present mainly in the amorphous domains of the polymer. The lifetime of *o*-Ps depends on the overlap of the Ps wave function with the wave function of electron in the free-volume cavity. Hence, larger is the hole size, smaller is the overlap and hence longer the lifetime. So, *o*-Ps pick-off lifetime ( $\tau_3$ ) and its intensity ( $I_3$ ) are a measure of the free volume size and their relative number density, respectively in condensed medium.<sup>23</sup> Positron lifetime measurements were carried out using a standard fast-fast coincidence system with conically shaped BaF<sub>2</sub> scintillators, coupled to photomultiplier tubes of type XP2020/Q with quartz window as detectors. The coincidence lifetime spectrometer had a time resolution of 220 ps. All measurements were made at room ambience. The source sample sandwich geometry was used for positron lifetime measurements. A 17  $\mu\text{Ci}$  Na<sup>22</sup> positron source deposited at the centre of a square kapton foil of 0.0127mm thick was used.

The experimental and data collection procedural details of this technique could be found in references.<sup>19,22</sup> Typical spectrum accumulation time in the present system was around 2 h with more than 10<sup>6</sup> 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 computer program RESOLUTION.<sup>24</sup> The lifetime spectra so acquired were analyzed using PATFIT-88 computer program<sup>24</sup> with proper source and background corrections applied. The analysis was done with three lifetime components fit. This resulted in better  $\chi^2$  values and standard deviations. For each sample, three lifetime spectra were accumulated and analyzed. The reproducibility of the results was found to be very good.

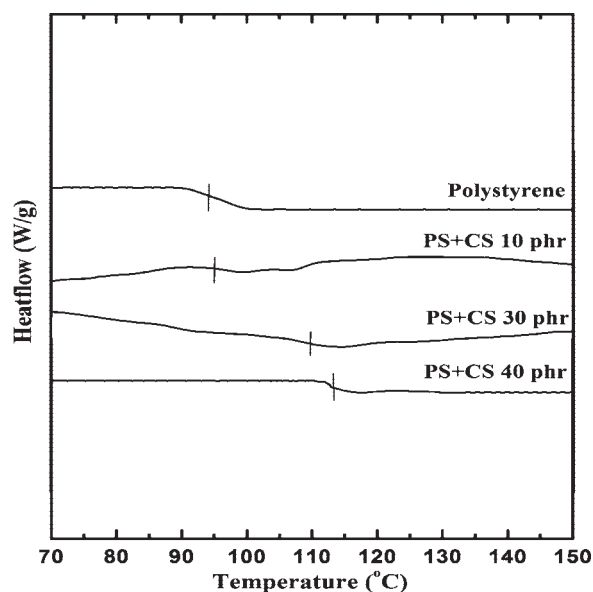
## RESULTS AND DISCUSSIONS

### Differential scanning calorimetry results

Figures 4 and 5 depict DSC scans for polystyrene and its composites with fly ash and cenospheres, respectively. In either case, the value of  $T_g$  was found to increase with increased filler content. For the FA loaded composite the  $T_g$  value increased from 97 to 102°C (20 phr), a shift of almost 5°C compared to polystyrene pure sample. For CS loaded composite  $T_g$  increased to 109.7°C at 30 phr, which further shifted to 113.5°C for 40 phr compared to pure polystyrene sample. The shifting to higher value in  $T_g$  can be interpreted as due to improved interaction between filler and the polymer matrix (details provided at the end of this section), good adhesion at the interface and hence be inferred as improved thermal stability of the composites. From Figure 6, we see that for calcium aluminosilicate filled composite a decrease in  $T_g$  for 15 phr (89.7°C) is observed compared to polystyrene pure sample. This decrease in  $T_g$  with lower filler load may be attributed to less number of interactions of fillers with polystyrene due to higher density and hence poor dispersion of CAS particles.<sup>25</sup> Thereafter, we observe increase in  $T_g$  for 20 and 40 phr of calcium aluminosilicate (95.6 and 101°C). The increase in  $T_g$  is in consonance with inference detailed earlier. For the results observed earlier, it is also believed that the elevated  $T_g$  due to fillers can be attributed to reduced chain flexibility.<sup>26</sup> The cenospheres owing to their low density (0.6 g/cc) appear to disperse well in the matrix and so hinder the motion of segments of the macromolecules more effectively, thus leading to a higher value of  $T_g$  for CS-polystyrene



**Figure 4** DSC scans of pure PS and fly ash filled composites.

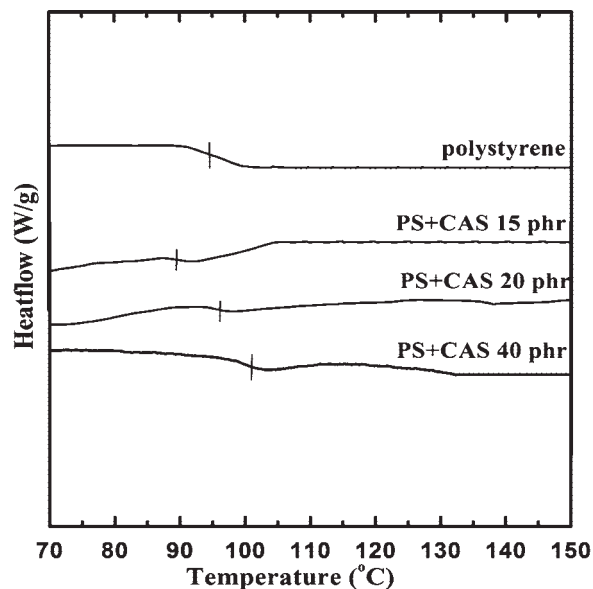


**Figure 5** DSC scans of pure PS and cenospheres filled composites.

composite than FA (0.9 g/cc) and CAS (2.46 g/cc) filled composites.

### Free volume and its correlation to mechanical properties

The measured positron lifetime spectra were resolved into three lifetime components  $\tau_1$ ,  $\tau_2$ , and  $\tau_3$ , with intensities  $I_1$ ,  $I_2$ , and  $I_3$ , respectively. The general interpretation of these lifetime components is as follows: The shortest lifetime component  $\tau_1$ , with intensity  $I_1$  is attributed to p-Ps and free positron annihilations.  $\tau_2$  with intensity  $I_2$  is usually



**Figure 6** DSC scans of pure PS and calcium aluminosilicate filled composites.

**TABLE 1**  
**Mechanical Properties and PLS Data for PS/FA Composites**

Sample	$\tau_3 \pm 0.02$ (ns)	$I_3 \pm 0.28$ (%)	$V_f \pm 0.6$ ( $\text{\AA}^3$ )	$F_v$ (%)	TS (MPa)	TM (MPa)	EB (%)
Polystyrene (PS)	1.98	24.73	95.28	4.24	5.18	41.69	23.92
PS + FA 5 phr	2.05	23.36	102.22	4.29	3.28	30.76	10.00
PS + FA 10 phr	2.04	22.75	100.89	4.13	3.84	45.48	9.93
PS + FA 15 phr	2.01	25.57	97.84	4.50	4.94	101.33	8.05
PS + FA 20 phr	1.96	24.87	93.59	4.19	5.23	102.93	6.02

attributed to trapped positrons annihilation at defects present in the crystalline regions or at crystalline – amorphous interface regions. The longest lifetime  $\tau_3$  with its intensity  $I_3$  is due to pick-off annihilation of o-Ps from the free volume sites in the amorphous regions of the polymeric material.<sup>27</sup> This is the parameter of importance in polymers and polymer-based systems because it provides the information on free volume size and its relative content. From  $\tau_3$ , we can calculate the radius of the free volume hole or cavity ( $R$ ) using the following relation developed by Nakanishi et al.<sup>27</sup> based on the original works of Tao and Eldrup.<sup>28–30</sup>

$$(\tau_3)^{-1} = 2 \left[ 1 - \frac{R}{R_0} + \frac{1}{2\pi} \sin\left(\frac{2\pi R}{R_0}\right) \right] \text{ns}^{-1} \quad (1)$$

Where  $R_0 = R + dR$  and  $dR$  is an adjustable parameter. By fitting eq (1) with  $\tau_3$  values for known hole sizes in porous materials like zeolites, a value of  $dR = 0.166$  nm was obtained. Using this value in eq (1), the  $R$  values for measured  $\tau_3$  were calculated and then the average size of the free volume holes  $V_f$  is calculated as  $V_f = (4/3) \pi R^3$ . Then the fractional free volume  $F_v$  is calculated as  $F_v = CV_f I_3$ , in which  $C$  is a constant and its value<sup>23</sup> of  $0.0018 \text{ \AA}^{-3}$  is used in calculating the fractional free volume of the polystyrene and the composites.

The measured mechanical properties of the pure polystyrene, fly ash up to 20 phr, cenospheres, and calcium aluminosilicate filled composites up to 40 phr and their corresponding free volume data are shown in Tables I–III. From the tables we can see that on addition of fillers the mechanical properties namely TS and TM increases and EB decreases with increasing filler phr content while the free volume hole size decreases with increasing filler content.

This shows that additions of fillers are important to the matrix, and the fillers initiate interaction between polystyrene and fillers and adhesion at the interface.

It has been well established that in polymeric systems, macroscopic properties such as tensile strength, modulus, and toughness depends on the microstructural properties of the system. This microstructural property in the present case is free volume cavities and their concentration, which had been used in understanding visco-elastic properties of many polymeric systems.<sup>18–23,25–33</sup> This property depends on chain morphology of the system i.e. they depend on the ease, with which the chains can slide past each other under the influence of any external force. Therefore, decrease in  $V_f$  due to close packing, provides less space for the chain movement and hence we expect TS and TM to be greater if the free volume is less, i.e., when the  $V_f$  is smaller and this behavior can be observed from the data in Tables I–III.

In Figure 7, we show the variation of  $V_f$ , TS, TM, and EB as a function of FA filler content: At low filler content (i.e. upto 5 phr) we see a decrease in all the mechanical properties. With more particles loading, the TS and TM show an increase, while EB stabilizes. At all composition of particle loading we observe a reverse correlation between free volume size  $V_f$  and mechanical properties namely TS and TM. This was also true in the other composites studied here and thus the mechanical properties appear to correlate well with the positron parameters in our study.

The initial decrease in EB with the addition of fly ash could be seen as little brittleness brought in the composites and may be attributed to less elasticity between PS and the filler.<sup>34–36</sup> Normally addition of rigid particulate fillers to a polymer matrix decreases

**TABLE 2**  
**Mechanical Properties and PLS Data for PS/CS Composites**

Sample	$\tau_3 \pm 0.02$ (ns)	$I_3 \pm 0.28$ (%)	$V_f \pm 0.6$ ( $\text{\AA}^3$ )	$F_v$ (%)	TS (MPa)	TM (MPa)	EB (%)
Polystyrene(PS)	1.98	24.73	95.28	4.24	5.18	41.69	23.92
PS + CS 10 phr	2.05	22.95	101.78	4.21	3.24	30.44	14.20
PS + CS 20 phr	1.98	24.23	95.82	4.15	3.52	40.18	10.31
PS + CS 30 phr	1.98	19.16	94.85	3.27	4.07	113.91	5.15
PS + CS 40 phr	1.97	16.25	94.02	2.75	4.32	117.48	3.80

TABLE 3  
Mechanical Properties and PLS Data for PS/CAS Composites

Sample	$\tau_3 \pm 0.02$ (ns)	$I_3 \pm 0.28$ (%)	$V_f \pm 0.6$ ( $\text{\AA}^3$ )	$F_v$ (%)	TS (MPa)	TM (MPa)	EB (%)
Polystyrene(PS)	1.98	24.73	95.28	4.24	5.18	41.69	23.92
PS + CAS 5 phr	1.98	27.65	95.71	4.76	5.00	78.52	9.35
PS + CAS 10 phr	1.99	28.25	96.13	4.88	4.98	75.47	9.85
PS + CAS 15 phr	2.01	22.75	97.41	3.98	4.63	70.76	9.90
PS + CAS 20 phr	1.98	22.34	95.28	3.83	5.30	92.93	9.50
PS + CAS 30 phr	1.95	21.79	94.85	3.72	5.68	110.16	5.87
PS + CAS 40 phr	1.96	21.61	92.76	3.61	9.97	121.97	5.00

the elongation at break owing to the overall stiffening and load sharing provided by the filler.<sup>37</sup> Only in rare instances, if there is a good reinforcement between polymer and the filler, the fracture goes from particle to particle rather than following a direct path, and these filled polymers have nearly equal elongations at break when compared with pure polymer.<sup>34</sup> Filler-PS composites seems to suggest good adhesion in terms of nearly same elongation at break values.

In Figure 8, we show the results for CS filled composites. We observe here also, a similar variation in  $V_f$  and the mechanical properties like fly ash filled ones. However, after the initial drop in TS and TM,

the increase observed for higher filler content is less compared to FA filled composites. The increase in  $V_f$  at lower CS phr up to 10 phr is possibly due to inability of the fillers to support stresses transferred from the polymer matrices during the loading process.<sup>35</sup>

From Figure 9(a), we see again a decrease in EB with increasing CAS filler and increase in  $V_f$  up to 15 phr and then decrease with increasing of CAS filler. Figure 9(b,c) shows the variation in tensile strength (TS), modulus (TM), and free volume hole size ( $V_f$ ). As can be seen, the correlation among  $V_f$ , TS and TM is more or less of same trend observed for the previous composites but with a difference.

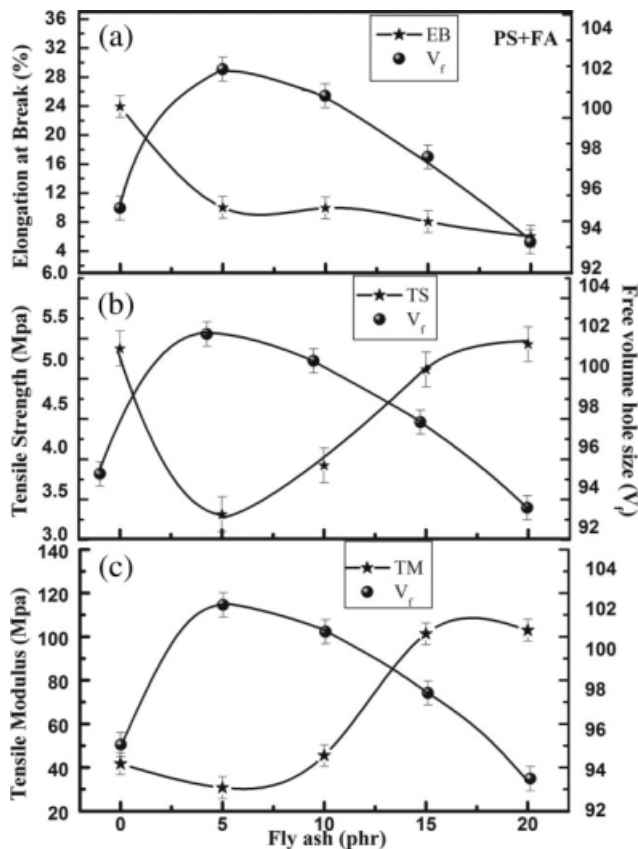


Figure 7 Plot of Free volume hole size,  $V_f$  against (a) percent elongation at break, (b) Tensile Strength, (c) Tensile modulus for polystyrene/Fly ash composites.

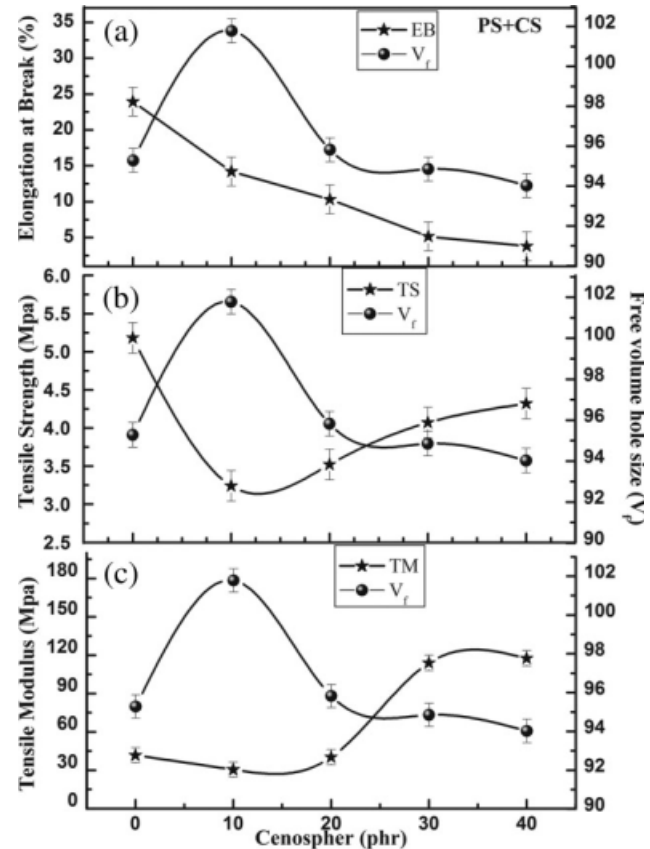
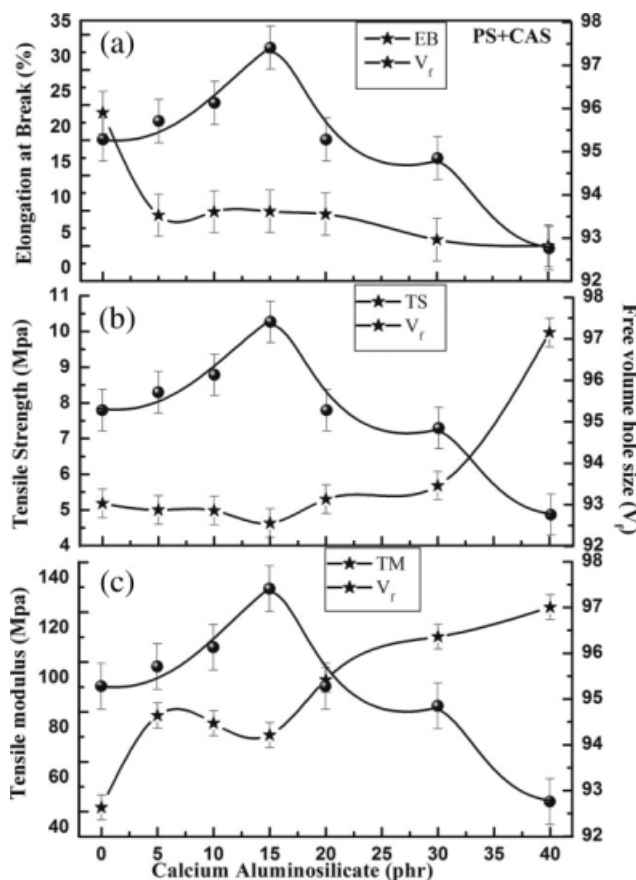


Figure 8 Plot of Free volume hole size,  $V_f$  against (a) percent elongation at break, (b) Tensile Strength, (c) Tensile modulus for polystyrene/Cenosphere composites.



**Figure 9** Plot of free volume hole size,  $V_f$  against (a) percent elongation at break, (b) Tensile Strength, (c) Tensile modulus for polystyrene/Calcium aluminosilicate composites.

That is TS changes by large magnitude. TS remains more or else at the same value up to 15 phr loading and thereafter it increases from around 5–10 Mpa at 40% CAS loading.

From the earlier discussion, it is clear that there is a significant improvement in mechanical properties (TS and TM) of calcium aluminosilicate filled composites compared to fly ash and cenospheres filled ones. The factors effecting to this end result may be manifold. The particle size and composition, and particle–matrix interaction appear to be the key factors. In a recent review on this subject, Fu et al.<sup>38</sup> have discussed the dependence of mechanical properties of particulate–polymer composites on the particle size, particle–matrix interface adhesion and particle loading. They conclude that: composite strength and toughness are strongly affected by all these three factors, especially particle/matrix adhesion, because strength depends on effective stress transfer between filler and matrix, and toughness/brittleness is controlled by adhesion. Various trends of the effect of particle loading on composite strength and toughness have been observed due to the interplay between these three factors, which cannot always be

separated. For poorly bonded particles, the stress transfer at the particle/polymer interface is inefficient. Discontinuity in the form of debonding exists because of nonadherence of particle to polymer. Thus, the particle cannot carry any load and the composite strength decreases with increasing particle loading. However, for composites containing well-bonded particles, addition of particles to a polymer will lead to an increase in strength especially for nanoparticles with high surface areas. The composite stiffness (tensile modulus) depends significantly on particle loading, not particle/matrix adhesion, as the fillers have much larger modulus than the matrix. There is also a critical particle size, usually in nano-scale, below which the composite stiffness is greatly enhanced due to the significant effect of the particle size, probably caused by the much larger surface areas imparting a “nano”- effect.

The Particle Size Distribution (PSD) measurements in this study show that calcium aluminosilicate are of smaller size (4.82  $\mu\text{m}$ ) than fly ash particles (19.0  $\mu\text{m}$ ) and cenospheres (256.3  $\mu\text{m}$ ). The higher specific surface area of CAS and hence more efficient stress transfer between it and the matrix may be one of reasons for the significant improvement of the mechanical properties (mainly the TS, as it is sensitive to filler size) of 40 phr CAS loaded composite. As the fillers are of microsize and not nanosize, the size-effect may not be a too significant factor unlike in nanoparticles. The general fact that particle loading improved the mechanical properties (TS and TM) of all the composites clearly suggests that the interfacial adhesion between matrix and filler has improved with loading, which happens for well-bonded particles. This is further confirmed by the overall decreasing trend of  $V_f$  and increased thermal stability of composites (from increased  $T_g$  results from DSC) compared to the neat polymer. It is known that when silica is loaded directly into a matrix, they tend to agglomerate among themselves (more so at higher loading) resulting in a filler–filler interaction only due to the hydroxyl groups of silica,<sup>39</sup> but to be remembered that hydrogen bonding is not possible with polystyrene, as a result poor interfacial bonding between matrix and filler occurs. However, the improved mechanical properties in our study vitiate this possibility and imply a good interfacial bonding between matrix and filler.

CAS, besides, being small in size, has also the highest amount of silica. As may be seen, the mechanical properties have improved with increase in silica content of the fillers. We therefore, believe that higher silica content of calcium aluminosilicate (73.64%) compared to cenospheres (60%) and fly ash (40%) is particularly responsible for the enhancement in mechanical properties in calcium aluminosilicate filled composites. We anticipate this due to

different possible interactions between PS matrix and the silica filler, namely the Van der Waals forces of attraction, electrostatic attraction between the electron rich phenyl ring of PS matrix and the electro-positive silica of the filler particles. Based on a recent study, we can also expect a hydrophilic affinity of the PS surface to the hydroxyl groups of the silica.<sup>40</sup> The possibility of these interactions may result to an appreciable interfacial adhesion between the particles and the matrix (due to higher silica content CAS brings in more such interactions) thereby mechanical properties improved. Cenospheres and Fly ash, with lesser silica content, fail to establish similar amount of interaction with the matrix resulting in less improvement in mechanical properties.

### CONCLUSIONS

The mechanical properties, free volume data, and DSC results for PS/FA, PS/CS, and PS/CAS composites revealed the following facts:

- The presence of fly ash, cenospheres, and calcium aluminosilicate particulates in general reduced the tensile strength and modulus of the composites up to 5, 10, and 15 phr loading, respectively and thereafter an increase with increasing of fillers. The free volume cell size on the other hand increases up to 5, 10, and 15 phr and thereafter decreases at higher fillers content due to good interfacial adhesion.
- Presence of the fillers improved the thermal stability of the composites as the  $T_g$  of the composites increased as revealed by the DSC data due to increased filler matrix interactions.
- We found a good correlation among the free volume cell size  $V_f$ , and TS and TM for all the fillers and improvement is more in CAS filled composites due higher silica content resulting in more interactions between the polymer matrix and the filler.
- The particulate's size may be another factor influencing the mechanical properties to some extent.

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