

## Eco-friendly cardanol-based phenalkamine cured epoxy-cenosphere syntactic foams: Fabrication and characterisation

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**ABSTRACT:** The performance of epoxy/cenosphere syntactic foams cured using phenalkamine (PA) were analyzed and characterized. The PA system was found to cure faster at room temperature, had lower density, and lower water absorption values. The thermogravimetric analysis result implied higher thermal stability. The cure studies using DSC inferred faster cure reaction in the ambient temperature conditions. The compression studies confirmed that unlike the epoxy system based on conventional triethylenetetramine curative, PA-based system did not undergo brittle failure. This was also confirmed with the scanning electron microscope images. Dynamic mechanical analysis inferred the glass transition temperatures ( $T_g$ ) as 81.4 °C. The specific modulus and specific strength were higher for 40% cenosphere loading in PA-based syntactic foams. As the need for light weight core materials is continually increasing, there is a great possibility for the utilization of this novel bio-based curing agent to produce sustainable products. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 44189.

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### INTRODUCTION

In the current technological age, strength to weight ratio is a very important aspect.

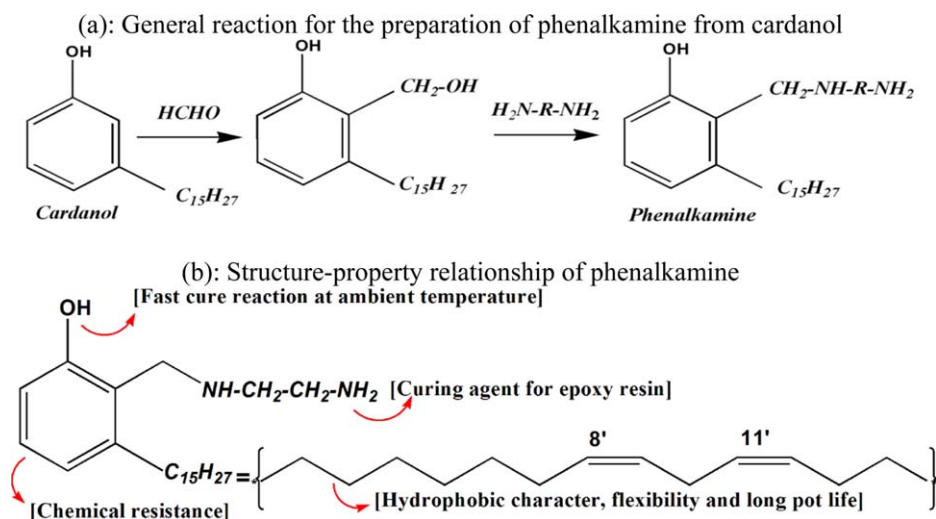
Syntactic foams are being extensively investigated mainly based on this motivating factor. These are well known for their unique physical properties such as stiffness, high compressive strength, low moisture absorption, and high thermal stability.<sup>1,2</sup> Hence, these are ideal materials for lightweight structural applications and buoyancy aid marine applications.<sup>3,4</sup> Syntactic foams are defined as particulate composites consisting of inorganic or polymeric hollow spheres dispersed in a polymeric, metallic, or ceramic matrix.<sup>5–8</sup> These can be employed as core materials in sandwich composites for weight sensitive structural applications.

In this study, epoxy resin was used as the matrix for the fabrication of syntactic foams. Epoxy resin is proven to be of high strength, stiffness, good chemical resistance, and electrical resistance in addition it can be cured without evolution of volatiles or by products.<sup>9</sup> Polyfunctional aliphatic amine—triethylenetetramine (TETA)—is one of the conventionally used curative for epoxy resins. It reacts with the epoxy group through the active amine hydrogen at ambient temperature. The cured product retains physical properties for a long-term, has an excellent chemical and solvent resistance. One major setback of this polymeric resin is its poor resistance to crack

initiation and growth. This is thus rendered as brittle along with low impact strength.<sup>10</sup>

The objective of this work was to reduce the brittleness of the epoxy matrix in an eco-friendly way. Here phenalkamine (PA), a new class of curing agent for epoxy was employed.<sup>11,12</sup> It is a bio-based curative synthesized from cardanol derived from cashew nut-shell liquid [Figure 1(a)]. Phenalkamine has a distinctive structure with diverse properties that are most sought-after. When they are used as a curing agent for epoxy these properties were also imparted to the cured system. Chemical resistance was imparted by aromatic backbone present in PA. The alkyl side chain was responsible for hydrophobic character, flexibility, and long pot life. The amine side chain reacted with the epoxide group present in the epoxy resin and resulted in highly crosslinked product. The name PA aptly stated alkyl-aromatic structure [Figure 1(b)] with an active amine group that aided as an epoxy curing agent. Presence of the phenolic OH group was responsible for high activity of PA even at ambient temperature. These curatives were known for low toxicity which makes them eco-friendly. Efficient curing of the resin was achieved at ambient temperature which was confirmed by Differential Scanning Calorimetry (DSC) studies. The brittleness of the epoxy resin was reduced because of the flexibility provided by the long linear side chain present in cardanol.<sup>11</sup>

The possibility of tailoring the syntactic foams according to the required product makes this class of materials very unique. The



**Figure 1.** (a) General reaction for the preparation of PA from cardanol. (b) Structure–property relationship of PA. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

desired properties can be achieved by choosing the appropriate matrix and hollow spheres. Additional phase like hollow microspheres in optimum loadings can decrease the weight and at the same time increase performance of epoxy matrix.<sup>13,14</sup> Maximum incorporation of the hollow spheres helps in achieving low density materials with high specific strength.<sup>15–17</sup> It also helps to decrease the cost of preparation. Cenosphere is one of the by-products obtained from thermal power plants. Cenosphere cannot be disposed directly in to the environment and these particles find only a few environmental friendly applications.<sup>18</sup> In an objective to utilize these by products, cenosphere was used as the particulate filler for the preparation of the syntactic foams. These ceramic hollow microspheres had good compatibility with epoxy and consequently did not require any modification or surface treatment.

Previous studies are focused on estimating the mechanical properties of conventionally prepared epoxy syntactic foams.<sup>8,11,14–16,18,19</sup> An attempt was made in this study to analyze the performance of bio-based PA cured epoxy–cenosphere syntactic foams using various techniques like DSC, thermogravimetric analysis (TGA), scanning electron microscope (SEM), dynamic mechanical analyzer (DMA), hygrothermal studies, and compression studies.

## EXPERIMENTAL

### Constituent Materials

Epoxy resin (LY556) was purchased from Javanthi enterprises Pvt., Ltd., India. Cardanol-based PA curative was obtained from Sathya Cashews Pvt., Ltd., India. Cenosphere (CIL 150) was purchased from Cenosphere India Pvt. Ltd., India. The details of CIL 150 are shown in Table I. Sea water was fetched from Bay of Bengal. All materials were used without any chemical modification or surface treatment.

### Specimen Preparation

Phenalkamine-based epoxy–cenosphere syntactic foams were prepared by stir-casting technique. Cenosphere are light weight particles with a bulk density of 0.4 g/cc. Owing to such a low

density of cenosphere when compared to resin they tend to float on top. So a calculated quantity of cenosphere was added in parts with the epoxy. After addition of each part, the mixture was thoroughly stirred such that the cenosphere was completely wetted and dispersed in the epoxy matrix. Generally, lower percentage of cenosphere was avoided due to the problem of filler floatation. Stirring time was more for lower weight percentage of cenosphere to ensure uniform distribution.<sup>20</sup> Required

**Table I.** (a) Sieve Analyses and (b) Chemical Composition of Cenosphere (CIL 150) as Provided by the Supplier

(a)		
S. No.	Particle size	Percentage
1	+ 30 # (500 Micron)	Nil
2	+ 60 # (250 Micron)	Nil
3	+100 # (150 Micron)	Nil
4	+120 # (125 Micron)	Nil
5	+150 # (106 Micron)	0–10
6	+ 240 # (63 Micron)	70–95
7	–240 #	0–30
(b)		
S. No.	Compound	Weight % (%)
1	SiO <sub>2</sub>	52–62
2	Al <sub>2</sub> O <sub>3</sub>	30–36
3	CaO	0.1–0.5
4	K <sub>2</sub> O	1.2–3.2
5	Fe <sub>2</sub> O <sub>3</sub>	1.0–3.0
6	TiO <sub>2</sub>	0.8–1.3
7	MgO	1.0–2.5
8	Na <sub>2</sub> O	0.2–0.6
9	Carbon dioxide	70
10	Nitrogen	30

**Table II.** Theoretical Density, Measured Density, and Void Fraction of PASF

CIL (wt %)	Sample name	PASF density (g/cc)			Void fraction (%)
		Theoretical	Measured	Relative	
0	PA0	1.04	0.99	1.00	5
10	PA10	0.97	0.91	0.91	6
20	PA20	0.91	0.86	0.86	5
30	PA30	0.84	0.77	0.77	8
40	PA40	0.78	0.69	0.69	12
50	PA50	0.72	0.62	0.62	14

quantity of the curative was added to this mixture and stirred further according to the pot life of the curative. The pot life was nearly 18 min for the PA curative derived from cardanol. This may be due to the long side chain present in cardanol which reduces the mobility of the curing agent thereby increasing the pot life.<sup>11</sup> Syntactic foams were fabricated using equal quantities of PA and epoxy on weight/weight basis. The porosity fraction in syntactic foams was varied by the addition of different weight percentages of cenosphere (0–50). Mixing was done at very low speed to minimize damage to the cenosphere particles. The homogenous mixture was poured into the greased mold [150 mm × 150 mm × 13 mm] from one corner. A wooden dipper tilted at an angle of 45° was used to pour the mixture in order to eliminate entrapment of air. Silica wax was used as a greasing agent to prevent adhesion between the mold and polymeric material. During the fabrication process, vacuum or pressure were avoided to prevent fracture of the cenosphere particles.

The fact that air gets trapped in the matrix during mechanical mixing cannot be ruled out and it remains in the cast syntactic foam. The presence of voids is detrimental as it weakens the foam and may lead to increased moisture absorption.<sup>16</sup> The percentage of air entrapped in the matrix is termed as void fraction. The rule of mixture was used to calculate the theoretical density which was consecutively used to calculate the void fraction ( $V_v$ ) using eq. (1).

$$V_v = [(\rho_{th} - \rho_m) / \rho_{th}] \times 100 \quad (1)$$

where,  $\rho_{th}$  and  $\rho_m$  represents the theoretical and measured densities correspondingly. The void fractions for different compositions of syntactic foams are given in Table II.

The crosslinking process for all the molds was completed after 24 h at room temperature. The casts were then post cured in oven at 100 °C for 3 h. High temperature was avoided to prevent the heat induced stress in the syntactic foams. The molds were cut for specific tests according to the ASTM standards. The following terminology has been used in the subsequent discussions:

- Epoxy-PA as PASF.
- 0–50 percentage of cenosphere in epoxy-PA syntactic foams as [PA0, PA10, PA20, PA30, PA40, PA50]
- For hygrothermal studies, room temperature as (RT), high temperature as (HT), deionized water as (DI), and sea water as (SW)

## CHARACTERIZATION

The density of syntactic foams was measured according to the ASTM C 271-94. Theoretical density was calculated as per ASTM standard D2534-9. Chemical structure of PA curative was studied using Agilent Cary630 FTIR. The frequency range of 400–4000  $\text{cm}^{-1}$  was used to measure the IR spectra. DSC Q20 V23.10, TA instrument was used for cure studies neat epoxy-PA systems. The extent of cure after 8, 16, 24 h and post cured samples were analyzed along with freshly prepared samples. About 6–7 mg of the prepared samples were analyzed from 35 °C to 350 °C at a scanning rate of 10 °C/min under nitrogen atmosphere. The moisture absorption study was done as per ASTM D 5229-92 procedure B. Two different temperature conditions [room temperature (RT) and high temperature (HT)] and two different mediums [deionized water (DI) and sea water (SW)] were used for the study. High temperature samples were maintained at 70 °C. Specimens were immersed in moisture till they reached saturation stage. The saturated samples were evaluated for their compressive property after exposure to varying environments. Thermal properties were analyzed using SDT Q600 V8.0, TA instrument. Samples were analyzed from room temperature to 800 °C at a scanning rate of 20 °C/min. SEM analysis was done using Hitachi instrument with an accelerating voltage of 30 kV. As the syntactic foams were non-conducting in nature, samples were coated with gold before imaging. Neat PA cured sample and cenosphere filled epoxy syntactic foams were fractured by impact and then analyzed. Compressed samples were also studied for failure analysis. Rectangular specimens having a size of 50 mm × 10 mm × 3 mm were analyzed using a frequency of 1 Hz from room temperature to 200 °C at a heating rate of 2 °C/min using DMA (S II EXSTAR 6100 DMS). Compression tests were performed using Universal Testing Machine at a speed of about 1.3 mm/min. Edge wise compression and flat wise compression were carried out as per ASTM D695-94 and C 365-94.

## RESULTS AND DISCUSSION

### Effect of Cenosphere Loading on Density

Rule of mixtures states that density of syntactic foams is the summation of density multiplied by volume fraction of all the constituents (epoxy resin, PA curative, and cenosphere). When there is an increase in the content of constituent with lesser density, the overall density decreases proportionally. The density of cenosphere is comparatively lesser than the density of epoxy

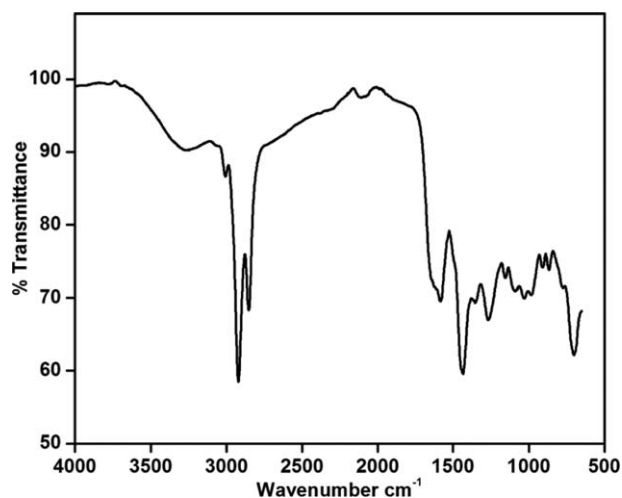


Figure 2. FTIR spectrum of the cardanol-based PA.

and PA. So, as the content of cenosphere increases in PASF, the density value decreases. The linear decrease in the density values with the increase in cenosphere content was in par with rule of mixtures.<sup>14,15,17–19</sup> With 50% loading of cenosphere, the density of the foams decreased by nearly 40% as shown in Table II. The density of the PASF samples was found to be lower almost close to one. This may be due to the free volume contributed by aromatic rings and the long alkyl side chain present in the cardanol from which the PA curative was derived. The relative density of syntactic foam was calculated as the ratio of density of syntactic foam to the density of neat sample. The values for different compositions are given in Table II.

#### Chemical Structure of Phenalkamine Curative

FTIR spectra (Figure 2) for the PA curative derived from cardanol exhibited characteristic absorption peaks for methylene group and C–H stretching for methyl group at  $2921\text{ cm}^{-1}$  and  $2852\text{ cm}^{-1}$  which confirmed the presence of the alkyl side chain of cardanol.<sup>11,13</sup> This was further confirmed by the peaks at  $3003\text{ cm}^{-1}$  for C–H stretching, characteristic for alkene and  $774\text{ cm}^{-1}$  for C–H out-of-plane bend. These peaks can be

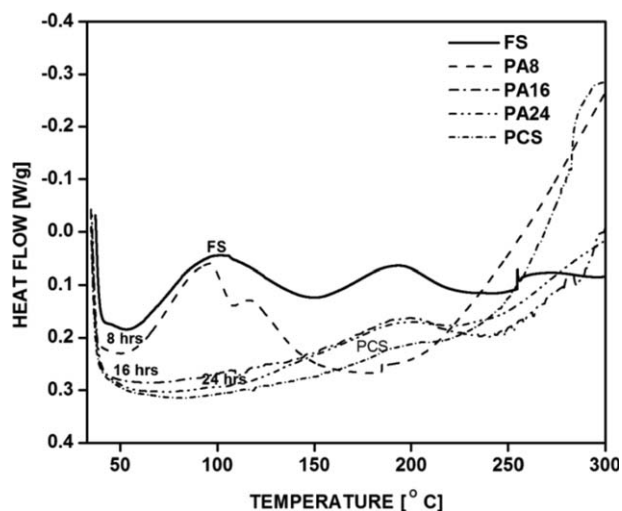


Figure 3. DSC thermograms of PA cured epoxy.

observed in FTIR spectrum of cardanol which indicated that side chain remained almost unaltered and unaffected in the PA curative.<sup>11,12</sup> The presence of aromatic ring was confirmed by the peak observed at  $1584\text{ cm}^{-1}$  which is characteristic of stretch for C=C present in aromatic structures. The peak at  $1433\text{ cm}^{-1}$  representative of the phenolic O–H bond established the presence of the hydroxyl group present on the aromatic ring. Characteristic peak at  $1087\text{ cm}^{-1}$  and  $3269\text{ cm}^{-1}$  for C–N stretching and N–H stretching confirmed the presence of primary amine.

#### Cure Studies

The degree of cure at different time intervals for PA curatives was studied by measuring the heat of the reaction using DSC. This heat was generated by the epoxidic ring opening reaction which occurred when liquid epoxy resin was mixed with the curative.<sup>11,21</sup> From peak pattern and area (Figure 3) it was inferred that thermograms were affected by time which indicated the extent of completion of the reaction. The exothermic peak due to crosslinking reaction between the epoxide group in epoxy resin and the amine group in PA curative resulted in the cured product. The thermograms for PA16, PA24, and PCS samples did not show any exothermic peak below the temperature of  $150^\circ\text{C}$  which inferred that crosslinking had taken place to a good extent after 16 h of cure at room temperature. The presence of phenolic hydroxyl groups in PA [Figure 1(b)] acted as the acid catalyst and facilitated the ring-opening reaction of epoxy.<sup>11</sup> This facilitated in the fast cure reaction even at ambient temperatures. The second large hump in the curve at a higher temperature nearly  $200^\circ\text{C}$  was because of the reaction of the unsaturated sites present in the side chain of PA derived from cardanol.<sup>22</sup>

#### Effect of Cenosphere Loading on Hygrothermal Properties

High temperature samples were kept in a hot air oven maintained at  $70^\circ\text{C}$ . Closed containers were used to avoid the change in salt concentration and to minimize the evaporation. Samples were briefly taken out and care was taken to wipe off excess surface water before weighing the specimens at regular

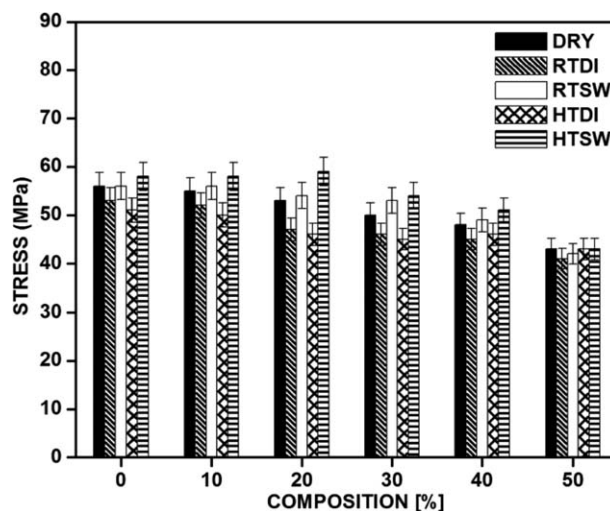


Figure 4. Failure strength of wet and dry PASF [Number of samples tested: 5].

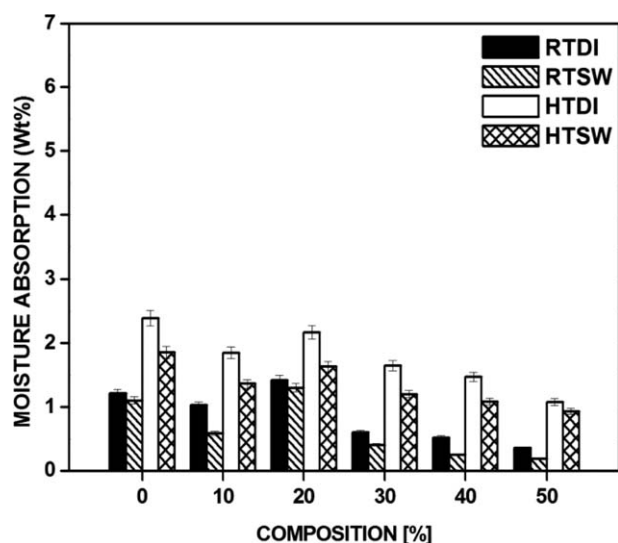


Figure 5. Moisture absorption of PASF at RT and HT condition.

intervals. To avoid thermal induced errors in weighing, the high temperature samples were brought to room temperature by placing them in air for about 5 min. Water diffused into the samples as the edges were not given any treatment to prevent absorption. Five samples were tested under each condition and the overall influence was depicted in the compression test conducted on the wet samples (Figure 4). Epoxy-based syntactic foams absorb less water and correlation of compressive strength with absorption level is uncommon.<sup>23</sup> Despite this fact, hygrothermal tests were conducted in order to get an opinion about moisture absorption in PASF. A marginal change in compressive strength due to the ingress of moisture in samples exposed to different hygrothermal conditions implied that moisture absorption had a minimal effect on syntactic foams. This fact was also supported by data found in the literature.<sup>23</sup> The compression tests conducted on the samples exposed to SW condition exhibited a rise in peak compressive strength compared to the dry sample. This ascendant trend could be credited to the presence of massive ions like the chloride ions, which being larger in size, exerted a compressive force. The need to overcome this compressive force resulted in higher strength values for seawater immersed samples. A similar trend was also found in literature.<sup>23</sup> Moisture absorption was reasonable in the PASF samples in both HT and RT conditions (Figure 5). This result was as expected because of the presence of hydrophobic long alkyl side

chain in PA.<sup>9</sup> According to cenosphere datasheet, the spherical cenosphere particles have virtually no water absorbing property. When the composition of such particles increased in the matrix, it aided in the reduction of moisture absorption. Hence the syntactic foams with 10% cenosphere showed a drop in moisture absorption value when compared to the neat resin samples. Besides, in general, syntactic foams are well known for low water absorption property. This was supported by various works found in literature.<sup>24</sup> Higher absorption values in HT condition may be due to enhanced kinetics owing to high temperature which aids the diffusion of water into the voids present in the samples. Water absorption in SW exposed samples was lower than DI exposed samples. This decrease in the absorption may be due to the presence of the big ionic species in the sea water.<sup>23</sup>

#### Effect of Cenosphere Loading on Thermal Properties

The char residue and  $T_{max}$  [thermal stability] values as given in Table III were found to increase with increase in percentage of thermally stable cenosphere in the resin.<sup>25</sup>  $T_{max}$  is defined as the temperature at which rate of decomposition is maximum. The percentage residue in the PA cured samples was more due to the presence of aromatic ring structure in the PA curative.<sup>26</sup>  $T_{10}$  is the temperature at which the sample experienced a weight loss of 10% due to degradation. Generally,  $T_{10}$  increased proportionally with cenosphere content but this trend was deviated in PA30. This discrepancy may be due to the minor error in the sample preparation.  $T_{max}$  [thermal stability] increased with the increase in cenosphere content by 11% for PA50 in comparison to the neat sample PA0. Epoxy syntactic foams based on conventional TETA curative were also fabricated and analyzed. PASF has  $T_{max}$  value which was comparable with the conventional TETA cured epoxy system as evident from Table III. Hence these syntactic foams were found to have a good thermal stability up a temperature of nearly 330 °C.

#### Morphology Characterization

The SEM images of samples that were fractured by impact revealed scales in epoxy system based on conventional TETA curative. These scales implied brittle nature [Figure 6(a)]. On the other hand, the smooth surface in PASF indicated the reduction of brittleness in an eco-friendly way by the use of bio-based PA curative [Figure 6(b)]. From the SEM micrographs of compression failed samples, brittle failure was evident in the epoxy system based on conventional TETA curative and reduced brittleness was obvious in the PA-based system [Figure 6(c,d)]. The micrographs

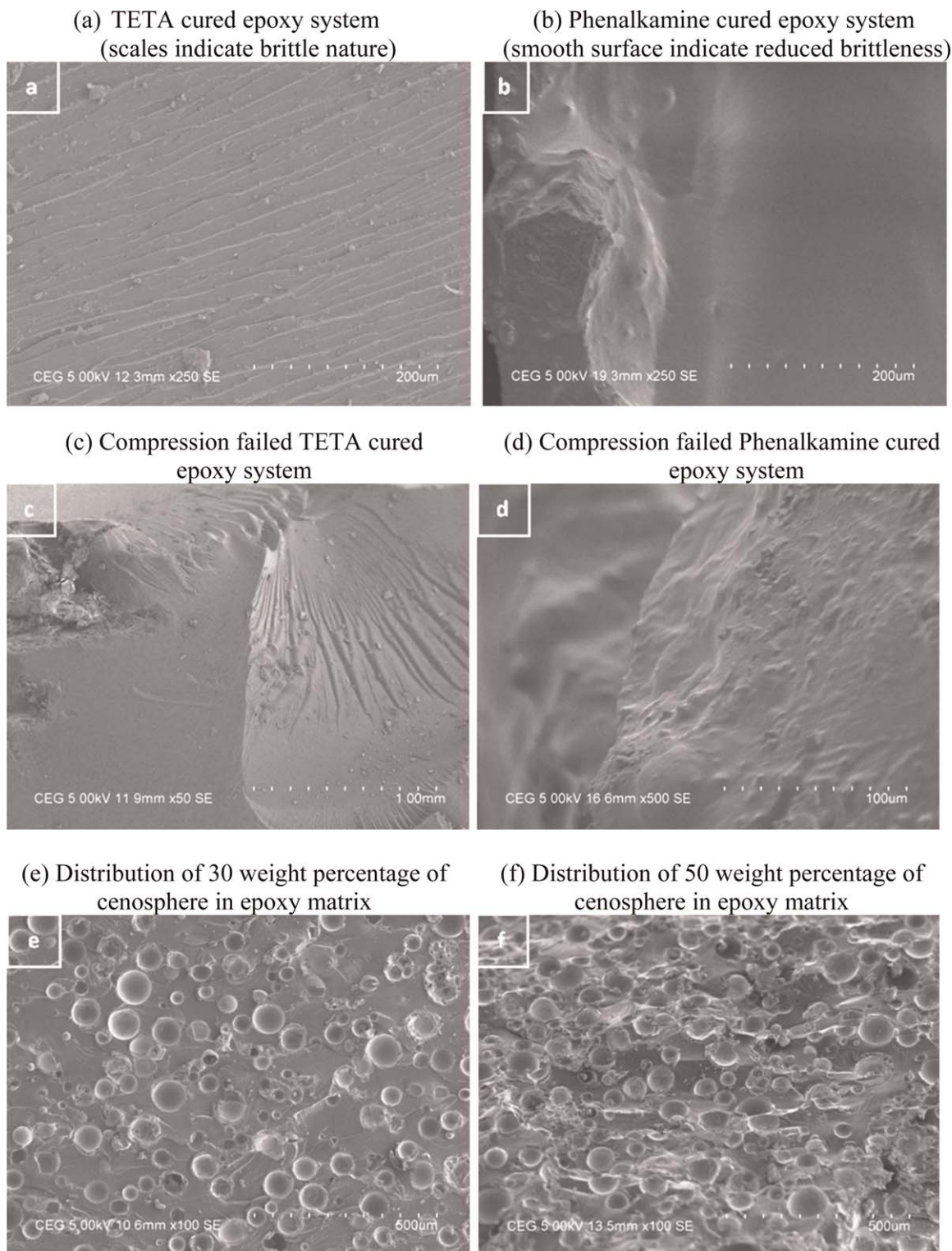
Table III. Thermogravimetric Values for PASF

S. No.	CIL (wt %)	$T_{10}$ (°C) (PASF)	$T_{max}$ (°C) (PASF)	Residue (%) (PASF)	$T_{max}$ (°C) (Conventional)
1	0	351	386	0.6	406
2	10	343	389	4.6	418
3	20	349	392	8.7	421
4	30	353	400	16.3	428
5	40	356	410	23.2	436
6	50	359	429	25.9	462

CIL: cenosphere,  $T_{10}$ : Temperature of 10% degradation,  $T_{max}$ : Temperature of maximum degradation.

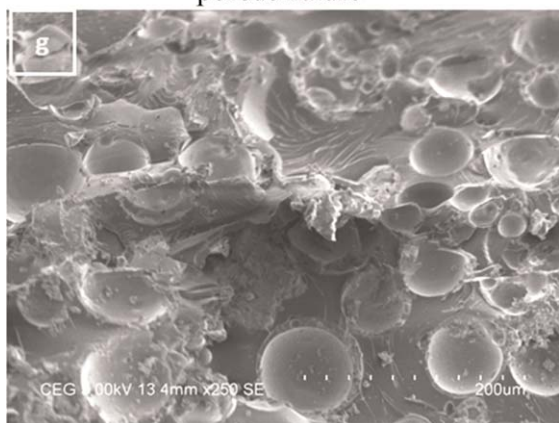
in Figure 6(e,f) revealed the uniform distribution of hollow spheres in 30 and 50 weight percentage of cenosphere in epoxy matrix. The SEM image of the failed cenosphere in the syntactic

foam subjected to compression test is given in Figure 6(g). The crushed shells of cenosphere particles when examined under high magnification clearly depicted the porous nature. The walls of



**Figure 6.** SEM images. (a) TETA cured epoxy system (scales indicate brittle nature), (b) PA cured epoxy system (smooth surface indicate reduced brittleness), (c) compression failed TETA cured epoxy system, (d) compression failed PA cured epoxy system, (e) distribution of 30 weight percentage of cenosphere in epoxy matrix, (f) distribution of 50 weight percentage of cenosphere in epoxy matrix, (g) crushed shells of cenosphere depicting porous nature, (h) white arrows shows broken cenosphere particles in porous shell.

(g) Crushed shells of cenosphere depicting porous nature



(h) White arrows shows broken cenosphere particles in porous shell

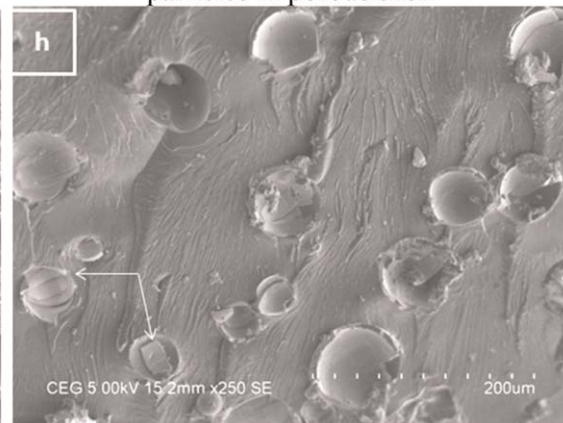
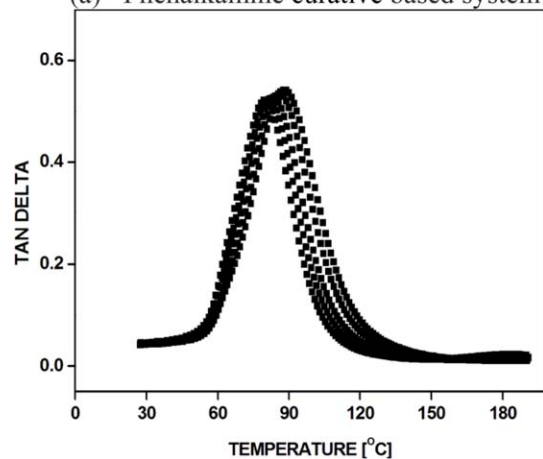
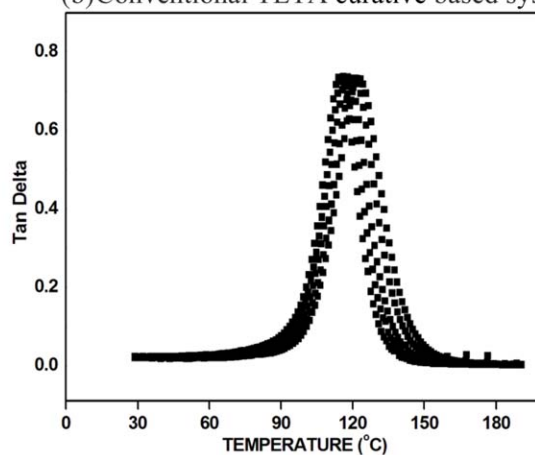


Figure 6. Continued.

(a) Phenalkamine curative based system

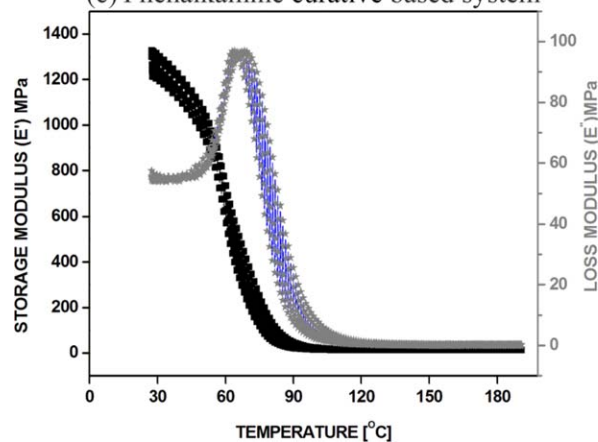


(b) Conventional TETA curative based system



The variation of loss moduli and storage moduli with temperature

(c) Phenalkamine curative based system



(d) Conventional curative TETA based system

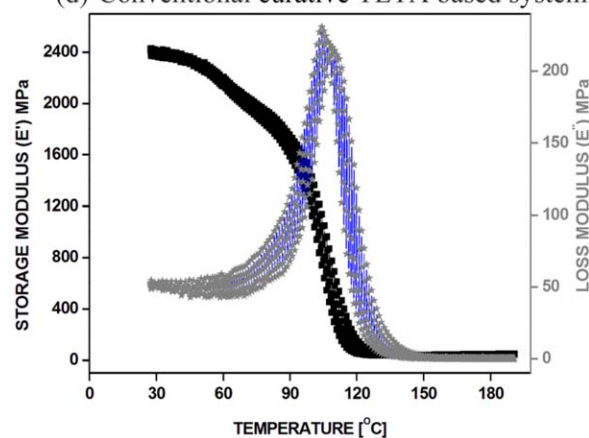
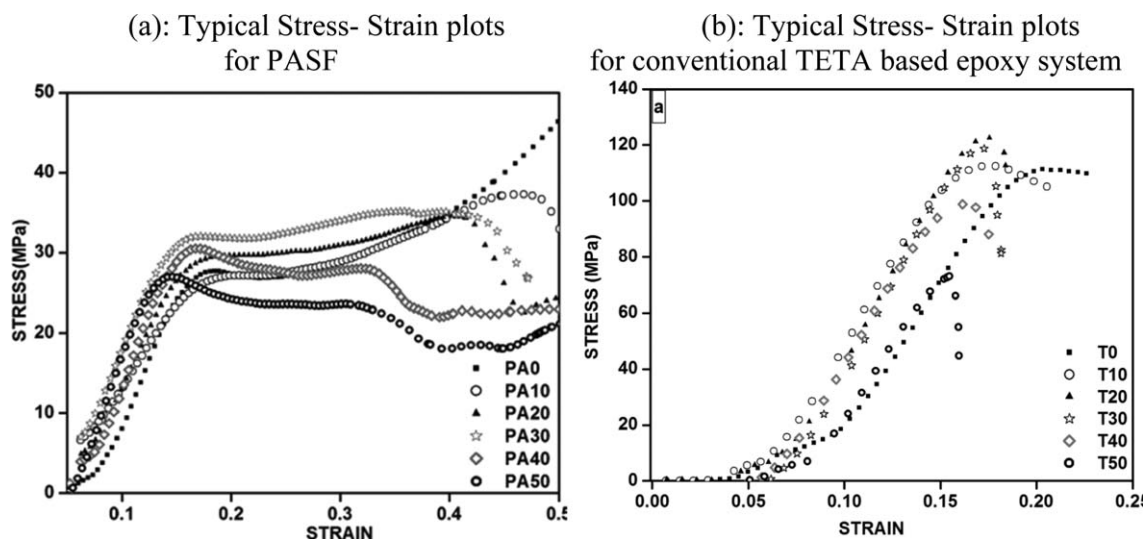


Figure 7. DMA Curves for neat sample. Effect of temperature on the tan delta value. (a) Phenalkamine curative based system. (b) Conventional TETA curative based system. (c) Phenalkamine curative based system. (d) Conventional curative TETA based system. The variation of loss moduli and storage moduli with temperature. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 8.** (a) Typical stress–strain plots for PASF. (b) Typical stress–strain plots for conventional TETA based epoxy system. F: Flat wise compression, eb: Edge wise big samples, es: Edge wise small samples, T: conventional TETA based epoxy system, 0–50: percentage composition of cenosphere.

cenosphere were found to have imperfections as these particles were the by-products from thermal power plants. Even though the structure lacked perfection, their incorporation provided improvement in the compressive modulus of syntactic foams. These waste by-products could thus be disposed in a sustainable way by their utilization in making useful composite products. Figure 6(h) shows how the broken pieces filled up the empty space that was accessible upon fracture of the cenosphere.

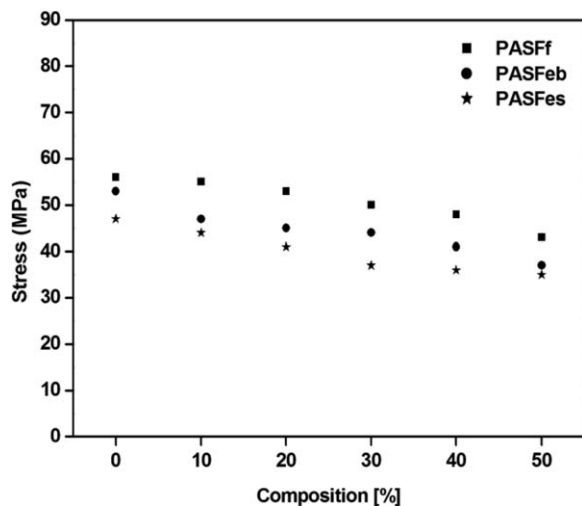
#### Dynamic Mechanical Analysis

The maximum value in the plot of  $\tan \delta$  with respect to temperature denoted the large scale cooperative segmental motion of the polymeric molecules typically called the glass transition temperature ( $T_g$ ). As evident from the DMA curves, the neat sample of PA curative based system had lower  $T_g$  value (81.4 °C) [Figure 7(a)] than the neat sample of conventional TETA curative based system (116 °C) [Figure 7(b)]. The reason for lower value of  $T_g$  may be the plasticizing effect of long alkyl

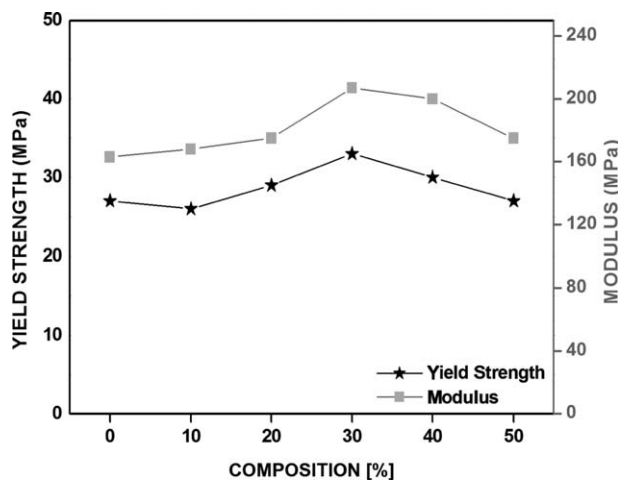
side chain that predominated in PA-based system. The loss modulus peak and the storage modulus for PA-based system are shown in Figure 7(c). The epoxy syntactic foams based on conventional TETA curative usually has a larger storage and loss modulus value that indicated the tighter network structure and higher stiffness which is the characteristic of the thermosetting resins Figure 7(d).

#### Mechanical Properties: Compression Tests

Edgewise compression tests were performed to find the difference in strength of the core when compressive loading is applied in in-plane direction and to predict the expected failure mode in this kind of compressive loading.<sup>25</sup> Such failure analysis is significant because these may lead to defects which may propagate and ultimately result in failure of the entire structure for which these cores may be employed. A typical stress–strain curve for compression consisting of a linear elastic region followed by a drop in stress value with the increase in strain is depicted in Figure 8(a). The plot for conventional TETA-based epoxy system showed a sharp drop in stress which indicated



**Figure 9.** Comparison of failure strength of PASF. PASFf: Flatwise sample, PASFeb: Edgewise big samples, PASFes: Edgewise small samples.



**Figure 10.** Yield strength and modulus of PASF.



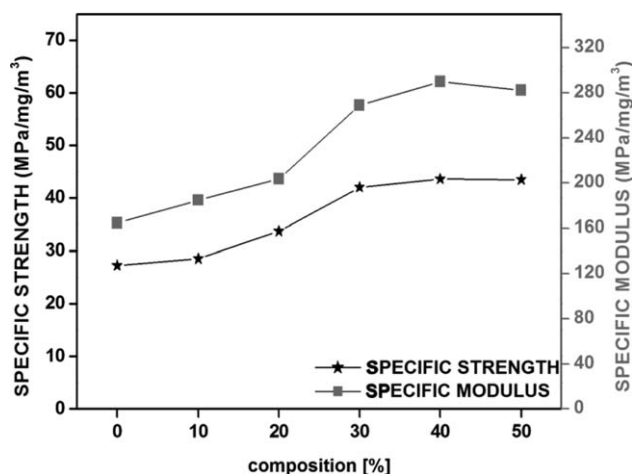


Figure 11. Specific strength and specific modulus of PASF.

brittle behavior [Figure 8(b)]. In general, epoxy syntactic foams based on conventional TETA curative survived very low strain values and samples exhibited brittle failure after they could take the maximum load. On the contrary, the drop in stress for PASF was not steep and was followed by a plateau region. This indicated that overall brittleness of the matrix was reduced. This could be credited to the flexibility of long alkyl side chain that aided in the reduction of the brittle nature in PA-based system. In the densification zone more and more cenosphere particles failed in the PASF samples under the compression load. Crack was initiated in the matrix at the maximum value of stress. The dip observed after reaching a peak yield strength value may be due to the collapse of cenosphere which left a void in syntactic foam.<sup>20</sup> This collapse of cenosphere was also evident from the SEM images [Figure 6(g)]. The broken pieces filled up in the void space present in the cenosphere, which opened due to the fracture of these particles under the compressive load. The result was an increase of the stress value until complete fracture of the sample. This was also apparent in the SEM image [Figure 6(h)]. It was evident that the strength required for failure of the samples decreased with increase in weight percentage of the cenosphere as shown in Figure 9. This trend was also cited in previous studies.<sup>17–21</sup>

#### Yield Strength and Modulus of PASF

Syntactic foams were able to sustain the load of compressive force applied at the center of the sample up to an optimum load where by the stiff spherical cenosphere could have provided the cushioning effect to the epoxy matrix. The yield strength increased by 22% and the modulus increased 27% in PA30 in comparison to PA0 samples (Figure 10). However the toughness value indicated by area under the stress–strain curves decreased with the increased percentage of cenosphere [Figure 8(a)]. This may be due to the increase in the breakability of syntactic foams with the addition of cenosphere.<sup>20</sup>

#### Specific Modulus and Specific Strength of PASF

The specific modulus increased by 72% for PA40 samples and the specific strength increased by 61% for PA40 sample when compared to PA0 sample (Figure 11). The probability of filler floatation in 10% and 20% loading of cenosphere and the possibility of damage to the hollow cenospheres during mechanical mixing at a

higher concentration cannot be ruled out. In the light of this fact, it can be assumed that there exists a strong particle–matrix interfacial bonding in 40% loading of cenosphere. This might be the reason for improved values in PA40 samples. The slight improvement of properties observed for 10% and 20% loading might hint at the possibility of uniform distribution although the probability of filler floatation cannot be ruled out completely.

#### CONCLUSIONS

As the scope for epoxy-based products is continually increasing, there is a great possibility for the utilization of this novel eco-friendly curing agent to produce improved products. The results revealed good thermal stability, lower water absorption, and appreciable water resistance in samples exposed to hygrothermal studies. The cure studies using DSC inferred faster cure reaction in PA system. The compression studies confirmed that unlike epoxy system based on conventional TETA curative, PA cured system did not undergo brittle failure. This was also established with the SEM images. The specific modulus and the specific strength were optimum in 40% cenosphere loading. This helped to reduce the cost of the preparation of the syntactic foams. Besides it also ensured effective utilization of the by-product from the thermal power plants. The use of equal amounts of the curative with the epoxy also aided in making the process more eco-friendly. DMA results revealed 81.4 °C as the  $T_g$  value of neat PA-based system. The compressive strength of PASF was lesser when compared to the epoxy syntactic foams based on conventional TETA curative. One reason for this drop in the strength may be the alkyl side chain in the PA which could have provided a plasticizing effect in PASF. Nevertheless, there is always a scope to increase the strength of the PA-based system. These light weight green foam core materials can therefore be explored for sandwich composites in various applications.

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#### REFERENCES

- Ashida, K. In *Handbook of Plastic Foams: Types, Properties, Manufacture and Applications*; Landrock, A. H., Ed.; Noyes Publications: New Jersey, **1995**; p 147.
- Shutov, F. A. In *Handbook of Polymer Foams and Foam Technology*; Klemmner, D., Frisch, K. C., Eds.; Hanser publishers: New York, **1991**; p 355.
- Malloy, R. A.; Hudson, J. A. In *International Encyclopaedia of Composites*; Lee, S. M., Ed.; Vancouver, VCH, **1990**, 365.
- Bardella, L.; Genna, F. *Int. J. Solids Struct.* **2001**, *38*, 7235.
- John, B.; Reghunadhan Nair, C. P. *Update on Syntactic Foams*; iSmithers Rapra: Shropshire, **2010**.
- Gupta, N.; Pinisetty, D.; Shunmugasamy, V. C. *Reinforced Polymer Matrix Syntactic Foams: Effect of Nano and Micro-Scale Reinforcement*; Springer: New York, **2013**.

7. Gibson, L. J.; Ashby, M. F. *Cellular Solids—Structure and Properties*, 2nd ed.; Cambridge University Press: UK, **1999**.
8. Woldesenbet, N.; Kishore, E. *J. Mater. Sci.* **2002**, *37*, 3199.
9. Shell Development Company, *EPON Resin Structural Reference Handbook*; Houston, Texas, **1983**.
10. Mohammed Altaweel, A. M. A.; Ranganathaiah, C.; Kothandaraman, B.; Raj, J. M.; Chandrashekhara, M. N. *Polym. Compos.* **2011**, *32*, 139.
11. Dal, Z.; Constantinescu, A.; Dalal, A.; Ford, C. Phenalkamine Multipurpose Epoxy Resin Curing Agents; Cardolite Corporation; Newark, New Jersey, p 1.
12. Liu, Y.; Wang, J.; Xu, S. *J. Polym. Sci. Part A: Polym. Chem.* **2014**, *52*, 472.
13. Dileep, T.; Archana, D.; Ramesh, C. *Int. J. Drug Dev. Res.* **2011**, *3*, 171.
14. Cai, C.; Shen, Z.; Wang, M.; Ma, S.; Xing, Y. *China Partic-uol.* **2003**, *1*, 156.
15. Suresha, B.; Siddaramaiah, G. C.; Jayaraju, T. *Polym. Compos.* **2008**, *29*, 307.
16. Gupta, N.; Priya, S.; Islam, R.; Ricci, W. *Ferroelectrics* **2006**, *345*, 1.
17. John, B.; Reghunadhan Nair, C. P.; Ambika Devi, K.; Ninan, K. N. *J. Mater. Sci.* **2007**, *42*, 5398.
18. Kadam, P.; Pawar, B.; Mhaske, S. *J. Miner. Mater. Character. Eng.* **2013**, *1*, 117.
19. Lin, T.; Gupta, N.; Talalayev, A. *J. Mater. Sci.* **2009**, *44*, 1520.
20. Swetha, C.; Kumar, R. *Mater. Des.* **2011**, *32*, 4152.
21. Rosu, D.; Cascaval, C. N.; Mustata, F.; Ciobanu, C. *Thermo-chim. Acta* **2002**, *383*, 119.
22. Kaur, M.; Jayakumari, L. S. *High Perform. Polym.*, **2016**, DOI: 10.1177/0954008316656923.
23. Wu, G. H.; Dou, Z. Y.; Sun, D. L.; Jiang, L. T.; Ding, B. S.; He, B. F. *Script. Mater.* **2007**, *56*, 221. Feb 28;
24. Gupta, N.; Woldesenbet, E.; Mensah, P. *Compos. Part A* **2004**, *35*, 103.
25. Velecela, O.; Soutis, C. *Compos. Part B* **2007**, *38*, 914.
26. Committee on Fire and Smoke Resistant Materials for Commercial Aircraft Interiors. *Fire and Smoke Resistant Interior Materials for Commercial Transport Aircraft*; National Academy Press, Washington, D.C. **1995**; Chapter 4, p 29, ISBN: 0-309-57834-5.