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Functionalized MWCNT, an efficient reinforcement for the preparation of eugenol based high performance PBz/BMI/CNT nanocomposite exhibiting outstanding thermo-mechanical properties

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Abstract The chemistry of benzoxazine synthesis offers wide molecular design flexibility and thus facilitates preparation of various polybenzoxazine based composites. In this paper, we reported the preparation of polybenzoxazine/BMI blend and subsequent preparation of nanocomposites with amine functionalized multiwalled carbon nanotubes (F-MWCNTs). The curing mechanism and the material properties of the blend and nanocomposites were studied extensively. DSC analysis showed two exothermic maxima, corresponding to benzoxazine and allyl group polymerization. Furthermore, by the incorporation of F-MWCNT into PBz/BMI system, the properties of PBz/BMI/F-MWCNT nanocomposites were improved significantly. The enhancement in the material properties is due to the strong interaction between F-MWCNTs and PBz, resulting in the formation of interpenetrating polymer network. The morphology and fracture surface of the nanocomposites were studied by scanning electron microscopy. The thermal, mechanical and dielectric properties of the nanocomposites are found to be outstanding when compared with the neat PBz and PBz/BMI blend.

Keywords: Eugenol, polybenzoxazine, bio-composite

1. Introduction

The development of environmentally friendly and sustainable polymers is one of the current challenges in polymer industry, nowadays. And therefore, both academics and industrialists show particular interest in the synthesis of organic materials from renewables. Bio-polymers are sustainable and renewable as they are made from plant materials, which can be grown indefinitely. Various renewable materials (such as diphenolic acids, cardanol, furfurylamine, stearylamine and guaiacol) have been used for the synthesis of bio-polymers¹. Recently, eugenol (4-allyl-2-methoxy phenol) has been extensively studied as a starting material for the synthesis of novel biobased polymeric materials. Eugenol is relatively cheap which makes it economically suitable for the synthesis of bio-based resins (in particular bio-based benzoxazines).

Polybenzoxazines (PBz), a novel class of phenolic resins, have gained a lot of attention these days because of their attractive characteristics, which includes i) near-zero volumetric change upon curing ii) low water absorption iii) glass transition temperature (T_g) much higher than the cure temperature iv)

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School of Chemical Engineering, Yeungnam University, South Korea E-mail: thiru.kumaran999@gmail.com stability and vi) good mechanical and excellent electrical properties^{2,3}. The straight and easy synthesis of benzoxazine monomer through Mannich condensation is another interesting fact to consider. This provides more flexibility to design their molecular structure and allows tailoring the properties of polybenzoxazine bv adding specific functionalities. Although PBz based materials offer several advantages, they are also associated with some disadvantages that includes i) requirement of high temperature for curing ii) the obtained products are brittle in nature iii) most of the monomers are solid, which limits their process-ability and iv) difficulty to prepare films (3). Several strategies such as i) synthesis of benzoxazine monomers with additional functionality⁴⁻⁸ ii) incorporation of benzoxazine in polymer chains and⁹⁻¹¹ iii) synthesis of benzoxazine-based composites or allovs have been adopted.

does not require strong acid catalyst for curing v) high thermal

Bismaleimide (BMI) has been used to stabilize the benzoxazine moiety as it undergoes co-polymerization through an eneaddition. BMIs are well known for their excellent mechanical properties, thermal stability, solvent resistance and electrical insulation properties over a wide range of temperature^{1,12}. BMI can undergo self-addition reaction resulting in the formation of dense crosslinked networks with high thermomechanical stability. However, the cured resins are brittle because of high crosslink density of these networks, which



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limits their application. And therefore, the toughness or impact strength of the materials has to be improved. This could be achieved by the formation of composites.

Carbon nanotubes (CNTs) hold the promise of delivering exceptional mechanical properties and multifunctional characteristics [Young's modulus as high as 1.2 TPa and tensile strength of 50-200 GPa]. The addition of CNTs to the polymer matrix can generally improve the strength and modulus of the polymer only when there is uniform dispersion of the nanoparticles (NPs) in the matrix, with the existence of strong interfacial bond between the NPs and the polymer. It is well known that dispersing NPs in a polymer matrix is a difficult task due to their tendency to form agglomerates^{13,14}. It is therefore necessary to functionalize the nanoparticles in order to obtain the expected improvements in the property of polymer nanoparticles. This study investigates the effect of functionalization of CNTs in the ternary system (Bzo/BMI/F-MWCNTs). The curing behavior and the material properties of the ternary system have been studied extensively.

2. Experimental

2.1 Materials

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Eugenol was purchased from Sigma-Aldrich, Indonesia; paraformaldehyde was purchased from Sigma-Aldrich, Germany; N,N- dimethylformamide (DMF), Ferric chloride, dioxane, sodium hydroxide, THF and ethanol were purchased from Merck Limited, India; potassium carbonate (K₂CO₃) was purchased from s d fine-chem limited, India, hydrazine monohydrate was purchased from Spectrochem Pvt. Ltd., India; p-chloronitrobenzene and 10% Pd/C from Sisco Research Laboratories, Pvt. Ltd. India; hydroquinone was purchased from Fisher Scientific (a part of Thermo Fisher Scientific, Pvt. Ltd., India; Multiwalled cabon nanotube was purchased from Iljin Nanotech Co. Ltd., Korea. All chemicals and solvents were used without further purification.

2.2 Characterization methods

Fourier transform infrared (FTIR) spectra of the samples were obtained using an ABB Bomen (Model MB 3000) Spectrometer. The samples were ground with spectroscopy grade KBr and made into pellets. ¹H (600 mHz) & ¹³C (125 mHz) nuclear magnetic resonance (NMR) spectra were recorded on a Joel Spectrometer with tetramethylsilane (TMS) as the internal standard. Solutions were prepared in DMSO-d₆. Differential Scanning Calorimetry was performed in a TA instrument Q₁₀ model using 5-10 mg of the sample at a heating rate of 10 °C/min in N₂ atmosphere. Dielectric constant and dielectric loss measurements were carried out with an impedance analyzer (Solatron 1260 Impedance/Gain-phase Analyzer) at room temperature. Samples of 1 mm thickness × 12 mm dia. were prepared using platinum (Pt) electrode sandwich model

in the frequency range of 1 kHz – 6 MHz at room temperature. The dielectric constant and dielectric loss of the samples were determined using ε' and ε'' as the standard relations. The morphology of the material was examined by scanning electron microscopy (FESEM, Hitachi S-4800) at an accelerating voltage of 30 kV, Dynamic mechanical analysis (DMA) was carried out using a Netzsch 242 DMA at a heating rate of 10 °C/min from 30 to 250 °C. Thermogravimetric analysis (TGA) was performed using a TA Q 600 thermal analyzer. Cured samples were analyzed in open silicon pan at a heating rate of 20 °C/min in N₂ atmosphere, up to a maximum temperature of 800 °C.

3. Synthesis of diamine

3.1 Synthesis of 1, 4 [bis (4'-aminophenoxy) benzene] [BAPB]

The diamine 1, 4 [bis (4'-aminophenoxy) benzene] was synthesized according to Zhang et al and Thirukumaran et $al^{15,16}$ as shown in Scheme 1.

FT-IR (KBr, cm⁻¹): 3042 (C-H, aromatic), 1495 (C=C, aromatic), 1271 (C-O-C), 3313 (N-H, asymmetric stretching), 3225 (N-H, symmetric stretching); ¹H-NMR (DMSO-d₆, ppm): 4.5 (s, -NH₂), 7.3 (d, -CH=C-N), 7.7 (d, -CH=C-O), 8.0 (d, -CH=C-O); ¹³C-NMR (DMSO-d₆, ppm): 125 (C=*C-NH₂), 100 (*C=C-NH₂), 115 (*C=C-O), 143 (C=*C-O).



Scheme 1: Synthesis of diamine

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4. Synthesis of benzoxazine monomers

4.1 Synthesis of bis (6-allyl-8-methoxy-3-phenyloxy-3, 4-dihydro-2H-1, 3-benzoxazinyl) oxane [Bzo-PHE]

The benzoxazine monomer bis (6-allyl-8-methoxy-3-phenyloxy-3, 4-dihydro-2H-1, 3-benzoxazinyl) oxane [Bz-PHE] was synthesized as described¹⁶ with some modifications as shown in Scheme 2.

In a 500 mL round bottomed three necked flask 1, 4 [bis (4'aminophenoxy) benzene] [BAPB] (0.05 m, 16.0 g), eugenol (0.1 m, 16.4 g) and 1, 4-dioxane (150 mL) were taken and stirred well to get a homogenous solution. Paraformaldehyde (0.3 m, 12.0 g) was added to the solution and the mixture was heated at 120 °C for 8 h in an oil bath with reflex condenser, and then reaction mixture was cooled to room temperature and finally poured into 1 L of aqueous sodium hydroxide solution (0.5 N). The precipitate formed was collected by filtration, washed several times with water. After drying at 60 °C in a vacuum oven, pale yellow powder was obtained (86% yield, m.p. 90 °C). FT-IR (KBr, cm⁻¹) 3044 (C-H), 1593 (C=C), 1327 (CH₂), 942 (oxazine ring), 1029, and 1233 (C-O-C), 1193 (C-N-C); ¹H-NMR (DMSO-d₆, ppm) 4.6 (s, Ar-CH₂-O), 5.3 (s, O-CH₂-N), 3.6 (s, -OCH₃), 3.3 (d, -CH₂*-CH=CH₂), 5.9 (m, -CH₂-CH*=CH₂), 5.0 (d, -CH₂-CH=CH₂^{*}), 6.5-7.5(m, aromatic protons); ¹³C-NMR (DMSOd₆, ppm) 49 (Ar-CH₂-O), 80 (O-CH₂-N), 56.0 (-OCH₃), 116.0 (-*CH₂-CH=CH₂), 137 (-CH₂-*CH=CH₂), 40 (-CH₂-CH=*CH₂).



Scheme 2: Synthesis of benzoxazine monomer

4.2 Functionalization of MWCNT

Multiwalled carbon nanotube was functionalized with ethylene amine by following the synthesis procedure of S. M. Yeun et al¹⁸. The FT-IR spectra of CNT and functionalized CNT are shown in Figure 1.



Figure 1: FT-IR spectra of a) MWCNT b) Acid functionalized MWCNT and c) Amine functionalized MWCNT

4.3 Preparation of Bzo/BMI blend and Bzo/BMI/CNT nanocomposites with different ratio

Synthesized benzoxazine monomer (5 g) and BMI (5 g) was dissolved in THF (10 mL) and stirred for 1 h at room temperature. To the solution 0.1 g of amine functionalized MWCNT was added and stirred at 80 °C to evaporate most of the solvent (THF).



Then the mixture was subjected to sonication to ensure that F-MWCNT was well dispersed in the mixture. After complete dispersion (of F-MWCNT) and evaporation of the solvent, a dark brown colored resin was obtained. Bzo/BMI/F-MWCNT nanocomposites were prepared by varying the F-MWCNT content (say 0, 1, 3 and 5 wt %). Each resin was introduced into a stainless steel mould and then step cured in an air circulating oven by following the cure cycle (100, 150, 200 °C each for an hour) and then finally post cured at 220 °C/1 h. All the cured samples are black colored with 3mm thickness (Scheme 3).

5.Results and Discussion

5.1 Structural analysis of benzoxazine

Chemical structure of the monomers was confirmed by FT-IR, ¹H NMR & ¹³C NMR spectral methods.

Eugenol based benzoxazine monomer (Bzo-PHE) was synthesised by the condensation reaction of eugenol with formaldehyde and amine as shown in Scheme 2. The FT-IR spectrum (Fig. 2) of the benzoxazine monomer shows characteristic absorption bands at 1233 cm⁻¹ (asymmetric stretching of C-O-C), 1029 cm⁻¹ (symmetric stretching of C-O-C) and 942 cm⁻¹ which is typical of benzoxazine ring structure ¹⁹. The spectrum also shows a band at 1376 cm⁻¹ due to tetra substituted benzene ring. Other aromatic vibrations are observed at 1593 and 1504 cm⁻¹. C-H stretching vibration of oxazine ring appears at 3044 cm⁻¹ and the peaks at 2934 and 2899 cm⁻¹ are owing to the asymmetric and symmetric stretching vibrations of the methylene group of the oxazine ring as well as alkyl side chain of eugenol ^{20,21}.



Figure 2: FT-IR spectrum of benzoxazine monomer

Fig. 3 shows the ¹H-NMR spectrum of the benzoxazine monomer. The characteristic oxazine ring protons appear as two singlets at 4.6 and 5.3 ppm which are assigned to the methylene protons of C-CH₂-N and O-CH₂-N respectively ²².

Fig. 4 shows the ¹³C-NMR spectrum of the benzoxazine monomer. The characteristic carbon resonances of the oxazine ring are found at 49 and 80 ppm, corresponding to the methylene carbons of Ar-CH₂-N and N-CH₂-O respectively. The peak at 56 ppm is attributed to the -OCH₃ carbon of eugenol moiety and the peaks at 116, 137 and 40 ppm are assigned to the allyl carbons [CH₂=CH-CH₂-], respectively.



Figure 3: ¹H-NMR spectrum of benzoxazine monomer



Figure 4: ¹³C-NMR spectrum of benzoxazine monomer

5.2 Curing profile of Bzo, Bzo/BMI blend and Bzo/BMI/F-MWCNT nanocomposites

DSC Analysis

The curing behavior of Bzo, Bzo/BMI blend and Bzo/BMI/F-MWCNT nanocomposites investigated by differential scanning

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calorimetry is shown in Fig. 5 and their values are tabulated in Table 1. The DSC thermogram of the benzoxazine monomer showed an endotherm and an exotherm. The endotherm at

90 °C is due to the melting point of the benzoxazine monomer.

The exotherm at 250 $^{\circ}\mathrm{C}$ is attributed to the ring opening of the benzoxazine monomer.

The influence of BMI in the polymerizability of the Bzo/BMI blend and Bzo/BMI/F-MWCNT nanocomposites was studied by DSC. All the DSC curves showed an endotherm at 90 °C, corresponding to the melting point of the benzoxazine monomer. This shows that there is complete miscibility of all the compounds (i.e., Bzo, BMI and F-MWCNT) in the blend and nanocomposites. Two exotherms were observed in the thermograms, one at 175 °C and the other at 250 °C, representing the curing reaction. As there are two exothermic curves, we can say that two different types of curing reactions should have taken place ¹.

The first exotherm is associated with the reaction between the maleimide group (of BMI) and allyl group (of Bzo monomer). The second exotherm is associated with the ring opening polymerization of benzoxazine. Moreover, due to the presence of allyl group (in Bzo), all the maleimide groups (of BMI) reacts with this allyl group and further there are no more maleimide group available for homopolymerization to occur²⁴.

The exothermic curing profile of Bzo/BMI/F-MWCNT nanocomposites is similar to that of Bzo/BMI blend, except for the one with high ratio of F-MWCNT. The Bzo/BMI/F-MWCNT (5%) nanocomposite showed a slight increase in the peak curing temperature. The processing window for Bzo/BMI blend and Bzo/BMI/F-MWCNT nanocomposites were around 60 °C, showing wide range of processability. Moreover, the blend (Bzo/BMI) and the nanocomposites (Bzo/BMI/F-MWCNT) showed another exotherm centered at 345 °C, indicating the degradation of aliphatic chains present in it.



Figure 5: DSC curves of a) Bzo b) Bzo/BMI c) Bzo/BMI/F-MWCNT (1%) d) Bzo/BMI/F-MWCNT (3%) and e) Bzo/BMI/F-MWCNT (5%)

S. No.	Samples	T _m (°C)	T _{onset} (°C)	T _{max} (°C)	ΔH ₁ (kJ/ mol)	ΔH₂ (kJ/mol)
1.	Bzo	90	225	248	-	29.8
2.	Bzo/BMI (1:1)	90	226	250	88.7	30.6
3.	Bzo/BMI/CNT (1%)	90	227	251	89.4	31.4
4.	Bzo/BMI/CNT (3%)	90	230	252	90.5	31.2
5.	Bzo/BMI/CNT (5%)	90	234	254	89.3	30.6

Table 1: DSC values of PBz, PBz/BMI blend and PBz/BMI/CNT.

 ΔH_1 : Amount of heat liberated of BMI react with allyl group ΔH_2 : Amount of heat liberated of Bzo ring opening

5.3 FT-IR analysis

nanocomposites

The curing reaction of Bzo and Bzo/BMI/F-MWCNT at different temperatures (say 100, 150, 200 and 250 °C) was monitored by FT-IR and are depicted in Figs. 6 & 7, respectively. The curing profile of the Bzo/BMI blend system was monitored by observing the changes in the peaks at 834 cm⁻¹ (=C-H of maleimide), at 939 cm⁻¹ (oxazine ring), at 1634 and 996 cm⁻¹ (allyl group), at 1711 cm⁻¹ (-C=O), at 1387 cm⁻¹ (-CN) and at 692 and 758 cm⁻¹ (imide ring), respectively. Upon curing, the intensity of the allyl peaks at 1634 and 996 cm⁻¹ and imide ring at 1387 and 834 cm⁻¹ decreased, which indicates that reaction occurred between allyl and maleimide groups. And further, the bands due to the imide ring at 692 and 758 cm⁻¹ disappears. On the other hand, the typical benzoxazine band at 939 cm⁻¹ decreased its intensity and finally disappeared during the curing process. Meanwhile, the -OH band at 3300 cm⁻¹ increased its intensity as the cure reaction advanced indicating that benzoxazine ring opening could be considered as one mode of polymerization²⁴. Thus, the spectral evidences mentioned above are in supportive of the expected cure sequence. Benzoxazine polymerization was completed between 200 - 250 °C, whereas the allyl group polymerization was comleted at 200 °C.

In the FT-IR spectra of Bzo/BMI/F-MWCNT nanocomposites, there are two regions of interest to study, in which one is the carbonyl region (between 1750 - 1650 cm⁻¹) and the other is the hydroxyl region (between 3500 - 3000 cm⁻¹). The characteristic carbonyl band was observed at 1711 cm⁻¹. In addition to it, two weak bands were observed at 1689 and 1704 cm⁻¹, respectively. These bands are a result of two types of intermolecular H-bonding interactions. Of which, one is between the carbonyl group of BMI and the hydroxyl group of PBz and the other is between the hydroxyl groups of PBz ²⁵.

From the above interpretation, it is clearly seen that the allyl group plays an active role in the polymerization of PBz/BMI/F-MWCNT nanocomposites. Benzoxazine ring also

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involves in the curing of blend and the nanocomposites and thus forms a well crosslinked polymer network.



Figure 6: FT-IR spectra of benzoxazine monomer at different curing temperatures





5.4 Di-electric profile of PBz, PBz/BMI blend and PBz/BMI/F-MWCNT nanocomposites

The effect of BMI and F-MWCNT on the dielectric constant and dielectric loss of polybenzoxazine were measured by using an impedance analyzer in the frequency range of 1 - 6 Hz at 30 °C. Fig. 8 and Table 2 show the dielectric curves and dielectric values of PBz, PBz/BMI blend and PBz/BMI/F-MWCNT nanocomposites. The dielectric constant values of the PBz/BMI/F-MWCNT nanocomposites increased incredibly with increasing content of F-MWCNT. Neat PBz and PBz/BMI blend have relatively poor ability for electrical conductivity [Neat PBz: 3.1, PBz/BMI: 3.2] due to its high organic Acoptente Nevertheless, on the addition of POLFLMWCNT, JOCHER conductivities have been significantly enhanced [PBz/BMI/F-MWCNT (1, 3 & 5%): 4.8, 6.7 & 8.4]. The functionalized MWCNT, even in less quantity (say 5%) disperse more homogeneously in the polymer matrix and thus results in producing polybenzoxazine nanocomposites with high conductivity 26,27 .



Figure 8: Dielectric constant of a) PBz b) PBz/BMI c) PBz/BMI/F-MWCNT (1%) d) PBz/BMI/F-MWCNT (3%) and e) PBz/BMI/F-MWCNT (5%)



Figure 9: Dielectric loss of a) PBz b) PBz/BMI c) PBz/BMI/F-MWCNT (1%) d) PBz/BMI/F-MWCNT (3%) and e) PBz/BMI/F-MWCNT (5%)

The dielectric loss of the nanocomposites also increased on increasing the weight percentage of F-MWCNT, as shown in Figure 9. Generally, the dielectric loss value of the material is contributed from three distinct factors, which includes direct

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current, conduction space charge migration and the dipole moment. The dielectric loss of neat PBz was found to be 1.5, for PBz/BMI blend it was found to be 1.7 and for the PBz/BMI/F-MWCNT (1, 3 & 5%) nanocomposites it was found to be 2.3, 3.1 and 3.7, respectively. This indicates that the network structure of PBz/BMI/F-MWCNT nanocomposites is highly crosslinked. Moreover, F-MWCNT restricted the mobility of the chains in the nanocomposites and thus hindered the curing of BMI, resulting in an increased dielectric loss factor. On the whole, both the dielectric constant and dielectric loss of PBz/BMI/F-MWCNT nanocomposites increased when compared with the neat PBz and PBz/BMI blend. It could be concluded that suitable content of F-MWCNT (say 5 wt %) in the PBz/BMI/F-MWCNT nanocomposites results in good dielectric property and retains good dielectric stability²⁸.

5.5 Morphology profile of PBz/BMI/F-MWCNT nanocomposites.

Fig. 10 illustrates the morphology of the fractured surface of PBz, PBz/BMI, F-MWCNT and PBz/BMI/F-MWCNT nanocomposites.



Figure 10: SEM images of a) PBz b) PBz/BMI c) F-MWCNT d) PBz/BMI/F-MWCNT (1%) e) PBz/BMI/F-MWCNT (3%) and f) PBz/BMI/F-MWCNT (5%)

The SEM micrograph of neat PBz displays a smooth and homogeneous surface. Whereas, the surface of PB2/BMI OFEnd is quite different, that shows dual phase morphology indicating apparent microphase separation. The degree of intermixing of benzoxazine and BMI is mainly affected by the compatibility between the two compounds²⁴. The degree of dispersion of F-MWCNT within the PBz/BMI matrix was investigated and their images are shown in Fig. 10 (d-f). The images show uniform and random dispersion of nanotubes in all the PBz/BMI/F-MWCNT nanocomposites. Moreover, the nanocomposites with low content of F-MWCNT i.e., 1 and 3 %, exhibits a homogeneous behavior. This fact is attributed to the miscibility of F-MWCNT with PBz/BMI matrix due to strong interfacial interaction (H-bonding) as well as chemical compatibility of PBz/BMI matrix with F-MWCNT. At higher F-MWCNT content (say 5 %), the surface of the nanocomposites seems to possess less amount of agglomeration.²⁷ These observations imply that even a minimum amount of functionalized MWCNT, when reinforced into the polymer matrix results in excellent thermal, electrical and mechanical properties of the polymer.

5.6 Dynamic mechanical properties of PBz, PBz/BMI blend and PBz/BMI/F-MWCNT nanocomposites

There are several important material parameters that could be derived from the DMA data. The storage modulus, ε' at 35 °C provides a measure of material's stiffness under shear deformation. The storage modulus of polybenzoxazine, their blend and nanocomposites are shown in Fig. 11 and the data are summarized in Table 2. The initial storage modulus of PBz was found to be 5.25 MPa, for PBz/BMI blend it was found to be 5.47 MPa and for PBz/BMI/F-MWCNT (1, 3 & 5%) nanocomposites it was found to be 5.78, 6.08 & 6.32 MPa, respectively. It was found that the storage modulus of the blend and the nanocomposites were found to be superior when compared with the neat PBz. This is attributed to the fact that in the case of PBz/BMI blend, the imide group (of BMI) and allyl group (of Bzo) involves in co-polymerization and forms a well cross-linked network^{1,24,29-31}. However, in the case of PBz/BMI/F-MWCNT nanocomposites, reaction between -NH₂ of F-MWCNT and C=C of BMI by Michael addition takes place. And there also exists π - π interaction between Bzo and CNT and as the CNT is functionalized with -NH₂ group, and Hbonding interaction between the -NH₂ group of F-MWCNT and -OH group of PBz. And due to these types of interactions, the movement of the main chain segments is restricted resulting in the formation of polymer nanocomposites with high crosslink densities.

The tan δ plots of PBz, PBz/BMI blend and PBz/BMI/F-MWCNT nanocomposites are shown in Fig. 12. The maximum peak temperature in the tan δ plots represents the glass transition temperature (Tg) of a material^{32}. The Tg value of the PBz/BMI [186 °C] and PBz/BMI/F-MWCNT (1, 3 & 5%) nanocomposites [221, 234 and 246 °C] increased when compared with neat PBz (162 °C).

 nanocomposites
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 S.No.
 Samples
 Dielectric
 DMA
 CLD x10⁵

Table 2: Dielectric, DMA and cross-link density values of PBz, PBz/BMI blend and PBz/BMI/CN/Ew Article Online

	–					
		constant, ε' (1 MHz)	loss, ɛ" (1 MHz)	Storage Modulus, ε' (GPa)	$T_{g}(^{\circ}C)$	(mol/m ³)
1.	PBz	3.24	0.16	5.25	162	6.83
2.	PBz/BMI (1:1)	3.32	0.19	5.47	186	7.12
3.	PBz/BMI/CNT (1%)	4.97	0.26	5.78	227	7.52
4.	PBz/BMI/CNT (3%)	6.63	0.31	6.08	234	7.91
5.	PBz/BMI/CNT (5%)	8.54	0.37	6.32	246	8.23



Figure 11: Storage modulus of a) PBz b) PBz/BMI c) PBz/BMI/F-MWCNT (1%) d) PBz/BMI/F-MWCNT (3%) and e) PBz/BMI/F-MWCNT (5%)

The crosslink density (CLD) of the polymer, their blend and nanocomposites was calculated from the storage modulus value at 35 °C. CLD is defined as the number of crosslink points per unit volume. The crosslink density may be in the order of 10^{-3} to 10^{-5} mol/cm³. For a typical rubbery material, there are about 15 to 15,000 monomeric unit between the crosslinks³³. The crosslink density of highly crosslinked thermoset can be determined by modulus measurement by using the following equation,

$v_c = \epsilon'/3RT$

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where ε' is the tensile storage modulus (MPa) of the polymer, T is the temperature (K) corresponding to the storage modulus value and R is the gas constant. The CLD values are tabulated in Table 2. The CLD of the PBz/BMI blend and PBz/BMI/F-MWCNT nanocomposites increased when compared with PBz and for the nanocomposites, it increased with higher loadings of F-MWCNT.



Figure 12: Curves showing tan δ values of a) PBz b) PBz/BMI c) PBz/BMI/F-MWCNT (1%) d) PBz/BMI/F-MWCNT (3%) and e) PBz/BMI/F-MWCNT (5%)

5.7 Thermal stability of PBz, PBz/BMI blend and PBz/BMI/F-MWCNT nanocomposites

Thermogravimetric analysis was performed to examine the effect of BMI and F-MWCNT on the thermal stability and decomposition behavior of PBz, as shown in Fig. 13 and their values are tabulated in Table 3. The thermal stability of PBz/BMI/F-MWCNT nanocomposites with increasing F-MWCNT content triggers a significant positive shift towards its degradation temperature. A noticeable increase in initial degradation temperature (T_i) was observed for the blend and nanocomposites when compared with pristine PBz. The initial degradation temperature was shifted from 251 °C (for PBz/BMI/F-MWCNT (1, 3 & 5) nanocomposites], respectively. In a similar way, degradation temperature at 5 and 10% weight loss (T₅ and T₁₀) were also shifted towards higher temperatures.

The incorporation of F-MWCNT into the PBz/BMI matrix was found to have a significant impact on the thermal properties of PBz. Indeed, it is well known that both F-MWCNT and Bzo will form π - π stacking with each other. As a result of this π - π stacking, there is a strong interfacial interaction between F-MWCNT and PBz in the supramolecular level. On the other hand, PBz/BMI/F-MWCNT nanocomposites have a network structure with high crosslink density that restricts the mobility of the chain segments ³⁴⁻³⁶. In addition to this, there is a network of H-bonding interactions, which makes the nanocomposites more stable than PBz. Moreover, the co-reaction (i.e., an alder-ene type of reaction) between PBz and BMI, results in the formation of single sphere system. This leads to an increase in char yield (at 800 °C) from 36.5 % (for PBz) to 39.2 % [for PBz/BMI] and 42.8, 44.0 & 46.3 % [for PBz/BMI/F-MWCNT (0.1, 0.3 & 0.5) nanocomposites], respectively.



Figure 13: TGA curves of a) PBz b) PBz/BMI c) PBz/BMI/F-MWCNT (1%) d) PBz/BMI/F-MWCNT (3%) and e) PBz/BMI/F-MWCNT (5%)

5.8 Flame retardant property of PBz/BMI/F-MWCNT nanocomposites

The flame retardancy or the non-flammability of neat PBz, PBz/BMI (1:1) blend and PBz/BMI/F-MWCNT nanocomposites is explained in terms of limiting oxygen index (LOI) value. LOI is defined as the minimum fraction of oxygen in a mixture of O_2 and N_2 that will support flaming combustion. The LOI values are calculated from the char yield (CY) values obtained from TGA analysis by using van Krevelan and Hofytzer equation ³⁷ as shown below,

LOI = 17.5 + 0.4 (CY)

The LOI value of PBz, PBz/BMI blend and PBz/BMI/F-MWCNT (1, 3 & 5%) nanocomposites were found to be 32.1, 32.7, 34.6, 35.1 and 36.0, respectively. As these values are greater than 26 (threshold value), we can say that these materials have good self-extinguishing and flame retardant properties ³⁸.

Table 3: TGA values of PBz, PBz/BM	II blend and PBz/BMI/CNT
nanocomposites	DOI: 10.1039/C7NJ00357A

S.No.	Samples	Ti	T 5	T ₁₀	CY	LO
		(°C)	(°C)	(°C)	(%)	Ι
1.	PBz	251	260	310	36.5	32.1
2.	PBz/BMI (1:1)	280	347	391	39.2	32.7
3.	PBz/BMI/CNT (1%)	294	362	403	42.8	34.5
4.	PBz/BMI/CNT (3%)	308	378	412	44.1	35.1
5.	PBz/BMI/CNT (5%)	315	391	428	46.3	36.9

6.Conclusion

The curing behavior, thermal, mechanical and dielectric properties of PBz/BMI blend and PBz/BMI/F-MWCNT nanocomposites have been investigated. BMI was used to stabilize the benzoxazine moiety, as it limits the thermal degradation of PBz by the formation of dense crosslinked network through ene-addition. During the curing process, the allyl functionality of eugenol undergoes heteropolymerization with BMI that prevents the homopolymerization of BMI itself. When combined as composites, the attractive characteristics of all the three components i.e., PBz, BMI and F-MWCNT are apparent. The introduction of F-MWCNT into PBz/BMI copolymer changed the chemical cross-linked network, which exerted a tremendous influence on the mechanical and thermal properties. Compared to PBz, the higher crosslinking density of PBz/BMI/F-MWCNT nanocomposites led to higher degradation temperature [T₅ of PBz/BMI/F-MWCNT (5%): 391 °C], mechanical stability [storage modulus of PBz/BMI/F-MWCNT (5%): 6.32 GPa] and glass transition temperature [Tg of PBz/BMI/F-MWCNT (5%): 246 °C] indicating better thermomechanical stability of the nanocomposites at service temperature. These enhancements are attributed to the effective participation of F-MWCNT in the formation of nanocomposite network, as these F-MWCNTs act as an internal reinforcing framework hindering volume changes in the nanocomposites. In addition, the excellent electrical property of CNT is preserved during curing, that results with materials possessing high conductivity [ɛ' of PBz/BMI/F-MWCNT (1, 3 & 5%): 4.97, 6.63 & 8.54]. In summary, F-MWCNT along with BMI paves a way for the preparation of sustainable high performance bio-based PBz/BMI/F-MWCNT nanocomposites which will find use for advanced high technology purposes.

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Functionalized MWCNT, an efficient reinforcement for the preparation of eugenol based high performance PBz/BMI/CNT nanocomposite exhibiting outstanding thermo-mechanical properties

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This work contemplates the stabilization of eugenol-based benzoxazine networks with the addition of BMI and amine functionalized multiwalled carbon nanotube.

