International Journal of Current Science Research
www.drbgrpublications.in

Enhancing Thermal and Mechanical Properties of Polybenzoxazine Composites through Methyl Substitution and Organoclay Incorporation

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Abstract

This study investigates the synthesis and characterization of polybenzoxazine (PBZ) composites derived from methylamine, bisphenol-A, and formaldehyde, focusing on the effects of methyl substitution and the incorporation of organoclay (montmorillonite) on their thermal and mechanical properties. Polybenzoxazine is a promising thermosetting phenolic resin known for its excellent properties, including low shrinkage, high char yield, and mechanical strength. However, challenges such as brittleness and low processability limit its applications. To address these issues, methylamine was utilized as a precursor to lower the polymerization temperature and reduce volatile emissions during curing. The synthesis involved the ring-opening polymerization of the methylamine-derived monomer, followed by the preparation of organoclay-loaded composites. The resulting materials were characterized using Fourier Transform Infrared (FTIR) spectroscopy, Field Emission Scanning Electron Microscopy (FESEM), and thermogravimetric analysis (TGA). FTIR analysis confirmed the successful formation of the benzoxazine structure, while FESEM images revealed uniform dispersion of the organoclay within the polymer matrix, which is crucial for enhancing mechanical properties. Mechanical characterization through Rockwell hardness tests indicated that the pristine PBZ exhibited a low hardness value of 11. In contrast, the incorporation of functionalized organoclay significantly improved hardness, with the optimal composite achieving a Rockwell Hardness Number (RHN) of 83. TGA results demonstrated that the thermal stability of the composites was markedly enhanced, with residual mass percentages of 40-49% at 600°C, indicating their suitability for high-temperature applications. Overall, this research highlights the potential of methyl-substituted polybenzoxazine composites as high-performance materials, offering improved thermal stability and mechanical strength. The findings suggest avenues for further exploration in optimizing synthesis processes and expanding the functional applications of these advanced composites in various industries, including aerospace and automotive sectors.

Keywords: Methyl-substituted polybenzoxazine, Rockwell Hardness, Thermal studies

Citation: S.Malathi Devi, D.Madhavan, and K.Jeyasubramanian. "Enhancing Thermal and Mechanical Properties of Polybenzoxazine Composites through Methyl Substitution and Organoclay Incorporation" International Journal of Current Science Research (IJCSR) e-ISSN: 2454-5422: 11.6 (2025): 41 - 57

Introduction

Polybenzoxazine is a new class of thermosetting phenolic resin obtained by the ring-opening polymerization of benzoxazine monomer. The wide variations in the starting material for the preparation of polybenzoxazine show tremendous molecular design flexibility which not only displays various properties such as near-zero shrinkage, high char yield, low water absorption, and excellent mechanical property, but has also been utilized in wide range of applications. Polybenzoxazine also has some shortcomings such as brittleness, low processability and need high temperature for the ring-opening polymerization. Earlier we have reported the thermal, mechanical properties of BXP derived from aniline (Sundaramoorthy *et al.*, 2022). Aiming for the lowering of polymerization temperature, altering the use of aniline with methylamine, such shortcomings shall be addressed. The change in the structural modifications of starting materials gives various functional applications in polybenzoxazines. To extend this knowledge, a series of structurally modified polybenzoxazines have been synthesized. In this work, we use methyl amine, a simple aliphatic amine, which is having high advantages in lowering the ring-opening temperature and reducing the amount of volatiles during curing.

In this context, numerous synthetic approaches have been adopted to isolate the substituted benzoxazine polymer. Arunthip Suesuwan *et al.* prepared four thymol-based benzoxazines using methylamine, ethylamine, 1-propylamine, and 1-butylamine and concluded that benzoxazines with respect to the N-substituent chain length showed an enhanced photoluminescent study, thermal study, water contact angle, anticorrosion performance. Min Zhong *et al*. synthesised a novel tri-functional benzoxazine using resveratrol and 2-thiophenemethylamine to develop the bio-benzoxazine monomer and investigated the thermal stability and flame retardancy of the polybenzoxazine by thermogravimetric analysis and microscale combustion calorimeter. Priyanka Madesh *et al.* synthesised hybrid benzoxazines from sustainable magnolol and found that polybenzoxazine containing ethynylaniline showed higher thermal stability, higher resistance to microbial growth and imparting low cytotoxicity against L-929 cell lines, hydrophobic nature of polybenzoxazines and dielectric constant. Mrinalini Shah *et al.* made cardanol-based mono, bi, and tetra-functional benzoxazines by reacting various aryl amines and cycloaliphatic amines with cardanol in the presence of paraformaldehyde by Mannich condensation and characterized their molecular structure, curing behavior, thermal stability, and hydrophobic nature. Soliman, Ahmed M. M. *et al.* synthesised 2-[(E)-(hexyl-imino)methyl] phenol by adding salicylaldehyde, n-hexylamine and sodium borohydride to produce 2-[(hexylamino)methyl] phenol and thermally polymerized at 210°C to give a polybenzoxazine. The as prepared sample was examined using FT-IR, 1H,13C NMR spectroscopy, DSC, TGA, SEM and XRD, and determine the thermal behavior, surface morphology and crystallinity. Qing Chen *et al.* prepared benzoxazine resins from the renewable daidzein and furfurylamine, together with polyetheramine, long aliphatic chain primary amines, and paraformaldehyde and reported high antibacterial rate, strong algae-killing ability and satisfied real-sea fouling resistance. Fangyu Li *et al.* explored a new bio-based benzoxazine monomer with two functionality from renewable *trans*-anethole and furfurylamine and indicated that polybenzoxazine would be a potential candidate for high-performance engineering applications.

Thirukumaran Periyasamy *et al.* developed a series of polybenzoxazine/*co*-polymer coatings which contains arbutin and silane functionalization and concluded that the coatings possess dual property i.e anti-corrosion and anti-biofouling property. Anun Wongpayakyotin *et al.* synthesized various polybenzoxazine composite materials by increasing the number and position of methyl groups and found that higher thermomechanical and wear resistance properties were obtained from polybenzoxazines with relatively high crosslink densities. Jing Wang *et al.* synthesize a new type of eugenol–furfurylamine benzoxazine and bisphenol A–furfurylamine benzoxazine to study infrared radiation spectroscopy, gel-permeation chromatograph, mass spectrometry, ^{1}H nuclear magnetic resonance, differential scanning calorimetry and dynamic mechanical analysis tests of the target molecules. Boyang Li *et al.* obtained a biobased bisphenol E epoxy thermosets from thymol and acetaldehyde using 4,4′-diaminodiphenyl sulfone and methyltetrahydrophthalic anhydride as curatives and found that the resulting thermosets exhibits lower dielectric constant, decreased water absorption, density, and thermal diffusivity and improved resistance to hygrothermal aging and good bulk mechanical properties. Lisa Guinebaud *et al.* produced bio-based benzoxazine from vanillylamine and melamine which possess lower curing temperatures, long and strong adhesive performance, efficient flame-retardants, limiting oxidation index value and also furnish a silver-colored paste with aluminium to afford a robust solid, which does not undergo contraction or deformation. Zhong-Qiong Qin *et al.* interpenetrated polybenzoxazine networks insisting of diphenolic acid-based benzoxazine (rigid segment) and cardanol-based benzoxazine (flexible segment), and found that cardanol-based benzoxazine possess high glass transition temperature, flame retardancy and toughness. Mohamed Mydeen *et al.* focused simple one-pot method to synthesis four unique set of thymol benzoxazines using varied nature of amines and concluded that the developed thymol polybenzoxazines and composites exhibited an excellent thermal and dielectric properties, making them suitable for sustainable, versatile coatings and microelectronics applications. Bhaskaranand Bhatt *et al.* explored polybenzoxazine resins to develop brake pads for passenger cars and found that dimethyl substituted polybenzoxazines resin based brake-pads showed a best tribological and noise vibration performance and also higher thermal stability, thermomechanical properties, higher fade ratio, wear resistance.

In this work, polybenzoxazine polymer was isolated using the precursors namely methylamine, bisphenol – A, and formaldehyde and their organo MMT clay-loaded composite in a simple method. The pristine polymer and its composite structure were characterized through FTIR, FESEM, with EDAX. The TGA and DTGA analyses were used to evaluate the thermal stability. Mechanical characterization was performed by Rockwell hardness method. Corrosion resistance property of plain varnish-coated steel, varnish dispersed with pristine polymer-coated steel and varnish dispersed with composite-coated steel was studied through potentiodynamic polarization studies. The results were compared with that of BXP fabricated using aniline instead of methylamine was reported by us earlier (Sundaramoorthy *et al.,* 2022).

Materials and Methods

The chemicals given in Table 1 was used in the present study are of research grade purity and used as such without any further purification.

Table 1 Chemicals used

S. No	Name of the Chemicals	Brand
1.	Bisphenol – A	E–Merck
2.	Aniline	E–Merck
3.	Methyl amine	E–Merck
4.	Formaldehyde	E–Merck
5.	Sodium chloride	E–Merck
6.	Ferric chloride	E–Merck
7.	Hydrochloric acid	E–Merck
8.	Montmorillonite clay	Alfa Aesar
9.	3-aminopropyltriethoxy silane	E–Merck
10.	Toluene	E–Merck

Preparation of Benzoxazine Polymer Using Methylamine (BXPME)

The polybenzoxazine polymer was prepared by mixing 0.005 moles bisphenol – A, 0.024 moles methyl amine and 0.017 moles paraformaldehyde. All these chemicals were accurately weighed and mixed together uniformly using pestle and mortar. The contents were transferred to a silicone rubber mold having circular disc-like pattern of diameter 2.5 cm. Then, it was kept inside the hot air oven and the temperature was increased from 25ºC to 110ºC at the heating rate of 2ºC / minute. At this condition, the contents were maintained for 15 minutes, while the benzoxazine monomer namely Bis (3,4–dihydro–2H–3–methyl–1,3–benzoxazinyl isopropane) was formed. After that, the temperature was further raised to 150ºC and held for three hours. At this condition the monomer undergoes ring opening polymerization to give polybenzoxazine. Then heating process was stopped, and the contents were allowed to attain the room temperature. After attaining room temperature, the disc–like polymer set was removed and stored in a desiccator. The polybenzoxazine polymer derived from methylamine as additive is designated as **BXPME**.

Preparation of ion-exchanged montmorillonite clays

10gm of Montmorillonite (MMT) clay was accurately weighed and mixed with 100ml 1M sodium chloride solution and stirred for three days in a mechanical stirrer and then filtered. The Na–exchanged MMT (NaMMT) obtained was washed liberally with distilled water followed by filtration and drying at 110ºC for 6 hours. Following a similar procedure, Fe^{2+} ion exchanged montmorillonite clay (FeMMT) was prepared by agitating NaMMT with 1M Ferric Chloride solution.

Functionalization of FeMMT Using APTES (FeMMT.APTES)

The cation–exchanged clays are hydrophilic and are naturally not able to mix uniformly with a polymer matrix while being added into polymeric resin. So, the respective surfaces of MMT and the metal ion-exchanged clays were functionalized by treating with 3-Aminopropyltriethoxy Silane (APTES), in order to give hydrophobicity. In a typical procedure for APTES functionalization of NAMMT, 10 gm of FeMMT was refluxed with 10 ml of APTES solution dissolved in 50ml of toluene at 60ºC for four hours with constant stirring. Then, the solvent was reduced to one third of its original volume. The concentrated sample was then kept in a refrigerator for one hour, and the FeMMT.APTES obtained was filtered and washed with adequate amounts of cold toluene and the obtained powder was dried at 105ºC for two hours in a hot air oven.

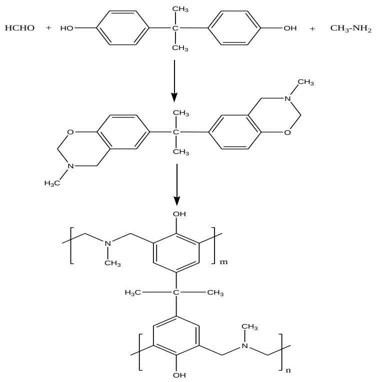
Fabrication of FeMMT.APTES loaded BXP composite

As prepared surface-modified metal ion-exchanged clays (FeMMT.APTES) were used as filler to obtain different composites. 0.05 g of FeMMT.APTES was taken along with 0.005 moles bisphenol – A, 0.024 moles methyl amine and 0.017 moles paraformaldehyde. The uniformity was ensured by thorough mixing. After that, the contents were taken in a silicone mold and heated to 110ºC for 15 minutes in a temperature-controlled hot air oven in order to get the monomer. Further, the temperature was raised to 150ºC and held for three hours which resulted in the polymerization to form the FeMMT.APTES@BXPME composite.

Results and Discussion

Fourier Transform Infrared spectroscopy analysis

The FTIR spectra of pristine polymer and their composites recorded in the region 400 cm^{-1} – 4000 cm^{-1} are shown in Figure1(a – c). Benzoxazine polymer is derived from formaldehyde, bisphenol – A, and methyl amine by heating from room temperature to 150ºC. The completion of the polymerization process was optimized from the time of heating[1]. After 15 minutes, a glassy matrix was obtained at 110ºC as an intermediate product (not shows higher toughness) which was broken and subjected to FTIR analysis. Based on the hardness data, it is ensured that the glassy matrix obtained after heating the precursor at 150ºC for three hours is a fully hardened benzoxazine polymer. The FTIR spectra clearly reveal the formation of monomer as intermediate at 110ºC and the final polymer with characteristics functional groups. On impregnating the surface-modified functionalized clay, it produces a clay-loaded BXPME composite. The following reaction scheme explains the formation of BXPME polymer via intermediate stage monomer formation and subsequently ended with the polybenzoxazine.



Bis (3.4-dihydro-2H-3-methyl l-1,3-benzoxazinyl) isopropane

Scheme 1 Formation of BX-ME and its subsequent polymerization

The FTIR spectra of intermediate compound obtained after heating at 110°C showed most of the vibrations as those are present in the monomer prepared using aniline as one of the precursors[1]. Similarly, the monomer obtained using methylamine also shows characteristic vibrations for the functional groups such as phenolic – OH and amine group along with other C – C and C – H vibrations (Figure 1a). On heating at 110ºC, the precursors get condensed together and form the corresponding benzoxazine monomer and its FTIR spectra is shown in Figure 1a.

The FTIR spectra of the polymer obtained at 150ºC and its clay composites are shown in Figure 1 b & c.

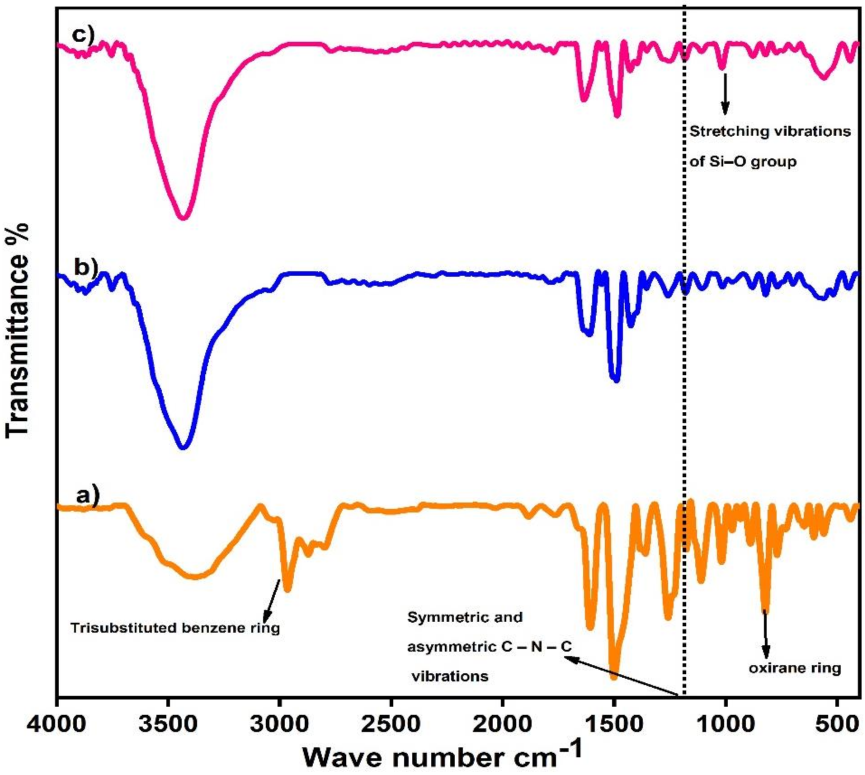


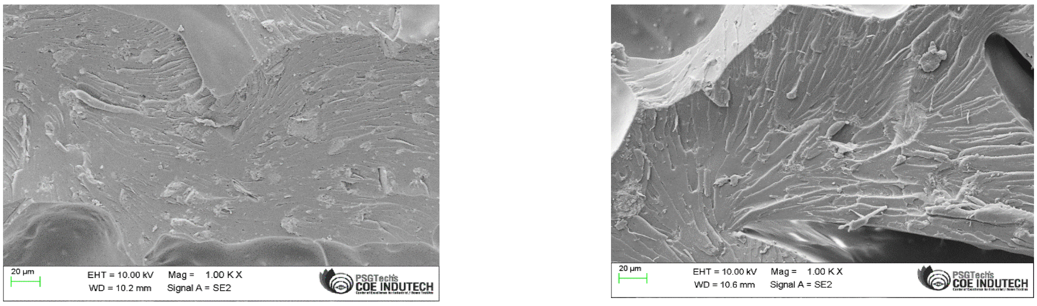
Figure 1: FTIR spectra of (a) Benzoxazine monomer (BX-ME),
(b) Pristine Polybenzoxazine (BXPME) and
(c) Clay loaded composite (FeMMT.APTES@BXPME2)

The FTIR spectra of the benzoxazine polymer display a broad peak at 3400 cm^{-1} due to the vibrations of phenolic -OH group [17]. A strong band found at 2964 and 2872 cm^{-1} are due to the stretching vibrations of C–N group [18]. The peaks observed at 1257 cm^{-1} and 1018 cm^{-1} are assigned to the asymmetric and symmetric stretching vibrations of C – O – C group existing in benzoxazine structure [19], and the peak at 972 cm^{-1} is assigned to the oxirane ring structure which further confirms the formation of benzoxazine monomer at 110ºC. The symmetric and asymmetric C – N – C vibrations are observed at 1178 cm^{-1} and 1111 cm^{-1} [18]. The monomer on further heating at 150^{0}C produces ring opening, and subsequent polymerization results in the formation of polymer network consisting a methyl group substituted benzoxazine backbone. The disappearance of peak at 972 cm^{-1} and appearance of a new peak at 1489 cm^{-1} confirm the polymerization. Notably, the disappearance of the peak at 2964 and 2872 cm^{-1} confirms the conversion of trisubstituted ring in to a tetra substituted ring. Bands at 648 cm^{-1} and 769 cm^{-1} correspond to the bending vibrations of C – H group present in benzoxazine[20].

On suspending 4.0% weight percentage of clay particles into the precursors and the subsequent heating offer its composites consisting of both BXPME and the clay particles. The FTIR spectra recorded in the region from 400 to 4000 cm^{-1} display the characteristic vibrations of both clay and the polymeric networks. The presence of clay particles exhibits a small sharp peak at 1355 cm^{-1} which is due to the deformation (wagging) vibrations of CH_2 group present in the APTES. The peak at 1016 cm^{-1} is attributable to the stretching vibrations of Si–O group that confirms the presence of the clay particles. The bands appeared at 690 cm^{-1}, 559 cm^{-1}, and 443 cm^{-1} are due to the bending vibrations of Si–O and bending vibrations of Al–O–Si, and Si–O–Si groups basically exist in clay particles further prove that the clay particles are embedded within the polymer network.

FESEM Analysis

The FESEM images of some of the representative composites were recorded by accelerating the electron beam at an operating voltage of 10 kV, and the images obtained are visualized at 100 kX magnification. The images shown in Figure 2 (a) correspond to the composite (FeMMT.APTES@BXPME2) consisting of 4.02 % weight of FeMMT.APTES dispersed in BXPME. The image clearly reveals the uniform dispersion of polymer, holding the APTES functionalized clay particles firmly. Such a uniform dispersion favors higher hardness. The FESEM image shown in Figure 2 (b) is corresponding to the composite prepared by dispersing 11.15 weight percentage of FeMMT.APTES@BXPME6 in which the agglomeration of clay is clearly visualized.



(a) **(b)**

Figure 2: FESEM images of (a) FeMMT.APTES@BXPME2 and (b) FeMMT.APTES@BXPME6

Rockwell Hardness (RHN)

The BXPME prepared by using a precursor of methyl amine instead of aniline also possesses excellent hardness property. The pristine BXPME polymer and the clay-dispersed composites FeMMT.APTES@BXPME were subjected to Rockwell hardness measurement test using 1/16 – inch diameter ball indenter by applying varying load from 60 kg to 100 kg. Rockwell Hardness Number (RHN) is a number derived from the net increase in depth impression while applying load on an indenter, which was conducted for all the prepared composite materials obtained in the form of circular disc as per ASTM D785-98 standards. All the prepared composites were cut into a spherical dimension of 20 mm dia with a thickness of 20 mm and then subjected to the hardness analysis. Hardness value of the composites were measured on three different points and an average value was taken under Rockwell B scale measurement by using Rockwell hardness tester (SAROJ Hardness Testers Model RAB-250, India).

From the RHN summarized in the Table 2, it is clear that the pristine BXPME prepared using methyl amine shows the least RHN of only 11 indicates its poor hardness. On suspending FeMMT.APTES, it exhibits increased hardness (60). Among the varying percentages of the clay dispersed into the BXPME, it is evident that about 4.02 weight % clay-dispersed composite shows a maximum RHN of about 83. FeMMT.APTES@BXPME3, FeMMT.APTES@BXPME4, FeMMT.APTES@BXPME5 and FeMMT.APTES@BXPME6 show a decrease in trend of RHN from 70, 59, 19, and 16 respectively. Such a decrease in trend is attributed to the dispersion ability of the host matrix (BXPME polymer) with respect to the added clay. On suspending higher % of clay into the constant amount of polymer does not provide uniform host–guest interaction[21]. Presence of higher amount of clay leads to its agglomeration, resulting in the reduction of hardness value.

Table 2 Hardness values with varying % of clay

S. No	Composite Specimen	Composition of FeMMT (% by weight)	RHN
1.	BXPME	---	11
2.	FeMMT.APTES@BXPME1	2.05	60
3.	FeMMT.APTES@BXPME2	4.02	83
4.	FeMMT.APTES@BXPME3	5.91	70
5.	FeMMT.APTES@BXPME4	7.72	59
6.	FeMMT.APTES@BXPME5	9.47	19
7.	FeMMT.APTES@BXPME6	11.15	16
8.	BXP	---	20[1]
9.	FeMMT.APTES@BXP3	7.5	79 [1]

When compared with BXP having similar weight percentage of clays, it can be seen that less quantity of clay can be dispersed in BXPME. It may be due to the difference in attraction between polymer molecules.

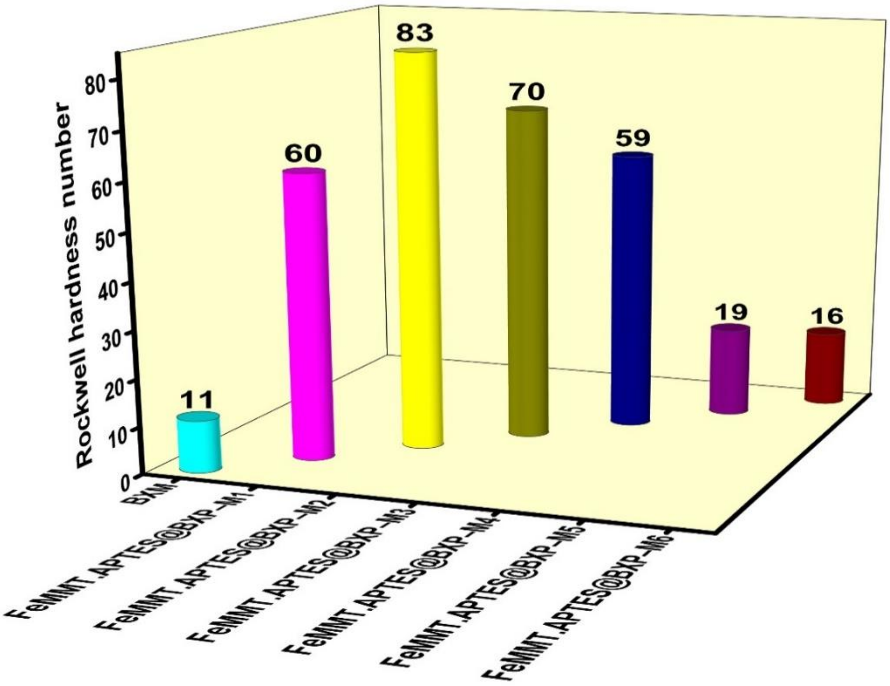


Figure 3 Effect of concentration of organoclay on RHN values

Thermal Analysis

Thermal degradation properties of pristine BXPME and the clay-loaded composites are shown in Figures 4 and 5. The figures clearly reveal the thermal characteristics of the polymer and their composites.

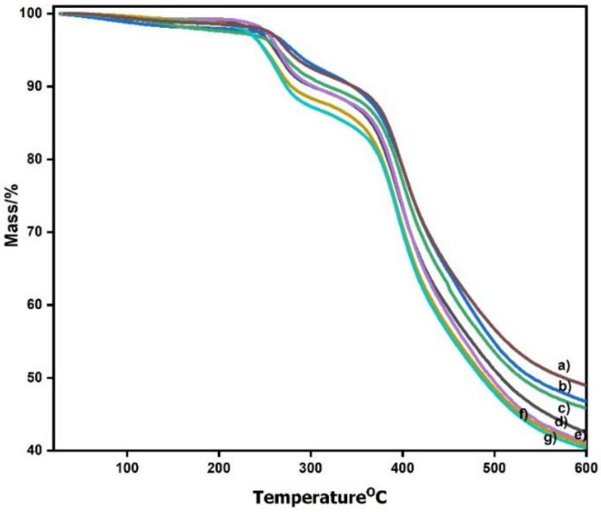


Figure 4 TGA graph of (a) FeMMT.APTES@BXPME6, (b)FeMMT.APTES@BXPME1, (c) FeMMT.APTES@BXPME2, (d)FeMMT.APTES@BXPME3, (e)FeMMT.APTES@BXPME4, (f) FeMMT.APTES@BXPME5 and (g) BXPME

A constant plateau is noticed in the temperature range from room temperature to 220ºC confirming its higher thermal stability. Owing to its higher stability, it can be used as a core polymer for high temperature applications. From 220ºC to 270ºC, the composites show 10% weight loss attributed to the loss of volatiles namely ammonia, CO, etc., From 270ºC to 330ºC, further loss in mass of 5% is noticed, which may be due to the start of the decomposition of carbonaceous network of the BXP-M matrix with the evolution of CO, CO_2, etc., After 380ºC, around 40 – 45% of the mass loss is noticed in this region, complete decomposition of BXP-M polymer backbone with the simultaneous evolution of CO_2, H_2O, CO and CH_4.

At about 600ºC, the complete degradation of carbonaceous polymer network occurred, and left out unburnt residue is called as char. As certain volume of the char residue is left, the composite can be used in high temperature applications[22]. Based on the data noticed at 600ºC, almost all composites display the residual mass of about 40 to 49%, that is, around 50% of the mass is left out as unburnt residue. From the TGA curve of all other composites containing different weight % of MMT, the temperature noticed for 5%, 10%, and 50% weight loss are summarized in Table 3.

Table 3 Effect of clay on thermal stability of BXPME composites

S. No	Specimen	Degradation temperature at 5% of weight loss (Td5 ºC)	Degradation temperature at 50% of weight loss (Td50°C)	Residue %
1.	BXPME	256.4	501.4	39.60
2.	FeMMT.APTES@BXPME1	271.9	531.9	46.77
3.	FeMMT.APTES@BXPME2	258.6	521.1	45.85
4.	FeMMT.APTES@BXPME3	261.7	491.7	41.22
5.	FeMMT.APTES@BXPME4	246.5	484.0	40.86
6.	FeMMT.APTES@BXPME5	245.8	480.8	40.39
7.	FeMMT.APTES@BXPME6	268.5	558.5	49.00
8.	BXP	220.71	433.21	33.72 [1]
9.	FeMMT.APTES@BXP3	256.91	---	63.88 [1]

From Table 3, it is evident that the temperatures corresponding to 5% weight loss and 10% loss are increasing when compared with that of pristine polymer. Such an increase in the decomposition temperature is attributed to the dispersion of the clay layers in a polymer matrix which acted as an effective barrier for oxidizing the constituents and enhance the thermal stability. However, beyond certain limiting concentration of clay, the thermal stability is found to decrease.

Figure 5 shows the DTGA plots of the BXPME and its clay-loaded composites recorded in between 200 – 500ºC in an inert atmosphere. The degradation process of BXPME and its clay-loaded composites noticed in the DTGA plots are divided into three stages which are shown in Figure 5.

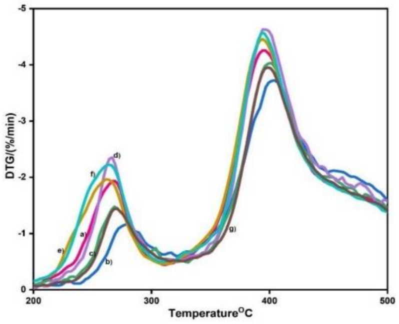


Figure 5 DTGA graph of (a) FeMMT.APTES@BXPME6, (b) FeMMT.APTES@ BXPME1, (c) FeMMT.APTES@BXPME2, (d) BXPME, (e) FeMMT.APTES@BXPME3, (f) FeMMT.APTES@BXPME4 and (g) FeMMT.APTES@BXPME5

On increasing the temperature from 200ºC, the first stage of degradation due to the cleavage of Mannich bridge is noticed in the region 270 – 280ºC. The degradation of the pristine polymer is noticed at 268.9ºC and the same phenomenon was noticed for the clay composite (FeMMT.APTES@BXPME1) at 279.4ºC which is higher in the order of 10.5ºC than the pristine BXPME. The second stage of degradation is due to the breakup of the isopropylidene linkage of the bisphenol A backbone occurring around 380 – 400ºC and also releases different substituted phenol fragments [23]. The third stage of degradation is found around 490ºC for pristine polymer and their composites in which phenol and many substituted benzenes were burned out due to the pyrolysis of the polymeric composites and finally the char only was left. Thus, the composite FeMMT.APTES@BXPME1 is more stable than pristine polymer. From the DTGA plots, the characteristics of first stage degradation, and the temperature at which maximum percentage of weight loss noticed with respect to the percentage of surface-modified clay are given in Table 4.

Table 4 Study of DTGA of BXPME composites

S. No	Specimen	Stage1 (ºC)	Stage3 (ºC)	Residue %
1.	BXPME	268.9	396.4	39.60
2.	FeMMT.APTES@BXPME1	279.4	404.4	46.77
3.	FeMMT.APTES@BXPME2	268.6	401.1	45.85
4.	FeMMT.APTES@BXPME3	266.7	394.2	41.22
5.	FeMMT.APTES@BXPME4	261.5	394.0	40.86
6.	FeMMT.APTES@BXPME5	263.3	393.3	40.39
7.	FeMMT.APTES@BXPME6	268.5	398.5	49.00
8.	BXP	243.91	463.79	33.72 [1]
9.	FeMMT.APTES@BXP3	286.77	460.99	63.88 [1]

It is clear from the Table 4 that the addition of 11.15 weight percentage of clay results in highest char residue of 49 % (FeMMT.APTES@BXPME6). The mass residue left after the combustion for all the remaining composites will be in the range of 40 to 46% which is high when compared to the pristine BXPME (39.6%) that proves their thermal stability. However, the composites are less stable (stable up to 268.6ºC) than the FEMMT.APTES @BXP composites (stable up to 286.7ºC) which contain phenyl group instead of methylamine group.

Conclusion

The polybenzoxazine polymer (BXPME) was successfully synthesized through the ring-opening polymerization of the methylamine-derived monomer. The process involved heating the precursors, resulting in a fully hardened polymer characterized by Fourier Transform Infrared (FTIR) spectroscopy. The FTIR analysis confirmed the formation of the benzoxazine structure, with distinct peaks indicating the presence of functional groups associated with both the polymer and the organoclay. Rockwell hardness tests demonstrated that the pristine BXPME exhibited a low hardness value of 11. However, the incorporation of functionalized organoclay (FeMMT.APTES) significantly enhanced the hardness, with the optimal composite (FeMMT.APTES@BXPME2) achieving a Rockwell Hardness Number (RHN) of 83. The mechanical performance was found to be dependent on the concentration of the organoclay, with lower concentrations yielding better dispersion and, consequently, improved hardness. Higher concentrations led to agglomeration, which negatively impacted the mechanical properties. Thermogravimetric analysis (TGA) revealed that the thermal stability of the composites was significantly enhanced compared to the pristine BXPME. The addition of organoclay acted as a barrier to thermal degradation, resulting in higher decomposition temperatures and increased char residue. The composites exhibited a residual mass of approximately 40-49% at 600°C, indicating their potential for high-temperature applications. Field Emission Scanning Electron Microscopy (FESEM) images indicated a uniform dispersion of the organoclay within the polymer matrix at optimal concentrations. This uniformity is crucial for achieving the desired mechanical properties and thermal stability. The findings suggest that these composites are suitable candidates for high-performance applications, particularly in environments requiring materials with excellent thermal stability and mechanical strength. Future work may focus on optimizing the synthesis process further and exploring additional functionalization strategies to enhance the properties of polybenzoxazine composites.

Acknowledgments

The authors are thankful to the Principal and the Management of Mepco Schlenk Engineering College, Sivakasi, India for their constant encouragement and support rendered for this research work.

Author contributions

Conception and design of study	:	MALATHI DEVI S and Madhavan Durairajan
Acquisition of data	:	MALATHI DEVI S and Madhavan Durairajan
Analysis and interpretation of data	:	Jeyasubramanian K and MALATHI DEVI S
Drafting the manuscript	:	MALATHI DEVI S and Madhavan Durairajan
Revising the manuscript critically for important intellectual content	:	Jeyasubramanian K

Conflicts of interests

The authors have no competing interests to declare that are relevant to the content of this article.

Compliance with Ethical Standards

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data and code availability: Not Applicable

Supplementary information: Not Applicable

Ethical approval: Not Applicable

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