Effect of Organo-Montmorillonite Nanoclay on Mechanical Properties, Thermal Stability and Ablative Rate of Carbon fiber /Polybenzoxazine Resin Composites

Golla Rama Rao[#,@], Ivautri Srikanth[#,*], and K. Laxma Reddy[@]

[#]DRDO-Advanced Systems Laboratory, Hyderabad - 500 058, India
[@]Department of Chemistry, National Institute of Technology, Warangal - 506 004, India
[*]E-mail: isrikanth@asl.drdo.in

ABSTRACT

Organo-Montmorillonite (o-MMT) nanoclay added polybenzoxazine resin (type I composites) were prepared with varying amounts of clay (0, 1, 2, 4 and 6 wt %). Clay dispersion, changes in curing behaviour and thermal stability were assessed in type I composites. Findings from these studies of type I composites were used to understand thermal stability, mechanical, and mass ablation rate behaviour of nanoclay added carbon fiber reinforced polybenzoxazine composites (type II). Interlaminar shear strength and flexural strength of type II composites increase by 25% and 27%, respectively at 2 wt% addition of clay. An oxy-acetylene torch test with a constant heat flux of 125 w/cm² was used to investigate mass ablation rate of type II composites. The ablation rate has increased as the weight percentage of clay has increased. This is contradicting to type I composites with up to 6 wt% clay and type II composites with up to 4 wt% clay, which have improved thermal stability. The microstructure of the ablated composites was examined using scanning electron microscopy. Increased ablation rates are due to the reaction of charred matrix with nanoclay, which exposes bare fibers to the ablation front, resulting in higher mechanical erosion losses.

Keywords: Carbon fiber; Polybenzoxazine resin; Organo-montmorillonite nanoclay; Thermomechanical properties; Ablation rate; Microstructure

1. INTRODUCTION

Composites made of phenolic matrix are used for high temperature thermal protection application due to their ability to provide good thermomechanical properties, thermal stability with low ablation rate. Phenolic resin has processing disadvantages such as volatiles evolution due to condensation polymerisation reaction. In addition to this, phenolic resin has low shelf life which adds to the processing cost[1-2]. In view of this, many researchers are exploring alternate resin systems for high temperature applications like cyanate ester resins, polyimide and benzoxazine resin (BZ). These resin systems undergo additional cured polymerisation giving no process volatiles. In addition, benzoxazine resin offers additional advantages such as good shelf life, and good flame retardant properties, coupled with good thermo mechanical properties with low volumetric shrinkage and moisture absorption[3-5]. Thus, there are many technical advantages in using BZ instead of phenolic resin. As a result, the current research focused on the carbon fibre reinforced polybenzoxazine resin composite as a candidate material for use in thermal protection systems (TPS).

Many studies on nanofillers such as nanosilica, nanographite, carbon nanotube, organo-nanoclay, polyhedral oligomer silsesquioxane (POSS), and nanozirconium have been published in the literature to improve the thermomechanical efficiency of high temperature polymer composites[6-11]. Organic treated montmorillonite nanoclay is the most commonly used filler since it is readily available and miscible with resin systems. Previous studies have shown that introducing nanoclay particles to polymer composites enhances their thermomechanical properties significantly[12-16]. TPS applications need excellent thermomechanical properties. It is reported that nanoclay can impart these properties to polymer matrices[17-18]. For instance, Agag[19], *et al.* reported organo-nanoclay modified polybenzoxazine nanocomposites with allyl dimethyl stearyl ammonium-montmorillonite and propyl dimethyl stearyl ammonium-montmorillonite with clay loadings (3,7,10 wt%). Organo-nanoclay catalysed polymerisation of benzoxazine resin was reported. It is also reported that thermal stability of resin has increased with increased nanoclay content[19]. Many researchers studied the thermal stability of nanoclay added polybenzoxazine composites and mechanical properties of glass fibre reinforced benzoxazine composites[20-24]. Furthermore, no studies on the ablative performance of benzoxazine resin composites have been published.

Although there is a lot of literature on nanoclay reinforced polybenzoxazine resin matrices, no research on nanoclay modified carbon fibre – polybenzoxazine matrix (C-BZ) composites has been done to the author's knowledge, despite the fact that carbon fibre composites are the most promising for end applications. The present work aims at addressing this gap.

Aims of the present research work are:

(i) To prepare o-MMT nanoclay added benzoxazine composites (type I) by adding various weight percentages of o-MMT nanoclay, studying clay dispersion in resin by using SAXS, and studying the curing behaviour and thermal stability changes due to clay addition.

(ii) Preparation of o-MMT nanoclay added carbon fibre-poly benzoxazine resin composites (type II) with various clay weight percentages (same as type I composites) to find out how clay influences on thermal stability, mechanical properties and ablation rate.

(iii) Correlating type II composite's thermomechanical and ablation properties with type I composite observations.

2. MATERIALS

Benzoxazine (BZ) resin based on aniline, formaldehyde, bisphenol F with the trade name Anazine was procured from M/s Anabond Limited, Chennai, India. Benzoxazine has 65 wt% solid content and remaining amount as solvent (methyl ether ketone). Char yield of the cured poly benzoxazine resin is about 48 wt % in inert atmosphere at temperature 900°C. PAN based carbon fabric having thickness of 0.38 mm (carbon fibre T 300, 3K, M/s Torayca) was selected. Montmorillonite nanoclay with organic treatment (o-MMT) (grade of clay is nanomer 1.31 PS) was selected in this study. Nanoclay contains 0.5 to 5% aminopropyl triethoxysilane and 15 to 35 % octadecyl amine in its organic portion.

3. EXPERIMENTAL

The experimental work is depicted in Fig. 1 as a schematic diagram.
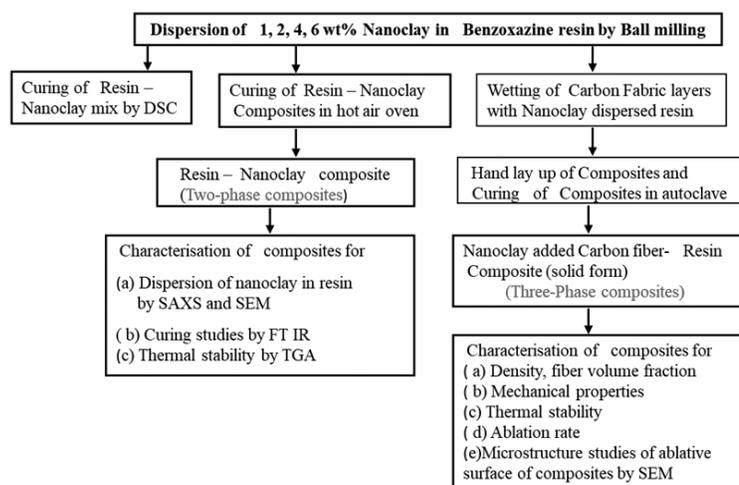
Figure 1. A schematic diagram for experimental work.

3.1 o-MMT Nanoclay Dispersion in Benzoxazine Resin

Benzoxazine resin was combined with nanoclay in a predetermined amount. In a stainless steel bowl with a capacity of 500 ml, approximately 200 g of this mixture was poured. Stainless steel balls were added to this mixture at 0.5:1 weight ratio. Nanoclay added resin mix was ball milled at 250 rpm for two hours. Thus nanoclay dispersed benzoxazine resin mixtures

were prepared with different wt % of clay. The addition of nanoclay to benzoxazine caused changes in viscosity, which were studied using a Brookfield viscometer. These mixtures were used to make two types of composites, as described below.

3.2 Preparation of Benzoxazine Resin - Nanoclay Composites

Volatiles in the resin were removed by heating the nanoclay dispersed resin mix in a petri dish at 60 °C / 1 hour. This resin –nanoclay mixture was polymerised in hot air circulating oven as per cure cycle of 60 °C /1 hour + 80 °C /1 hour + 140 °C /1 hour + 170 °C /3 hours + 180°C /2 hours + 200 °C / 4 hours. Table 1 lists benzoxazine resin - nanoclay composites (type I) that were produced.

Table 1. Description of type I and type II composites

Nanoclay (NC) (wt %) loading in resin	Type I composite	Type II composite
0	Benzoxazine resin (BZ)	C- BZ (blank)
1	1 NC- BZ	1 NC / C-BZ
2	2 NC- BZ	2 NC / C-BZ
4	4 NC- BZ	4 NC / C-BZ
6	6 NC-BZ	6 NC / C-BZ

3.3 Preparation of Nanoclay Added Carbon Fibre Reinforced Benzoxazine Resin Composites

For fabricating each of the type-II composite, twelve layers of carbon fabric with size of 300 x 300 mm were collected. These layers were applied with nanoclay dispersed benzoxazine mixture using nylon brush. Subsequently resin impregnated fabrics were laid on a mould and followed by vacuum bagging. This stack was cured in an autoclave at five bars of pressure and one bar of vacuum, following temperature cycle of 60 °C /1 hour + 80 °C /1 hour +140 °C /1 hour + 170 °C /3 hours + 180 °C /2 hours + 200 °C / 4 hours. Table 1 lists the o-MMT nanoclay added carbon fibre reinforced benzoxazine resin composites (type II) that were produced.

4. TESTING AND CHARACTERISATION

4.1 Curing studies of Benzoxazine Resin –nanoclay Composites

The curing behaviour of benzoxazine resin – nanoclay composites was investigated using differential scanning calorimetry (Q200, M/s Waters India Pvt limited). DSC was performed on 10 mg sample from 30 to 400 °C with rate of heating 10 °C/min in nitrogen atmosphere.

4.2 Nanoclay Dispersion Studies in Resin

Nanoclay dispersion in resin was examined with small angle X-ray scattering (SAXS). Scanning electron microscope (SEM) is used to study dispersion studies.

4.3 Fourier-Transform Infrared Spectroscopy (FTIR)

The Agilent 640 series with the Ge-ATR attachment was used to record FTIR spectra. As received nanoclay, nanoclay heated at 200 °C for 2 hours, liquid benzoxazine resin, cured benzoxazine resin and type I composites were studied in transmission mode and spectra from 4000 to 700 cm-1 were collected.

4.4 Volume Fraction of Fibre (%V_f)

V_f of fibre in nanoclay added carbon fibre reinforced benzoxazine resin composites was determined as per ASTM D 3171.

4.5 Thermal Degradation

Thermogravimetric analysis (Q500, M/s Waters India Pvt limited,) runs were performed on samples of o-MMT nanclay, composites of type I and type II from RT to 900 °C nitrogen atmosphere with heating rate 10 °C/minute. Temperature at 5% mass loss ($T_{5\%/^{\circ}C}$), residual carbonaceous char (CR) were recorded.

4.6 Interlaminar Shear Strength (ILSS) and Flexural Strength

samples were collected from nanoclay added carbon fibre reinforced benzoxazine resin composites for ILSS and flexural strength tests and samples were tested as per ASTM D 2344 and ASTM D 790 respectively. Minimum of six samples were tested for each property.

4.7 Mass Ablation Rate

o-MMT nanoclay added carbon fibre reinforced benzoxazine resin composites were tested for mass ablation rate by oxyacetylene torch test as per ASTM E 285. To conduct this test, samples measuring 10 cm × 10 cm x 0.42 cm were used. A flame source with heat flux of 125 w/cm^2 was used to expose samples for 60 seconds. The mass loss per second was measured for composites. The average mass ablation rate was calculated from two samples.

4.8 Characterisation of Microstructure

Microstructure of the type II composite samples exposed to oxyacetylene flame was studied with scanning electron microscope (SEM).

5. RESULTS AND DISCUSSION

5.1 The Curing Behaviour of Nanoclay Added Resin Composites

DSC scans for the neat Benzoxazine (BZ) resin, and nanoclay added BZ mixture in Fig. 2. Initially observed endothermic peaks can be ascribed to the process of evaporation of solvent from the resin. The cure characteristics temperatures namely initiation (Ti), onset (Te), Peak (Tp), end set (Tf), and heat of polymerisation reaction (ΔH) are all shown in Table 2. It was observed from Table 2, cure characteristic temperatures valued were shifted to lower values as relative to reference BZ. It's due to the reaction of organo nanoclay with BZ monomer in ring opening[19,25]. It can be seen that the ΔH
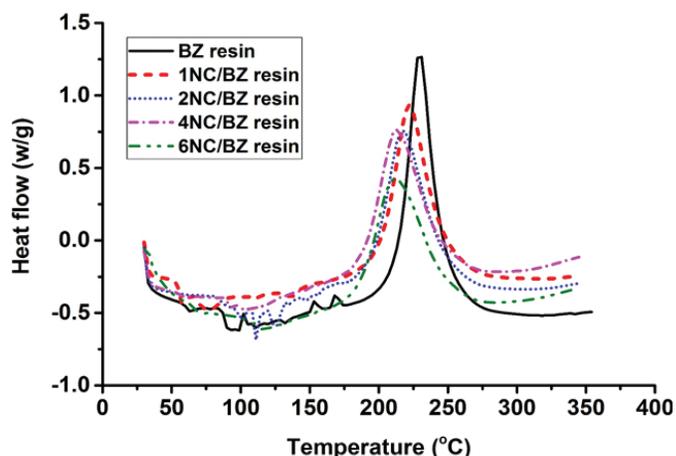
Figure 2. DSC scans for the neat Benzoxazine (BZ) resin, and nanoclay added BZ mixture.

Table 2. Cure temperatures and heat of reaction of resin with varying clay contents

Nanocomposites description	Nanoclay (by wt %)	Ti (⁰C)	Te (⁰C)	Tp (⁰C)	T_f (⁰C)	ΔH (J/g)
BZ resin	0	177	213	230	291	275
1 NC/ BZ	1	160	200	222	294	253
2 NC/BZ	2	158	195	217	299	247
4 NC/ BZ	4	113	186	212	295	300
6 NC/ BZ	6	110	183	211	286	285

is initially is coming down up to 2 wt% addition of nanoclay, followed by increase. Initially with the addition of nanoclay, hindrance for the diffusion of polymeric monomers during cross linking increases. This is reducing the overall cross link density. However, from 4 wt% nanoclay addition onwards, as the nanoclay is agglomerating and not spread throughout the matrix, it can't hinder the molecular diffusion during curing. However, as the organic part of nanoclay is playing the catalytic role with ring opening of BZ resin, it is triggering the reactions and acting as nucleating sites for their completing. This could have resulted in the higher ΔH at higher loading of o-MMT nanoclay. The observed patterns were found to be consistent with previously published heat of polymerisation data for nanoclay added polymers[19]. Thus, present study indicates that, o-MMT acts as catalyst for curing of benzoxazine resin.

5.2 Effect of Nanoclay in Curing of Benzoxazine Resin–nanoclay Composites

FTIR spectrums of as received nanoclay, nanoclay heated at 200 °C for 2 hours, liquid benzoxazine resin, cured benzoxazine resin and cured benzoxazine resin-nanoclay composites and resultant spectrum of subtracted spectrum cured benzoxazine from cured benzoxazine resin-nanoclay composite are shown in the Fig. 3.

Figure 3 (a) represent the spectrums of nanoclay and liquid BZ which shows the characteristic peaks of Siloxane at 1024^{-1} cm and 942,1027,1232 and 1490 cm^{-1} respectively. Fig. 3 (b) shows the FTIR spectrums of cured type I composite samples, cured benzoxazine resin and nanoclay sample heated at 200 °C. FTIR spectrums of cured type I composite samples and cured
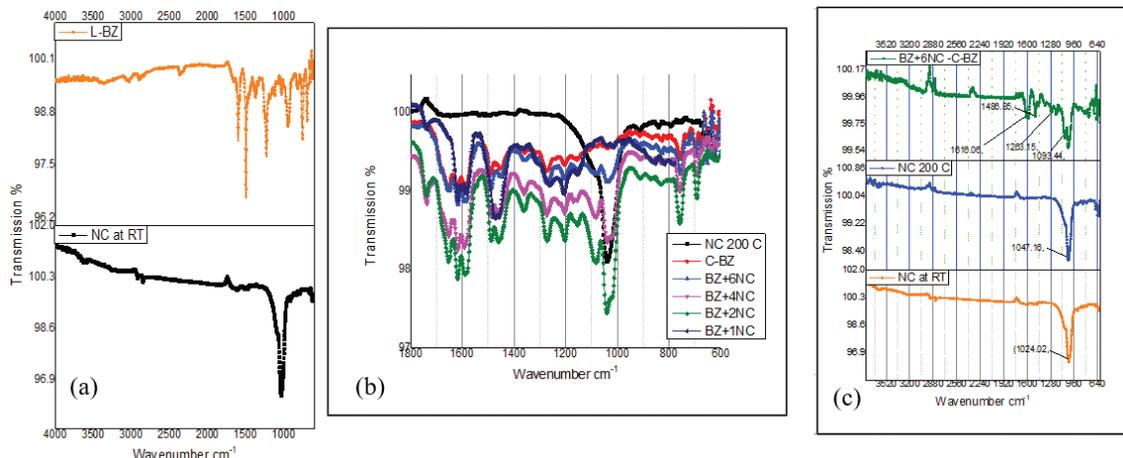
Figure 3. FTIR spectrums of (a) Nanoclay and Liquid BZ (b) heated Nanoclay, cured benzoxazine resin and type I composites (c) Nanoclay (as received), nano clay heated at 200 °C and resultant spectrum of nanoclay (subtracted BZ from B-NC composite).

benzoxazine shows the disappearance of all characterstic peaks of benzoxazine and appears a new peak at 1477 cm^{-1} indicates that complete polymerisation of benzoxazine in all composites samples. The effect of nanoclay in curing of benzoxazine resin – nanoclay (BZ-NC) composite was determined by FTIR subtraction method, in which cured BZ FTIR spectrum was subtracted from BZ-NC spectrum. Resultant FTIR subtracted spectrum was compared with that of NC before and after heated samples. Fig. 3(c) shows the FTIR spectrums of nanoclay (as received), nano clay heated at 200 °C and resultant spectrum of nanoclay (subtracted BZ from BZ-NC). Nanoclay before and after heating exhibits a large peak at 1027 cm^{-1} that matches to siloxane structure, indicating that siloxane and other functional groups do not change with heating. Subtracted FTIR spectrum shows that characteristic peak of nanoclay and also shows additional peaks at 758, 1083, 1202, 1265 & 1353 cm$^{-1,}$ which may be due to stretching and bending vibrations of new siloxane and secondary amine structures. FTIR subtracted spectrum indicates that the amine and hydroxyl groups present on the organo modified montmorillonite nanoclay participate in the ring opening reaction and also forms the part of the product.

5.3 Nanoclay Dispersion in Resin–nanoclay Composites

Figure 4 depicts the SAXS patterns of the nanoclay and resin-nanoclay composites.

The d-spacing of nanoclay and type I composites is measured using Bragg's law. Table 3 displays the results of d spacing values.

Figure 3 shows that the crystalline peak of o-MMT clay was not observed in 1 wt% and 2 wt% clay added composites, indicating that layers of clay were exfoliated in the benzoxazine. SAXS patterns of 1 wt% and 2 wt % nanoclay added Polybenzoxazine resin composite have not shown any crystalline peak of nanoclay at lower scattering vector (q). After 2 wt% addition of nanoclay, SAXS patterns have shown crystalline peaks and d spacing of nanoclay has increased from 32Å to 40Å. This indicates that the nanoclay in the 4 wt% and 6 wt% composites was partially intercalated.
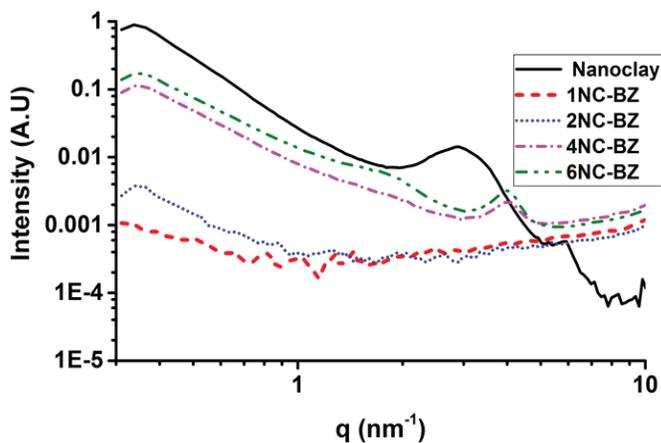
Figure 4. SAXS of o-MMT nanoclay clay and nanoclay dispersed resin composites.

Table 3. *d* spacing values for as received nanoclay and nanoclay dispersed in Polybenzoxazine resin composites

Nanocomposites description	% Nanoclay loading in resin	d 001 (Å)
Nanoclay	Nanomer 1.31 PS	32
1 NC-BZ	1 wt%	No crystalline peak
2 NC-BZ	2 wt%	No crystalline peak
4 NC-BZ	4 wt%	40
6 NC-bz	6 wt%	40

SAXS shows clay layers separation, while clay distribution in the matrix can be seen on a macroscopic scale in the scanning electron microscopy. SEM images of nanoclay distribution in clay added benzoxazine resin composites are shown in Figure 5. The silicon molecule, which is one of the key constituents of o-MMT nanoparticles, is associated with the white spots in the images in Fig. 5. As a result, more white spots with a uniform distribution around the exposed region suggest the presence of clay in resin.
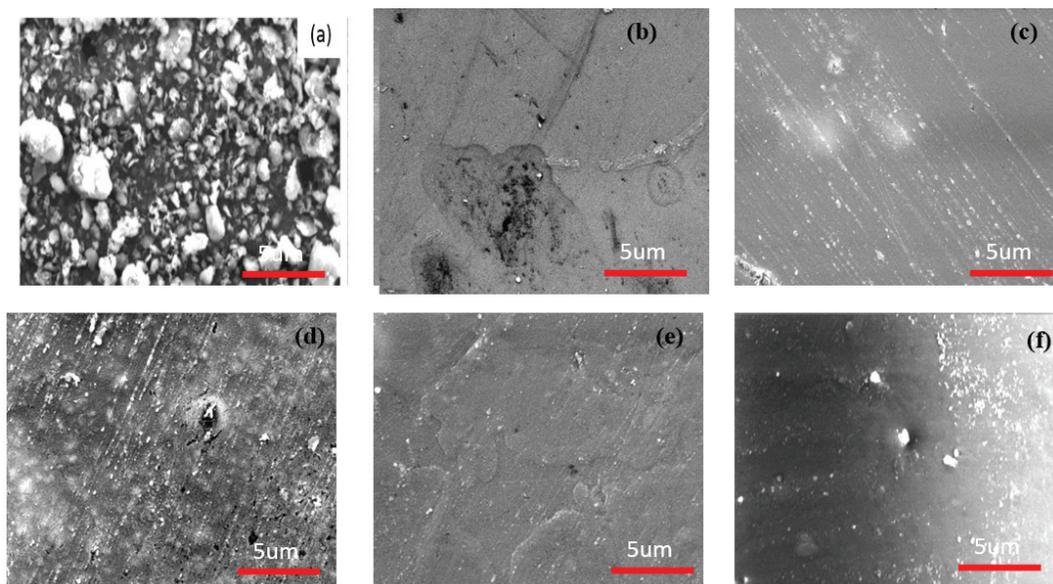
Figure 5. Scanning electron microscopy images of (a) nanoclay (b) 1 wt% nanoclay loaded benzoxazine composite (c) 2 wt% nanoclay loaded benzoxazine composite (d) 4 wt% nanoclay loaded benzoxazine composite (e) 6 wt% nanoclay loaded benzoxazine composite.

5.4 Volume Fraction of Fibre in Nanoclay Added C-BZ Composites

Table 4 shows that as the clay content increased in the resin, the volume fraction of fibre in composites decreased. It is owing to increased viscosity of the resin at higher nanoclay loadings, which do not squeeze out of the fabric layers during composite processing, resulting in a lower fibre volume fraction[8-13].

Table 4.   Volume fraction of fibre of nanoclay added C-BZ composites

Composite description	Clay content in resin (wt%)	Volume fraction of fibre (%)
C- BZ (blank)	0	58
1 NC / C-BZ	1	58
2 NC / C-BZ	2	56
4 NC / C-BZ	4	56
6 NC / C-BZ	6	53

5.5 Thermal Degradation of Nanoclay and Composites

Thermograms of nanoclay, nanoclay added BZ composites and nanoclay added C-BZ composites are shown in Fig. 6.

The results of temperature at 5% weight loss and char yield of resin-nanoclay composites and nanoclay added carbon fibre-resin composites are shown in Table 5.

Table 5.   Degradation temperature and char yield of type I and type II composites

%Nanoclay (by wt) in composite	$*T_{5\%/°C}$		% Char yield at 900 °C	
	Type I	Type II	Type I	Type II
0	303	405	48	84
1	315	413	46	84
2	315	415	47	83
4	325	414	45	83
6	340	390	45	80

*Temperature of the sample at 5% weight loss
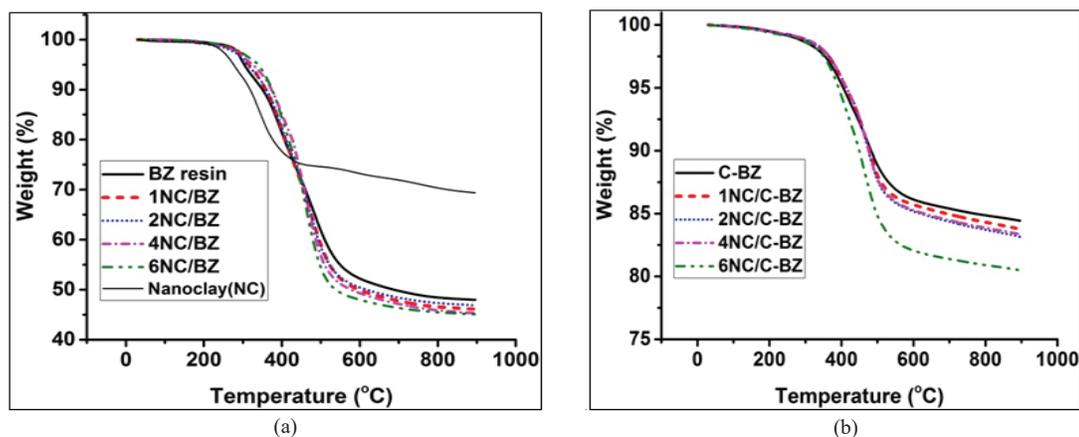
Figure 6. Thermograms of (a) nanoclay and clay added BZ composites (b) o-MMT nanoclay added C-BZ composites.

The thermal decomposition of the o-MMT nanoclay and subsequent weight loss began around 250 °C and ended around 450 °C, as can be seen. At 900 °C, the remaining weight of nanoclay means that about 70% of the o-MMT nanoclay is inorganic nature and the 30 % of clay is organic nature. Figure 4 shows that the char yield of benzoxazine resin is approximately 48 wt%. Type I composites with a nanoclay addition of up to 6% and type II composites with a nanoclay addition of up to 4% improved their thermal stability. Nanoclay provides a barrier to oxygen and matrix interactions, resulting in increased thermal stability[26-27] . T5 %/°C has decreased in relative to the blank at 6 wt% loading due to increased resin content in composites at higher loadings of nanoclay. Furthermore, the organic component of the nanoclay is known to generate oxidising volatiles, reducing the matrix's thermal stability. This effects becomes prominent at higher loading of the nanoclay[8].

5.6 Interlaminar Shear Strength of Nanoclay Added C-BZ Composites

ILSS values of nanoclay added C-BZ composites are shown in Fig. 7. With 1wt% loading of nanoclay, ILSS value increased (25% increase at 2 wt% loading) as relative to the reference C-BZ composite. This is because of the good miscibility of nanoclay in resin up to 2 wt%. ILSS began to decrease after 2 wt%, but it remain higher than reference C-BZ composites. The higher interfacial area of clay platelets and the ability of the organic component of nanoclay platelets to effectively bond with matrix can be attributed to increase ILSS due to nanoclay [28-30].
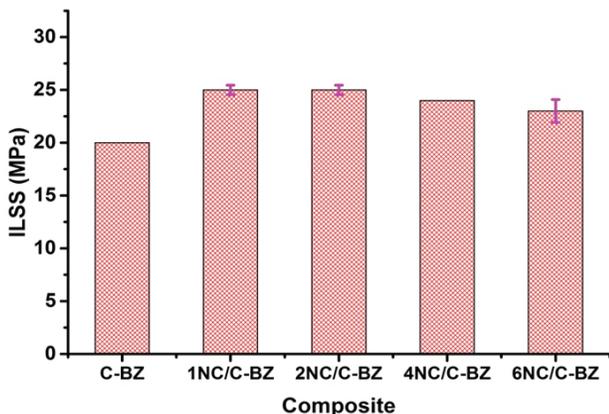
Figure 7. ILSS of o-MMT nanoclay added C-BZ composites.

5.7 Flexural Strength of Nanoclay Added C-BZ Composites

Flexural strength values of nanoclay added C-BZ composites are shown in Fig. 8

The addition of 1 wt% clay significantly increased flexural strength, with marginal improvements up to 2 wt% clay increasing flexural strength by about 27%. After 2 wt% nanoclay, flexural strength decreased. This is owing to good dispersion of nanoclay in resin up to 2 wt%. Nanoclay at 4 wt% and 6 wt% loadings in composites, on the other hand, has provided comparable flexural strength to blank composites, despite the fact that the fibre volume fraction in these composites is lower than in blank composites. This indicates, nanoclay
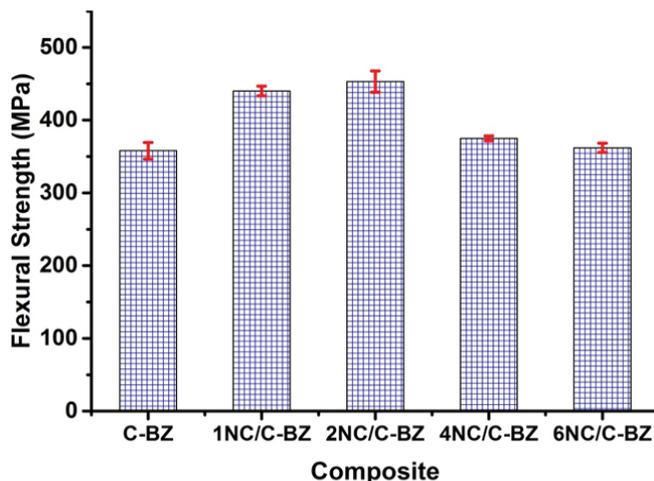
Figure 8. Flexural strength of o-MMT nanoclay added C-BZ composites.

platelets are strengthening the composite. Furthermore, the findings show that nanoclay platelets can improve the flexural strength of composites under exfoliated conditions by forming strong chemical bonds with the matrix, preventing cracking and deboning. The composites' overall strength is improved by the additional chemical bonds formed in the matrix.[31-33].

5.8 Mass Ablation Rate of Nanoclay Added C-BZ Composites

The mass ablation rates of nanoclay added C-BZ composites are shown in Table 6.

Table 6. Mass ablation rate of nanoclay added C-BZ composites

Composite description	% Nanoclay (by wt)	Mass ablation rate (mg/sec)	
C-BZ(blank)	0	115	-
1 NC/ C- BZ	1	133	(16 %)
2 NC/ C-BZ	2	154	(34 %)
4 NC/ C- BZ	4	163	(42 %)
6 NC/ C- BZ	6	179	(56%)

*In parenthesis, the % increase in mass ablation rate over a blank value is shown.

As the weight percentage of nanoclay content has increased, ablation rates have increased relative to blanks. Under inert conditions, the polybenzoxazine resin in the composite can degrade according to the reaction shown in Eqn (1)[34].

$$\text{Polybenzoxazine resin} \longrightarrow C \text{ (Char)} + CO + CO_2 + NH_3 - \text{Heat} \quad (1)$$
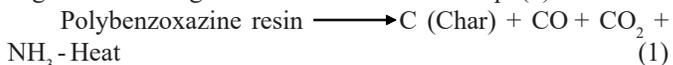
On the other hand, organic part of nanoclay degrades and gives oxygen as one of the byproducts.

Char formed in the reaction (1) can further react with the oxygen evolved from the organic part of the clay as per reaction (2) as shown below.

$$C \text{ (Char)} + O_2 \longrightarrow CO_2 + H_2O + CO - \text{Heat} \quad (2)$$
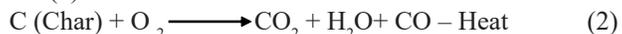
Because of the reaction shown in Eqn (2), char gets removed at a faster rate from the sample under ablation, thus bare fibres gets exposed to the flame thereby removing large chunks of composites. Effect of char removal and subsequent increase in the ablation rate will be more pronounced at higher
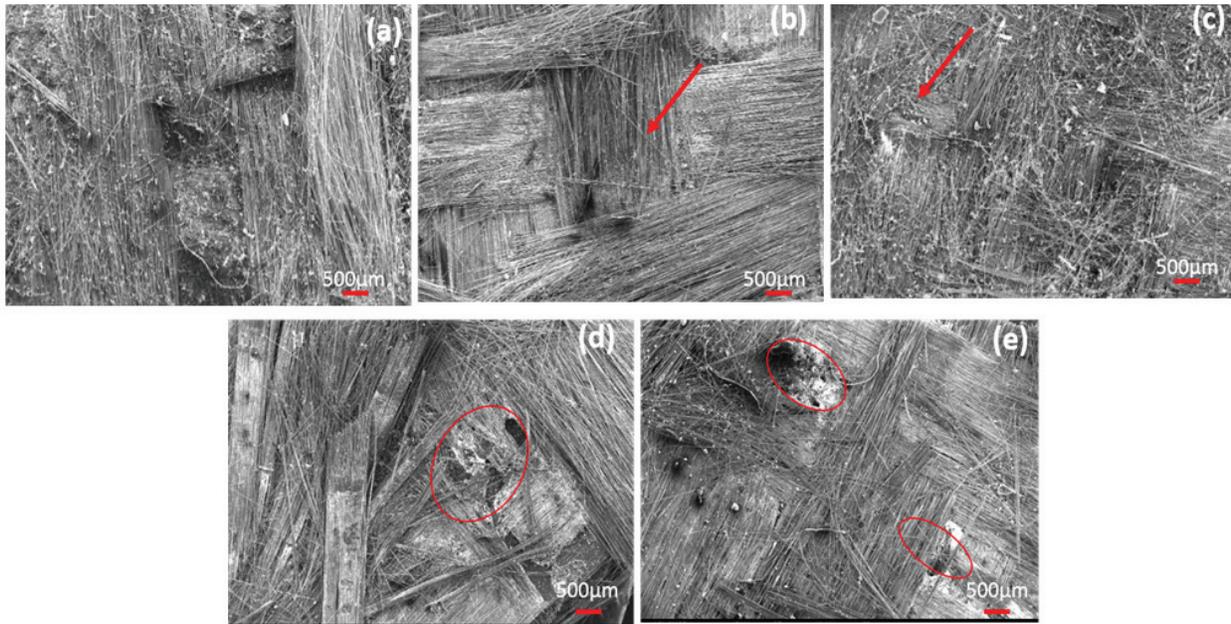
Figure 9. Microstructure of ablated samples (a) Blank C-BZ (b) 1 wt% nanoclay added C-BZ , arrow indicating minor fiber breakage with traces of matrix present (c) 2 wt% nanoclay added C-BZ , arrow increasing depth of damage on carbon fiber tows (d) 4 wt% nanoclay added C-BZ , encircled zone showing deep grooves of damage with large of chunks of composites removed (e) 6 wt% nanoclay added C-BZ , encircled zones showing deep grooves of damage with large of chunks of composites removed.

loading of o-MMT nanoclay leading to more ablation. This aspect can be understood from the microstructural changes of the ablated surfaces as discussed in subsequent sections.

5.9 Microstructure characterisation of ablated surface of Type II composites

Figure 9 depicts the microstructures of ablated surfaces.

Figure 9(a) shows the blank C-BZ composite after ablation. There is no major damage to the fibres in the blank C-BZ composite, as can be seen. Traces of charred matrix holding the fibres together can be noticed for blank C-BZ composite. However, in case of nanoclay added composites, because of reaction of char with nanoclay, bare fibres are being exposed. More is the nanoclay content, more is the damage to the matrix resulting in more damage area. At 4 wt% and 6 wt% nanoclay loading, deep grooves in the thickness direction of the composite can be seen (encircled zones in Figs. 9(d) & (e). This is because of the advancement of heat front ahead of ablation front which creates a situation, where, composite starts to degrade much ahead it sees the oxyacetylene flame. As the damage in the heat advancement zone increases, the erosive losses of the material when it sees the oxyacetylene flame will be more. The type II composites with nanoclay added have a higher ablation rate as a result of this.

6. CONCLUSIONS

The effect of adding different weight percentages (1, 2, 4 and 6 wt%) of o-MMT nanoclay on the thermal stability, mechanical properties and mass ablation rate of carbon fibre reinforced benzoxazine (type II) was investigated. To understand the changes in the curing behaviour and thermal stability of matrix part of the composite, nanoclay added

benzoxazine composites (type I) were also fabricated and the results obtained from type I composites were correlated with thermomechanical behaviour of type II composites. The following is a summary of the study findings.

- Up to 2 wt% addition of o-MMT nanoclay in benzoxazine resin, exfoliation of clay platelets in resin was observed, beyond which clay platelets are not getting segregated effectively.
- Thermal stability was increased in type I composites with a clay addition of up to 6% and type II composites with a clay addition of up to 4%.
- Interlaminar shear strength and flexural strength of type II composites increased by 25% and 27%, respectively, with a 2 wt% addition of nanoclay, and afterwards these parameters decreased.
- When the weight % of nanoclay in type II composites was increased in comparison to the reference, the mass ablation rate increased.
- Based on above properties, 1 wt% o-MMT nanoclay as filler is optimum for improving performance of carbon fibre reinforced polybenzoxazine resin composites without much compromise in the ablation performance.

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CONTRIBUTORS

Mr Golla Rama Rao has obtained his MSc (Chemical Science) from Pondicherry University, Pondicherry in 1997 and MTech (Polymer Science and Technology) from Indian Institute of Technology, Delhi in 1998. Currently pursuing his PhD from National Institute of Technology, Warangal. He is currently employed as a Scientist 'F' at the DRDO-Advanced Systems Laboratory, Hyderabad, where he is working on the development and characterisation of high performance polymers for fibre reinforced composite materials, as well as the characterisation of composite materials for the generation of design input data for aerospace applications. He has received Laboratory Scientist of the Year-2017 and Agni Award for Excellence in Self Reliance-2018. He has published so far 14 research articles.
His contributions in the present study are finalising the experimental plan, fabrication of samples, testing and results interpretation.

Dr Ivautri Srikanth has obtained MTech (Corrosion Science and Technology) from Indian Institute of Technology, Bombay in 2000, PhD (Metallurgical Engineering and Material Science) from Indian Institute of Technology, Hyderabad in 2014. Presently working as Scientist 'F' in DRDO-Advanced Systems Laboratory, Hyderabad. He has been working in the area of nano materials added carbon fibre reinforced polymer composites for enhanced mechanical, thermal and ablation resistance, development and fabrication structural stealth composites and development of high temperature ceramic matrix composite products for aerospace applications. He has thirty research papers and filed five Indian and one European Patents.
In the present study, his contributions in the present study are conceptualisation and designing experiments, guiding experimental work, SEM studies of ablated surface of type II composites and interpretation of test results.

Prof. K. Laxma Reddy has obtained his MSc with Inorganic Chemistry specialisation from Kakatiya University, Warangal in 1980 and PhD from coordination chemistry from Kakatiya University, Warangal in 1984. He is presently working as Professor (HAG) in the Department of Chemistry at National Institute of Technology, Warangal, Telangana. He has been working in the area of Coordination Chemistry, Supramolecular Chemistry, Bioinorganic Chemistry and Environmental Chemistry. He has published so far 82 research papers in International Journals and presented 75 papers at National and International Conferences.
In the present work, he has guided experimental work, monitored progress of research work and provided valuable suggestions from time to time. He has also contributed in the analysis of test results.