RSC Advances

Journal Name

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Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Thermo-mechanical and surface properties of POSS reinforced structurally different diamines cured epoxy nanocomposites.

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Received (in XXX, XXX) XthXXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

In the present study three structurally different diamines namely bisphenol- A based ether diamine, octane diol based ether diamine, and capron based diamine were synthesized and characterized using FT-IR, ^{1}H-NMR and ^{13}C-NMR spectra. These diamines were used to cure DGEBA epoxy resin and were reinforced with NH_2-POSS in different weight percentages (1%, 3% and 5% wt) to obtain epoxy matrices and composites. Data obtained from thermo-mechanical, dielectric and surface studies were compared with those of neat epoxy matrix cured with diamino diphenyl methane (DDM). The surface morphology was ascertained from the XRD and SEM analysis and the presence of POSS in the composites was ascertained from the TEM images. The capron based diamine cured epoxy matrix shows better improvement in tensile strength and impact strength of 39.8% and 137.0% respectively than those of neat epoxy cured with diamino diphenyl methane (DDM). The value of contact angle (91.3^{o}) of the capron based diamine cured epoxy composites infers that the epoxy matrix becomes hydrophobic nature. Data obtained from different studies suggest that the capron diamine cured epoxy matrix can be used in the form of coating, encapsulant, sealant for different industrial and engineering applications for better performance and improved longevity.

Introduction

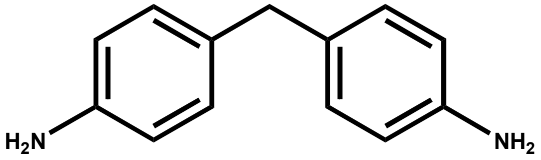
Thermosetting resins found many engineering applications because of their high strength and stiffness, good dielectric behavior, resistance to chemicals, corrosion and microbial organisms, low shrinkage during cure and good thermal characteristics [1-7]. Epoxy resins possess an excellent heat resistance, high modulus, enhanced heat and electrical resistant properties that are made epoxy resin suitable for coatings, structural adhesives, composite materials, and sealants for microelectronics [8]

Toughness, chemical resistance, mechanical properties ranging from extreme flexibility to high strength and hardness, high adhesive strength, good heat resistance and high electrical resistance, etc., are the properties, depend on the chemical structure of the curing agent used for epoxy resin and the curing conditions adapted [9]. Chemical modification of epoxy resin has greatly enhanced their utility towards industrial applications [10, 11]. Our research group has published several articles based on modifications of epoxy resin with different kinds of tougheners, polymeric intermediates and curatives to make epoxy resin suitable for high performance industrial applications [12, 13].

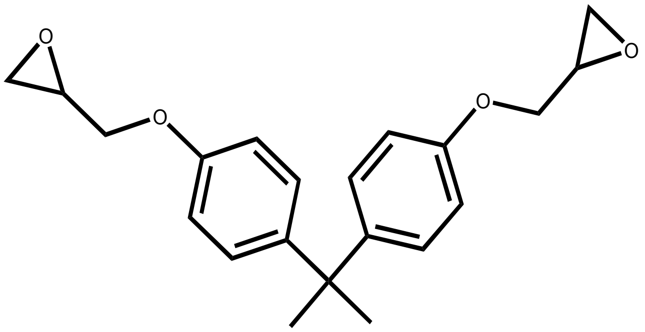
The properties such as crosslink density, molecular flexibility, spatial configuration and free volume in the network of the matrix are vary with nature of amine skeleton, curatives, which include functionally aliphatic, aromatic nature and flexible ether linkage in the molecular structure, etc. [14]. The effect of crosslinking on the glass transition temperature (Tg) is one of the fundamental indicators on the properties of the cured matrix.. Experimentally, it has been shown that Tg invariably increases with increase in crosslink density. In addition to the cross linking density, the value of Tg markedly depends on the molecular skeleton of the amine curatives [15, 16].

Polyhedral oligomeric silsesquioxanes (POSS) are a type of three-dimensional, structurally well-defined caged molecules with the general formula (RSiO1.5)n. It may be referred to as a silica nanoparticle consisting of a silica cage core, as well as other organic functional groups attached to the corners of the cage [17]. Several reports of organic-inorganic nanocomposites involving epoxy resin and POSS have reported, and POSS can endow the materials with improved thermo-mechanical and dielectric properties and flame retardance [18-19].

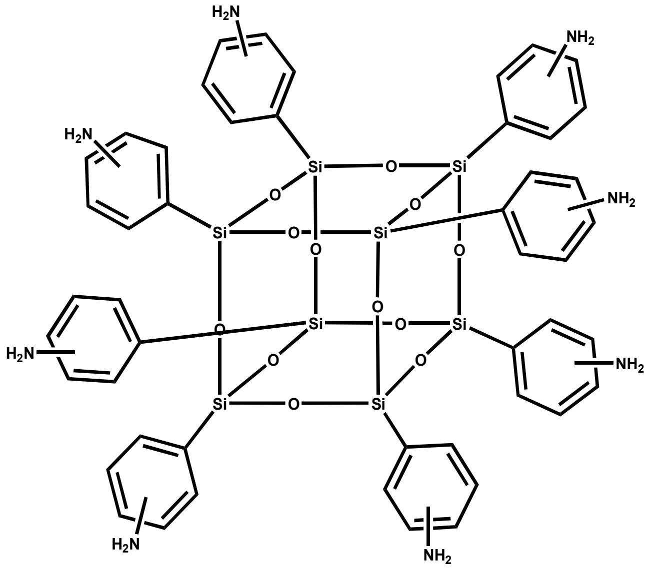
In the present work an attempt has been made to synthesize three different types of skeletally modified diamines and were used as curative for DGEBA epoxy resin and epoxy reinforced with different weight percentages of amine terminated POSS. Data resulted from thermo-mechanical, dielectric and surface studies and morphology of epoxy resin reinforced with varying weight percentages of POSS and cured with different diamines were compared with those of neat epoxy cured with diamino diphenyl methane (DDM) and are discussed and reported.



Diamino diphenyl methane (DDM)



Diglycidyl ether of bisphenol A



POSS-NH$_2$

Scheme 1 Chemical structures of DDM, DGEBA epoxy resin and POSS

Experimental

Materials

The commercially available epoxy resin (diglycidyl ether of bisphenol-A, DGEBA) LY 556 and 4, 4-diaminodiphenylmethane (DDM) were obtained from Ciba-Geigy Ltd., India. Bisphenol-A, 1, 8-octanediol, 6-aminocaproic acid, 1-chloro-4-nitrobenzene, potassium carbonate, N, N-dimethylformamide (DMF), ethanol, Pd/C (10%) and hydrazine hydrate were obtained from SRL and were used as received. The reinforcement POSS was synthesized as per the reported procedure [9].

Synthesis of N, N'-(4,4'-methylenebis (4,1-phenylene))bis(6-aminohexanamide)-(CPA)

In a 250 mL two neck round bottomed flask equipped with condenser, 100 mL of N-methyl pyrrolidone (NMP), 10g (0.0504 mol) of 6-aminocaproic acid, 13.2g (0.1008 mol) of 4-(4-aminobenzyl)benzenamine and a pinch of alkali hypo phosphate catalyst were added. The reactants were allowed react at 100 ^{o}C for 24 h with efficient agitation to facile completion of reaction. The product obtained was purified. (Yield 85%, M.Pt 124 °C). (Scheme S1a)

Synthesis of 1, 8-bis (4-aminophenoxy) octane (OMA)

In a 250 mL two neck round-bottomed flask, 100 mL of dry N, N-dimethylformamide (DMF), 23.2 g (0.4833 mol) of sodium hydride (50%) and 10 g (0.161 mol) of 1,8-octanediol were added. The reactants were stirred for 6 h at 50 °C and cooled to 0–5°C to get the sodium salt of diol. Further, at the same temperature, 50.7 g (0.322 mol) of 1-chloro-4-nitrobenzene was dissolved in 100 mL of DMF. After the complete addition, the temperature was raised to 30°C and stirred overnight. The reaction mass was quenched into the required amount of crushed ice, filtered, washed with distilled water and recrystallized with ethanol to yield 1,2-bis(4-nitrophenoxy) ethane with 89% and the melting point of 134 ^{0}C. Further the nitro compound was reduced to yield out the diamine. 1 g of 10% Pd/C was added to 10 g (0.3305 mol) of 1, 2-bis (4-nitrophenoxy) ethane dissolved in 100 mL of ethanol in a 250 mL round-bottomed flask.

The reaction temperature was raised to 50°C. To the mixture, then 20 mL of hydrazine hydrate was added and refluxed for 3 h. The hot filtrate of the product was allowed to cool to room temperature, to obtain a white crystalline product. (Yield 92%, M.Pt 120 °C). (Scheme S1b)

Synthesis of 4-(4-(2-(4-(4-aminosphenoxy) phenyl) propan-2-yl) phenoxy) benzenamine. (BPA)

To the 50 mL of N,N- dimethylformamide (DMF) in a 100 mL flask dissolved bisphenol-A (0.04 mol) and after the addition of potassium carbonate (0.12 mol) the reactants were stirred well for 30 min at 30°C, further 1-chloro-4-nitrobenzene (0.08 mol) was added and refluxed at 100 °C for 12 h and then cooled to 30 °C. Further pale yellow solid product was obtained by quenching the mixture with water. After thorough washing with water and methanol, the yellow solid product was dried under vacuum at 100 ^{o}C to get 2, 2-bis (4-(4-nitrophenoxy) phenyl) propane.

The purified 2, 2-bis (4-(4-nitrophenoxy)-phenyl)propane (0.04 mol) was dissolved in ethanol (100 mL) and 10% Pd/C (0.250 g) was added and refluxed at 50 °C. Further, hydrazine monohydrate (25 mL) was added slowly and heated to 80–90 °C for another 3 h. The hot filtrate was allowed to cool to room temperature, to obtain a white crystalline product. (Yield 85%, M.Pt 127 °C). (Scheme S1c)

Development of POSS reinforced epoxy composites cured with different diamines

The DGEBA epoxy resin 40 g and 1,3 and 5 wt% of POSS were added separately and stirred for 24 h using a mechanical stirrer and then a stoichiometric amount of diamine curing agent, corresponding to epoxy equivalents was added. The resulting product was poured into a pre-heated mould at 120˚ C for an hour, to remove the moisture and trapped air. The samples were cured successively cured at 120˚ C for 2 h, post cured at 180˚ C for 3 h, and removed from the mould and characterized (Schemes 1, 2 and 3).

Characterization

Fourier transform infrared (FT-IR) spectra for the samples were recorded on a Perkin Elmer 6X FT-IR spectrometer. The ^{1}HNMR and ^{13}CNMR spectra were recorded with a BRUCKER 300 MHz NMR spectrometer. Samples were diluted using deuterated chloroform (CDCl3), and tetramethylsilane (TMS) was used as an internal standard.The glass transition temperature (Tg) of the sample was determined using DSC 200 PC differential scanning calorimeter (DSC) (Netzsch Gerateban GmbH). Thermogravemetric analysis (TGA) was carried out using the DSTA 409 PC analyzer (Netzsch Gerateban GmbH). The surface morphology of the fractured surface of the samples was examined using scanning electron microscope (SEM; JEOL JSM Model 6360). A JEOL JEM-3010 analytical

transmission electron microscope operating at 80 kV with a measured point-to-point resolution of 0.23 nm was used to characterize the phase morphology of the developed nanocomposites.TEM samples were prepared by dispersing powder samples under sonication in ethanol and were mounted on carbon-coated Cu TEM grids and dried for 1 h at 70 ^{0}C to form a film of <100 nm. Contact angle measurements were carried out using 210 a Rame-hart Inc. goniometer (Succasunna, NJ, USA) with 5 ml of deionised water and diiodo methane (DIM).

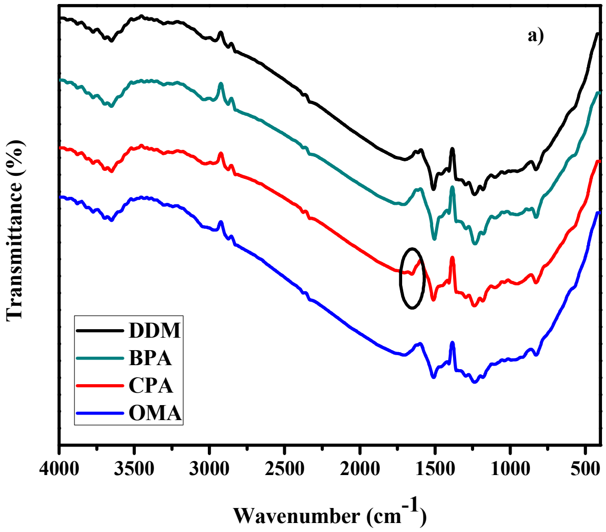
The dielectric studies were carried out with the help of an impedance analyser, Solartron impedance/gain phase analyzer 1260) at RT using platinum (Pt) electrode at 30 ^{o}C at a frequency of 1 MHz This experiment was repeated four times at the same conditions. X-ray diffraction patterns were recorded at room temperature, by monitoring the diffraction angle 2θ from 10 to 70˚ as the standard, on a Rich Seifert (Model 3000) X-ray powder diffractometer. The tensile (stress–strain) properties were determined, using INSTRON (Model 6025 UK) as per ASTM D 3039 at 10 mm min^{-1} cross-head speed, using specimen with dimensions of 100 mm×25 mm ×3 mm. The flexural strength and modulus were measured using INSTRON (Model 6025 UK) as per ASTM D 790, with specimen dimensions of 100 mm ×10 mm × 3 mm at 10 mm min^{-1} cross-head speed. The un-notched Izod impact strength of each sample was studied as per ASTM D 256, using specimen dimensions of 65 mm × 10 mm × 3 mm. The impact test was carried out at 25˚ C.

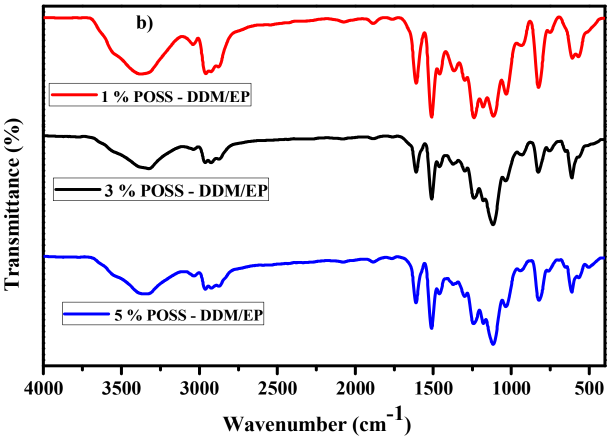
Results and Discussion

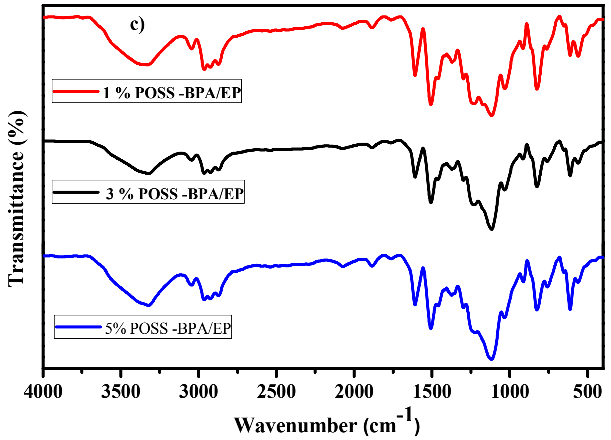
The molecular structure of capron based amine N,N'-(4,4'-methylenebis(4,1-phenylene))bis(6-aminohexanamide) **(CPA)** was confirmed with ^{1}H and ^{13}C NMR **(Figure S2a and S3a)**,in proton NMR whose δ values are 3 (for a methylene H^1), 6.6 (for b aromatic H^1), 6.9 (for c aromatic H^1), 6.8(for d amide H^1), 2.4 (for e aliphatic H^1), 1.6 (for f aliphatic H^1), 3.1 (for g aliphatic H^1) and 3.5 (for h amine H^1). In ^{13}C NMR the carbonyl carbon atoms appeared at 179 ppm, aromatic carbon atoms appeared between 115 and 144 ppm and aliphatic carbon atoms appeared between 23 and 42 ppm.

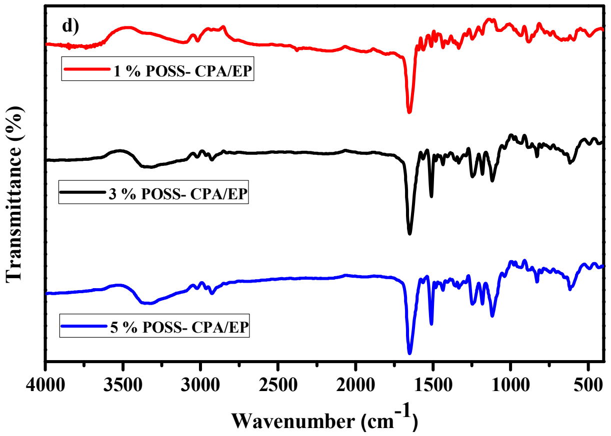
The molecular structure aliphatic C8 based ether linked diamine **1, 8-bis (4-aminophenoxy) octane (OMA)** was confirmed with ^{1}H and ^{13}C NMR **(Figure S2b and S3b)**, in proton NMR whose δ values are 1.4 (for a, b aliphatic H1), 1.7 (for c aliphatic H^1), 3.8 (for d aliphatic H^1), 6.5 (for e aromatic H^1), 6.6 (for f aromatic H^1). In ^{13}C NMR the carbon atoms bonded with ether appeared at 156 ppm, aromatic carbon atoms appeared between 116 and 148 ppm and aliphatic carbon atoms appeared between 31 and 41 ppm.

The molecular structure of aromatic bisphenol-A based ether linked amines **4-(4-(2-(4-(4-aminophenoxy) phenyl) propan-2-yl) phenoxy) benzenamine (BPA-NH$_2$)** was confirmed with ^{1}H and ^{13}C NMR **(Figure S2c and S3c)**, in proton NMR whose δ values are 1.6 (for a aliphatic H1), 7.1 (for b aliphatic H^1), 6.8 (for c and d aromatic H^1), 6.7 (for e aromatic H^1), 3.5 (for f amine H^1). In ^{13}C NMR the carbon atoms bonded with ether appeared at 152 ppm, aromatic carbon atoms appeared between 115 and 139 ppm, aliphatic carbon linked with ether appears at 68 pm and aliphatic carbons appears between 25 and 29 ppm.









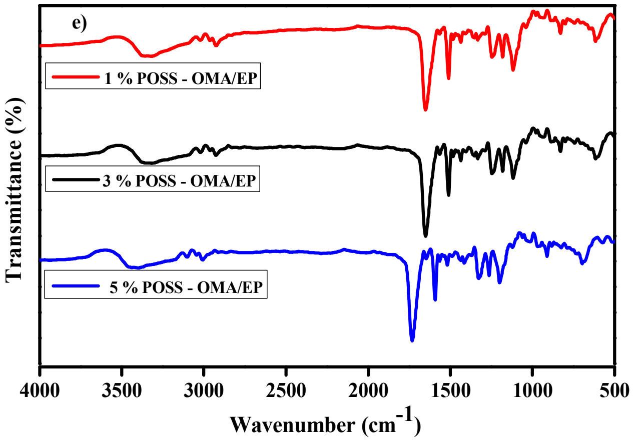
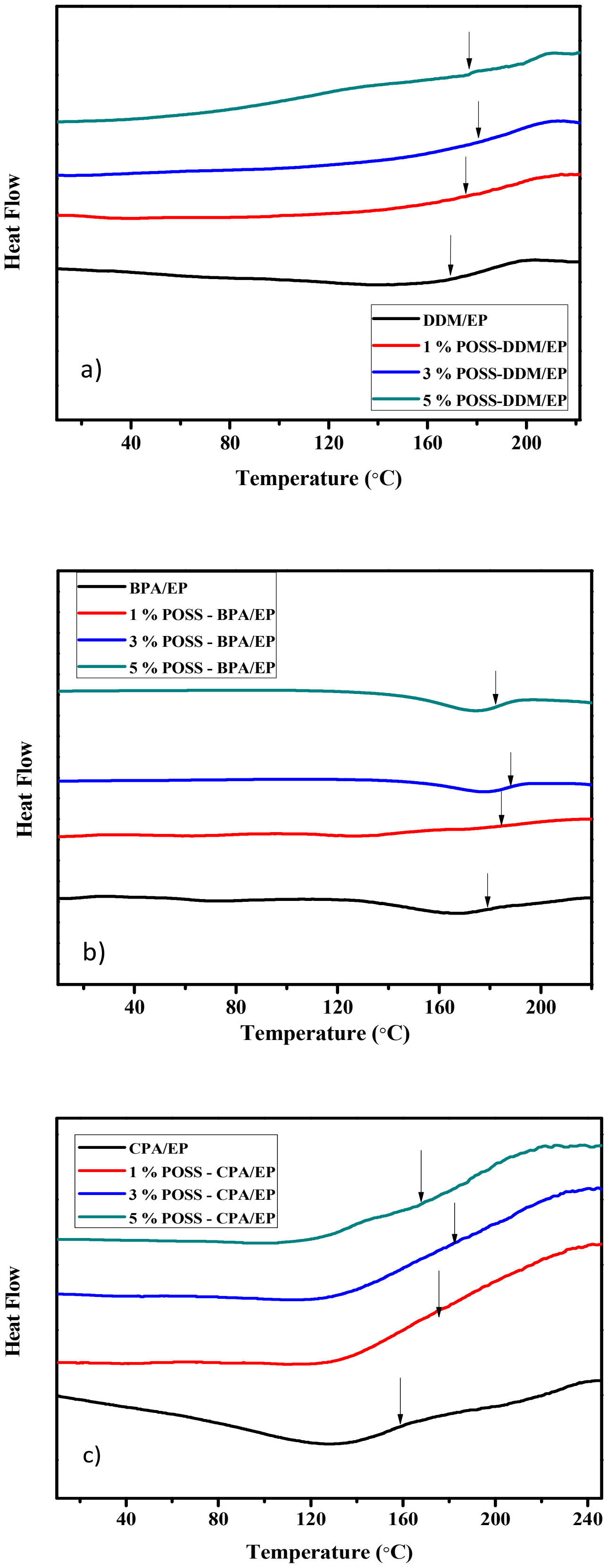


Figure 1 FT – IR Spectra of epoxy POSS composites

The curing of epoxy resin with BPA CPA and OMA diamines are illustrated in Figure 1. The disappearance of vibration band at 954 cm^{-1} indicates the ring opening curing mechanism of DGEBA. However the appearance of vibration bands at 3645, 1508, 1233 and 821 cm^{-1} confirm the presence of the -OH functionality, aromatic -C=C-, C-N stretching modes and aromatic C-H bending vibration respectively. The circle pointing at 1650 cm^{-1} indicates the C=O stretching of amide linked amine curative in the CPA diamine. Further, the presence of POSS was ascertained from the appearance of peak between 1070 cm^{-1} and 1110 cm^{-1} as illustrated in Figure 1b-d.



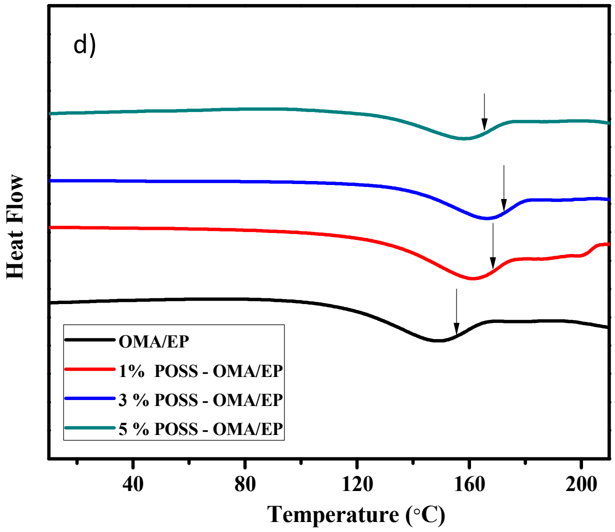


Figure 2 DSC profile of epoxy matrix and POSS composites

Miscibility of amine cured epoxy matrix can also be evidenced from the variation in the glass transition temperatures (Tg) with respect to their amine skeleton and interpenetration with the cross linked epoxy networks. The aliphatic skeletal diamines with long aliphatic chain have lower Tg value than that of aromatic skeletal diamine [15]. The values of Tg of four different diamines cured epoxy matrices are presented in Table 1. The value of Tg follow in the order BPA> DDM> CPA> OMA. Epoxy resin cured with BPA exhibits the highest value of Tg (178 ^{0}C) and with OMA possesses the lowest value of Tg (156 ^{0}C) and with CPA also exhibit the lowest value almost that of OMA (158 ^{0}C).The higher value of Tg observed in the cases of BPA and DDM may be explained due to the presence of rigid molecular skeleton, where as the lower values of Tg were observed for CPA and OMA cured matrices due to the presence of long and flexible aliphatic chain in the skeleton.

Because of their flexibility and long chain length provides an enhanced free volume with lower crosslink density and accelerates the reaction rate which in turn reduces the curing temperature (Figure 2). Further in the case of CPA the plasticization effect of the capron based amine is responsible for the lower value of Tg. This may be explained due to the chain lengthening and flexible nature of -NH-CO- linkage formed during the reaction of 6-aminocaproic acid which in turn decreased the effective crosslink density. This creates an excess free volume in the matrix system and leads to reduction in the values of Tg, of cured epoxy matrix [20]. This result is in good agreement with the previous similar reports using caprolactam as toughening agent [21, 22]. Furthermore, the values of Tg of POSS reinforced epoxy composites were enhanced upto 3 wt % of POSS in all the cases of composites (Table 1) due to enhanced crosslink density brought about the multifunctional POSS molecules. Beyond this concentration (above 3wt %) the reverse trend in the value of Tg was noticed due to agglomeration of POSS molecules in the epoxy matrix.

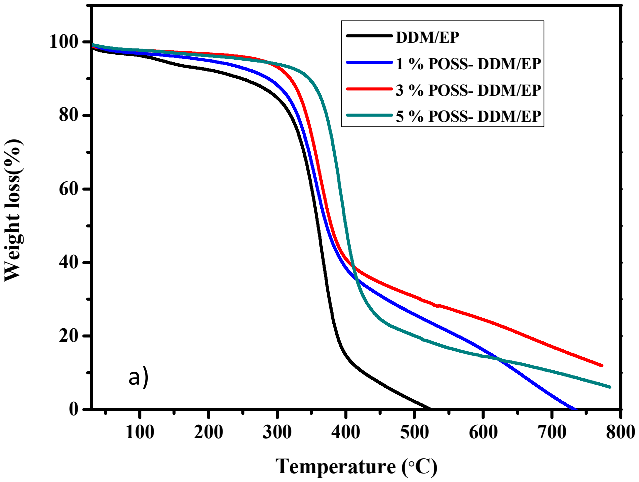
Table 1 Thermal properties

Sample	Weight loss (%)			Char Yield at 700 °C	T_g (°C)
	20 %	40 %	60 %		
DDM/EP	318.1	350.8	367.1	0 (517.0)	166
1% POSS – DDM/EP	330.4	359.0	390.6	3.5	175
3% POSS – DDM/EP	354.9	377.4	400.8	16.8	181
5% POSS – DDM/EP	371.2	391.6	411.0	10.7	177
BPA/EP	307.5	333.8	354.2	0 (400.0)	178
1% POSS – BPA/EP	310.9	348.1	380.8	0 (484.0)	185
3% POSS – BPA/EP	313.5	354.2	386.8	0 (546.1)	187
5% POSS – BPA/EP	319.5	362.4	397.1	0 (660.4)	184
CPA/EP	192.0	349.1	377.7	0 (579.8)	158
1% POSS – CPA/EP	200.1	353.2	381.8	0 (688.0)	174
3% POSS – CPA/EP	274.1	371.6	426.7	23.6	182
5% POSS – CPA/EP	340.9	377.7	455.3	24.8	169
OMA/EP	319.5	352.2	374.6	0 (497.1)	156
1% POSS – OMA/EP	331.8	358.3	380.8	0 (580.8)	168
3% POSS – OMA/EP	339.9	366.5	401.2	7.2	172
5% POSS – OMA/EP	346.0	377.6	417.5	14.0	166

Thermal stability of DDM, BPA, CPA and OMA diamines was studied using thermal analysis in the temperature range of 30–700° C. **Figure 3** illustrates the thermal degradation behavior of DDM, OMA, CPA and BPA cured DGEBA matrices and POSS reinforced composites. Data pertaining to the thermal stability of the matrices and POSS composites are presented in **Table 1.**

The degradation pattern was found varied with respect to the molecular structure of curatives, which provides the stability against thermal energy. Conventional DDM cured epoxy matrix shows only 7% weight loss up to 300 °C, which is due to the presence of water and solvent occluded in the DGEBA matrix and on further heating, it tends to show single degradation peak over the range of 350°C to 430° C, which attributes to degradation of hydrocarbon moiety of the matrix. The thermal stability of OMA diamine cured matrix has 11% degradation at 300 ^{0}C which is very close to the degradation value of conventional DDM cured matrix. Whereas in the cases of BPA and CPA cured matrices the degradation at 300 ^{0}C are 13 % and 31 % respectively.

This infers the poor thermal stability of flexible ether and amide linked BPA and CPA curatives. The POSS reinforced composites show a remarkable enhanced thermal stability. The char yield values of diamine cured matrices are presented in Table 1. From the Table it can be seen that all the diamines cured epoxy matrices have zero percent char yield at 700 ^{0}C. Whereas the POSS reinforcement enhances the char yield according to the weight percentage incorporation, the 5% wt POSS reinforced CPA has highest thermal stability with 25% char yield at 700 ^{0}C.



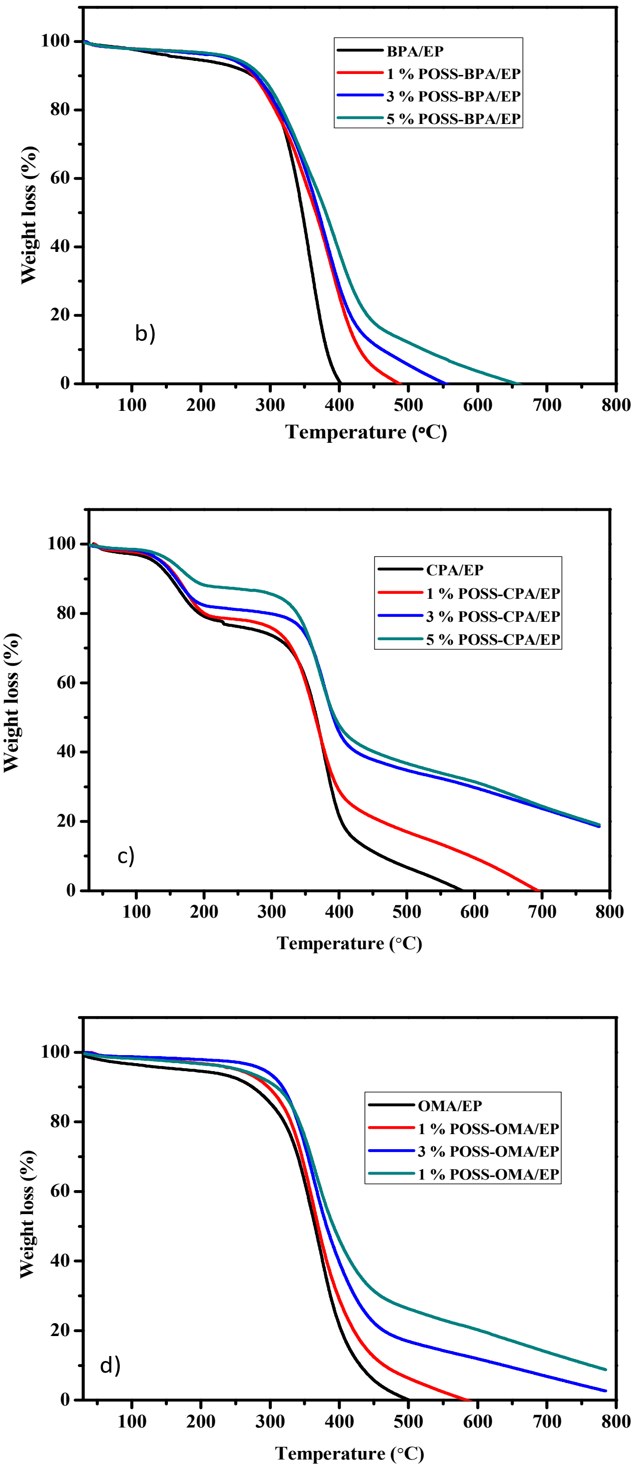


Figure 3 TGA profiles of epoxy matrix and POSS composites

The mechanical properties of DGEBA matrix cured with DDM, CPA, BPA and OMA diamines are presented in **Table 2 and Figure 4**. The impact strength of the DGEBA matrix cured with CPA based amine, OMA amine and BPA amine shows an improvement of 137%, 53.41% and 7.36% respectively when compared with that of conventional DDM amine cured neat epoxy matrix.

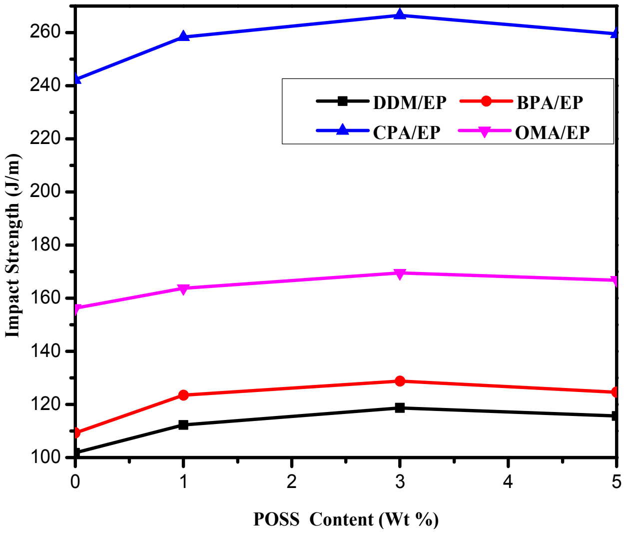


Figure 4 Effect of POSS reinforcement on impact strength of diamine cured epoxy composites

The improvement in impact strength is mainly attributed to the flexible linkages present in the skeleton of curatives. Thus capron based amine provides more flexible linkage with long symmetric carbon chain from the amide linkage and toughens the DGEBA matrix. However, among the ether linked amine, OMA amine shows a significant enhancement in the value of impact strength behavior which is also due to the presence long aliphatic chain. Thus the excess of free volume caused by the chain entanglement with high energy absorption is the key factor which determines the toughness behavior. Further with POSS reinforcement, the amount of free volume gets increased upto 3 wt% of POSS, whereas beyond 3wt% (ie 5wt%) the agglomeration of POSS results the reverse trend in strength behavior. Comparing the flexural strength of conventional DDM cured epoxy matrix with that of BPA, CPA and OMA diamines cured matrices, the bisphenol based amine (BPA) shows the highest value of flexural strength with 70.17 % improvement. Because of its rigid behaviour results from aromatic rigid cores which in turn contribute to prevent the chain entanglement in the matrix. Where as in the cases of OMA and CPA based diamines shows an improvement of only 44.56 % and 9.01 % respectively are observed due to the more plasticization effect and flexibility offered by the skeleton of diamines[23].. Further, with reinforcement of POSS the flexural strength increases up to 197.64 MPa (87 %) for 3 wt % of BPA cured matrix. The increase in the value of flexural strength of the POSS reinforced composites is due to the enhanced movement of molecules [24].

Tensile strength value of BPA based diamine cured matrix is not appreciable than that of neat DDM cured matrix. Whereas in the case of CPA diamine cured matrix an improvement of 39% the tensile strength was achieved. The amide linked CPA amine provides higher cross linking density, which imparts higher entanglement and results in less micro cracks. Comparing the tensile behavior of CPA based amine with other curatives, the hydrogen bonding formed between the –NH- of amide linkages (-CO-NH) provides higher stability to the matrix, whereas the other curatives have only ether linkages, which contributes only van der Waals forces of attraction. Further, the POSS reinforcement also show significant enhancement in the tensile behavior.

The silicon rich POSS molecules induce stress concentration effect which absorbs the stress due to deformation when the load is applied. The enhanced compatibility of amine terminated POSS also influences to obtain homogenous dispersion and hence affords strong adhesive forces between the reinforcement and matrix, which enhances the strength of the resultant composites [25].

Table 2 Mechanical and Dielectric properties

Sample	Tensile strength (MPa)	Flexural strength (MPa)	Impact strength (J/m)	Dielectric Constant (k)
DDM/EP	61.34	106.82	101.85	3.48
1% POSS – DDM/EP	66.46	112.47	112.34	3.22
3% POSS – DDM/EP	69.81	116.74	118.76	2.97
5% POSS – DDM/EP	67.89	110.59	115.67	2.76
BPA/EP	61.11	181.82	109.35	3.71
1% POSS – BPA/EP	67.34	193.50	123.51	3.37
3% POSS – BPA/EP	70.36	197.64	128.83	3.02
5% POSS – BPA/EP	68.25	188.58	124.66	2.78
CPA/EP	**85.71**	110.61	**242.20**	3.28
1% POSS – CPA/EP	**91.65**	116.58	**258.24**	3.05
3% POSS – CPA/EP	**97.57**	130.52	**266.47**	2.87
5% POSS – CPA/EP	**93.45**	125.16	**259.42**	2.57
OMA/EP	63.21	154.54	156.25	3.29
1% POSS – OMA/EP	67.99	165.27	163.75	3.11
3% POSS – OMA/EP	71.26	172.35	169.51	2.89
5% POSS – OMA/EP	69.43	169.50	166.79	2.63

The dielectric dependency with respect to the amine structure is clearly obtained from the values presented in **Table 2** at 1MHz. The skeletal modification of the skeleton of the amine yields the lower capacitive behavior amine dipole and thus reduces the value of dielectric constant. The lower value of dielectric constant of capron based diamine is due to the long alkyl chain, which in turn reduces the effective interaction of matrix molecules and further reinforcement of POSS provides an extra free volume in the matrix. Thus the 5% POSS reinforced capron diamine cured nanocomposites possesses the lowest value of dielectric constant (k = 2.57). Additionally, the value of dielectric loss was also found to be lowest in case of capron diamine cured matrix, which also contributes to an effective insulating behavior.

The contact angle measurements were performed using a goniometer and the values are presented in **Table 3**. The values of contact angle of DGEBA matrix cured with DDM, BPA, CPA and OMA diamines were 75.6°, 78.5°, 91.3° and 75.5° and respectively using 5 µl of deionised water as probe liquid, which infer that the matrices cured with ether linked amine curatives were less hydrophobic than that of amide linked capron amine curative. Similarly when diiodomethane was used as a dispersive liquid the values of contact angle were found to be 61.4°, 54.3°, 56.1°and 55.8° respectively. However, POSS reinforcement enhances the hydrophobic behavior of composites. For example, the capron diamine cured composites with 5wt% POSS reinforcement shows an increase in contact angle value from 91.3° to 95.3^{0}, due to the influencing effect of hydrophobic behavior of POSS. The value of contact angle observed for epoxy matrix with different curatives and POSS reinforcement makes the surface of composites from hydrophilic to hydrophobic nature. It was also inferred that, the chemical skeleton of capron based amine induces higher cross linking between the long chain amide linkage of capron amine and epoxy matrix, which makes the matrix become hydrophobic nature.

Table 3 contact angle and surface free energy

Sample	Contact angle (^{0})		Surface free energy		
	Water	DI	Υ^{d}	Υ^{p}	Γ (mJ/m^{2})
DDM/EP	75.6	40.5	39.4	6.4	45.8
1% POSS – DDM/EP	77.8	55.4	36.4	5.1	41.5
3% POSS – DDM/EP	80.3	61.4	34.5	4.0	38.5
5% POSS – DDM/EP	87.5	49.6	31.2	2.2	33.4
BPA/EP	78.5	54.3	35.6	3.4	39.0
1% POSS – BPA/EP	80.2	57.6	33.9	2.6	36.5
3% POSS – BPA/EP	84.7	50.5	32.2	1.9	34.1
5% POSS – BPA/EP	90.0	60.3	30.5	1.2	31.7
CPA/EP	91.3	53.7	34.0	8.2	42.2
1% POSS – CPA/EP	93.4	50.6	30.0	5.7	35.7
3% POSS – CPA/EP	94.0	56.6	28.4	3.1	31.5
5% POSS – CPA/EP	95.3	56.1	24.8	1.4	26.2
OMA/EP	75.5	40.9	40.3	6.7	47.0
1% POSS – OMA/EP	76.8	55.8	39.2	5.0	44.2
3% POSS – OMA/EP	78.4	48.3	35.2	5.2	40.4
5% POSS – OMA/EP	81.9	38.6	31.8	2.8	34.6

The contact angle values of water and diiodomethane can be used to estimate the surface free energy of composites surfaces. The surface free energy (Γ) decreases with decrease in polarity of the composites and is calculated according to the geometric mean model [26].

$$\cos\theta = 2/\gamma_L\ [(\gamma_L^{d}\ \gamma_s^{d})^{1/2} + (\gamma_L^{p}\ \gamma_s^{p})^{1/2} \qquad (1)$$

$$\gamma_s = \gamma_s^{d} + \gamma_s^{p} \qquad (2)$$

Where θ is the contact angle and γ_L is the liquid surface tension; and γ_s^{d} and γ_s^{p} are the dispersive and polar components of γ_L, respectively. It can be seen that the 5wt% POSS reinforced capron diamine cured epoxy composites exhibited the lowest value of surface free energy (26.2 mJ/m^2) when compared to that of other wt% POSS reinforced nanocomposites. This is attributed due to the less polar nature of the Si-O-Si linkage in the POSS and also the effective interaction occurred between the curatives and the epoxy matrix, which favors the reduced polarity of the resultant composites.

The morphological behavior of composites was characterized with XRD, SEM and TEM. The XRD diffractogram of diamine cured epoxy matrices and 3wt% POSS reinforced nanocomposites are illustrated in **Figure 5**.

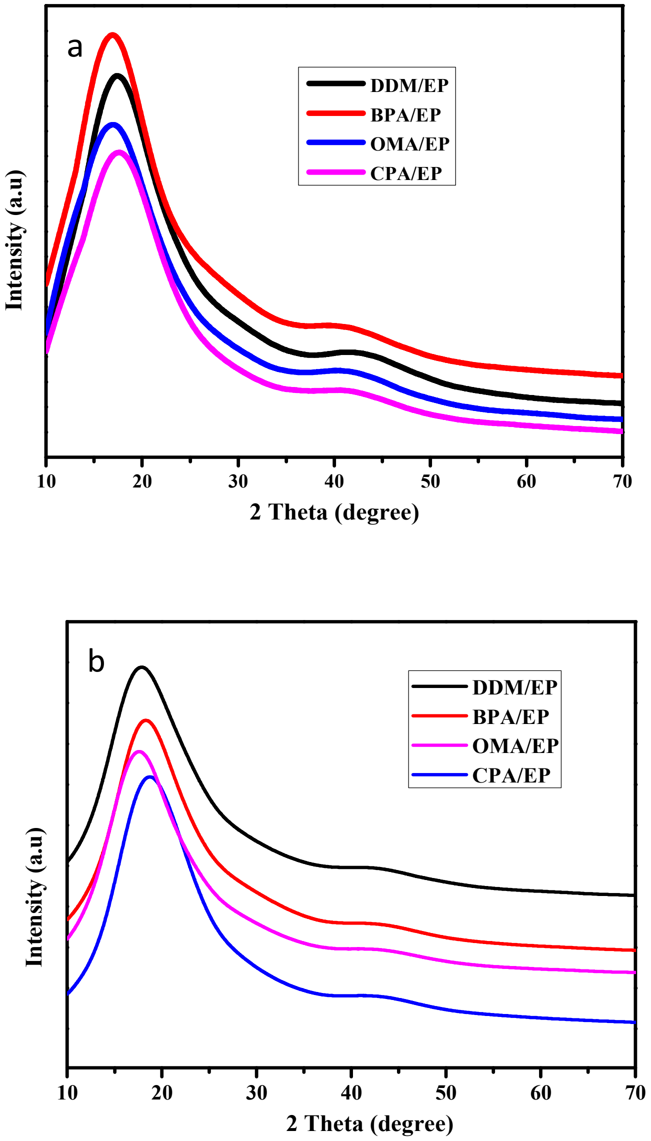


Figure 5 XRD diffractogram of (a) Diamine cured epoxy matrices and (b) 3wt% POSS reinforced diamine cured epoxy composites

The diffractogram of all diamine cured matrices exhibit a broad amorphous peak at 18.5 to 35 ° with peak maximum at 18.5 to 22.0 ° of 2θ value. Whereas in the case of POSS reinforced composites there was no change in the 2θ values but the amorphous nature of the composites is reduced slightly due to the presence of POSS molecule.

Figure **6** shows the fractured surface of 3wt% POSS reinforced nanocomposites of DGEBA cured with (a) DDM, (b) BPA, (c) OMA and (d) CPA diamine.

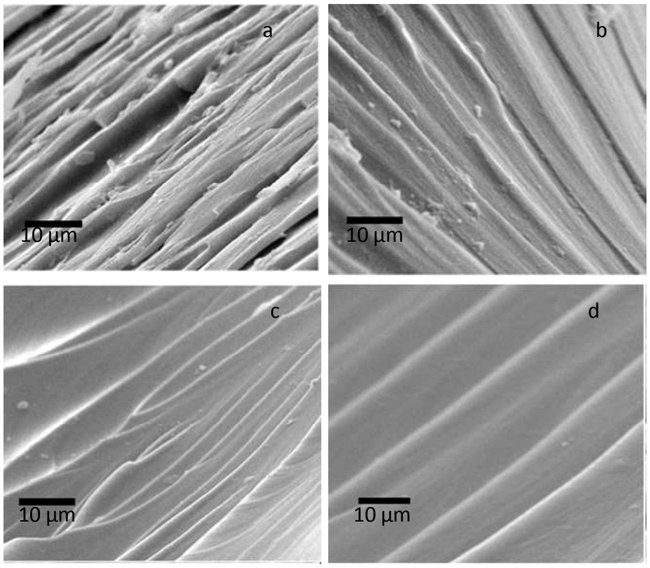


Figure 6 SEM micrograph of diamines cured epoxy matrices

The crack propagation of fractured surfaces of BPA, OMA and CPA diamine cured matrices is considered to be lower than those of DDM cured epoxy in the cross-section. A closer inspection of the fractured surface presented indicates that, the microstructure of the capron amine cured epoxy matrices shows a smooth and lower crack propagation, which lead to more energy dissipation with higher plastic deformation. In addition, the capron based diamine (CPA) cured epoxy matrix also shows a ductile fracture. The appearances of stretching and plastic deformation patterns on the fractured surfaces indicate an effective dissipation of fracture energy which contributes the higher impact strength to the matrices. In addition, it is also ascertained that the polyamide core of the capron based curative lead the bridging mechanism and thus contributes to higher impact behaviour. Further the reinforcement of 1, 3 and 5wt % of POSS in CPA amine cured composites at 20 nm magnification was ascertained from the TEM micrograph (Figure 7(a-c)). The micrograph illustrates the uniform dispersion of POSS core with homogeneity and it contributes to the good thermo-mechanical properties with hydrophobic surface.

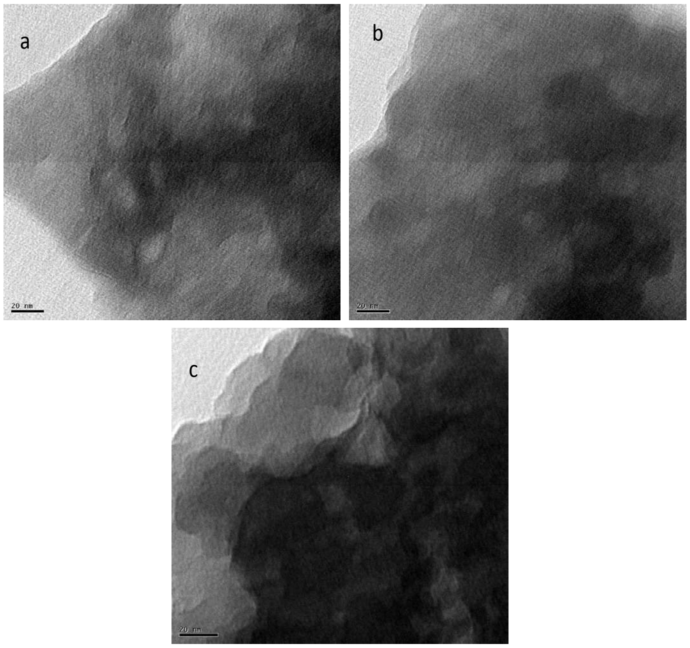


Figure 7 TEM micrograph of 1%, 3% and5 % POSS reinforced CPA diamines cured epoxy matrix

Conclusion

The ether linked aliphatic, aromatic diamine and amide linked diamine prepared in the present work were used to cure DGEBA resin similar to that of conventional DDM. The capron based amine with amide linkage possesses excellent mechanical behaviour, good hydrophobic behaviour and minimal micro cracks in the fractography. An improvement in the value of tensile strength and impact strength with 39.8% and 137.0% respectively were achieved when compared with those of DDM cured epoxy matrix. Data obtained from dielectric studies indicate that the capron diamine cured epoxy can be used for coating with less dissipation of dielectric even at low frequency. With POSS reinforcement the curatives developed in the present work were found to further enhancement in thermo-mechanical properties and hydrophobic behavior. Data obtained from different studies it is inferred that the capron diamine (CPA) cured system possess better properties than other diamine cured systems. CPA diamine cured epoxy matrix and composites can be used in the form of coatings, sealants and composites for better performance with prolonged longevity for different industrial and engineering applications.

Acknowledgement

The authors thank BRNS, G. No: 2012/37C/9/BRNS, Mumbai, Govt. of India., for the financial support and also thank Dr.Manmohan Kumar, Senior Scientific Officer, BARC, Mumbai.The authors thank to Dr. M.R.Vengatesan, Pusan National University, Busan, 609-735, South Korea, Dr. S. Devaraju, Sungkyunkwan University, Suwon, South Korea.

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Notes

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Supporting information

Scheme S1 (a-c). Schematic representation for synthesis of CPA, OMA and BPA diamines

Figure S2 (a-c). 1H NMR spectra of CPA, OMA and BPA diamines

Figure S3 (a-c). 13C NMR spectra of CPA, OMA and BPA diamines

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