

PREPARATION AND CHARACTERIZATION OF POLYBENZOXAZINE
INVOLVING VARIOUS ADDITIVES

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INVOLVING VARIOUS ADDITIVES**

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ABSTRACT

PREPARATION AND CHARACTERIZATION OF POLYBENZOXAZINE INVOLVING VARIOUS ADDITIVES

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Polybenzoxazines, a class of phenolic offering excellent mechanical and physical properties, have been developed to overcome the shortcomings of the traditional phenolic resins. The features of these polymers such as no requirement for harsh catalysts, releasing no by-product, molecular design flexibility and low melt viscosity make this class of polymers a promising candidate for various industrial and academic applications. Several methods such as preparation of alloys with other high performance polymers, designing of novel monomers and incorporation of additive compounds were employed to improve the performance of polybenzoxazines.

In this work, polybenzoxazine composites involving various types of additives namely aromatic diboronic acid, boric acid, clay, zirconium diboride and diglycidyl ether bisphenol-A epoxy resin were prepared to improve thermal properties. In the first part, phenol and aniline based benzoxazine monomer, in the second part, difunctional benzoxazine monomer were synthesized and their composites were prepared.

The structural and thermal characteristics of the benzoxazine monomers, polybenzoxazines and polybenzoxazine composites were analyzed by NMR, FTIR,

DSC, TGA, XRD, DMA and DP-MS techniques. Improvement in the thermal characteristics were recorded by the incorporation of additives of the benzoxazine monomers.

Keywords: Polybenzoxazine, Thermal Properties, Direct Pyrolysis Mass Spectrometry, Aromatic diboronic acid, Boric acid, Clay, Zirconium diboride, Epoxy



ÖZ

ÇEŞİTLİ KATKI MADDELERİNİ İÇEREN POLİBENZOKSAZİN KOMPOZİTLERİNİN HAZIRLANMASI VE KARAKTERİZASYONU

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Fenolik reçinelerin üstün mekanik ve fiziksel özellikler gösteren bir sınıfı olan polibenzoksazinler, geleneksel fenoliklerin eksikliklerini gidermek için geliştirilmiştir. Polibenzoksazinler sert katalizörlere ihtiyaç duymama, yan ürün oluşturmama, moleküler tasarım esnekliği ve düşük eriyik viskozitesi gibi yüksek performans özellikleri gösterirler. Bu sayede polibenzoksazinler çeşitli endüstriyel ve akademik uygulamalar için umut verici bir adaydır. Polibenzoksazinlerin performansını iyileştirmek için yüksek performanslı polimerler ile alaşımlama, yeni monomerlerin tasarımı ve katkı maddeleri ile birlikte kürleştirme yöntemleri denenmiştir.

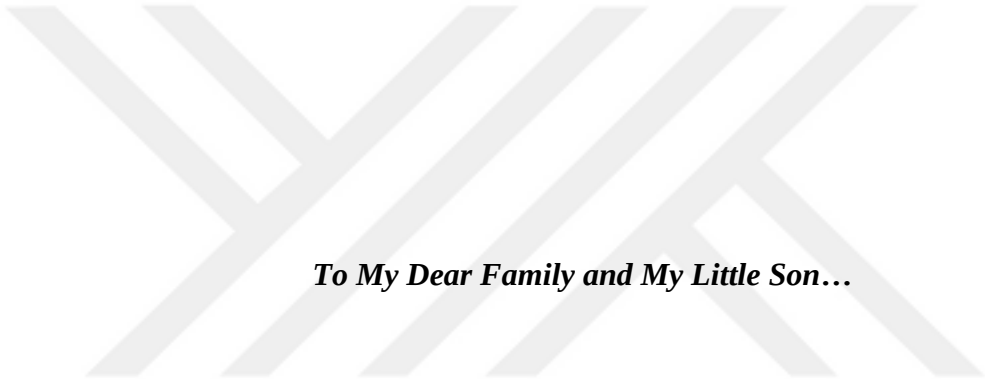
Bu çalışmada, termal özellikleri iyileştirmek için aromatik diboronik asit, borik asit, kil, zirkoniyum diborid, epoksi gibi çeşitli katkı maddelerini içeren polibenzoksazin kompozitleri hazırlanmıştır. İlk bölümde fenol ve anilin bazlı benzoksazin monomeri, ikinci bölümde çift fonksiyonlu benzoksazin monomeri sentezlenmiş ve kompozitleri olgunlaştırma programları ile hazırlanmıştır.

Benzoksazin monomerlerin, polibenzoksazinlerin ve polibenzoksazin kompozitlerinin yapısal ve termal özellikleri NMR, FTIR, DSC, TGA, XRD, DMA

ve DP-MS teknikleri ile analiz edilmiştir. Katkı malzemelerin kullanılmasıyla polibenzoksazinlerin termal karakteristiklerinde iyileşme gözlemlenmiştir.

Anahtar Kelimeler: Polibenzoksazin, Isıl karakterizasyon, Direkt Piroliz Kütle Spektrometresi, Aromatik borik asit, Borik asit, Kil, Zirkonyum diborid, Epoksi





To My Dear Family and My Little Son...

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LIST OF ABBREVIATIONS

ABBREVIATIONS

NMR	Nuclear Magnetic Resonance Spectroscopy
FTIR	Fourier Transform Infrared Spectroscopy
DSC	Differential Scanning Calorimetry
TGA	Thermal Gravimetric Analysis
XRD	X-Ray Diffraction
DP-MS	Direct Pyrolysis Mass Spectrometry
CNT	Carbon Nanotube
NMP	N-methylpyrrolidone
BDBA	Benzene-1,4-diboronic acid
BA	Boric acid
C10A	Cloisite 10A
EP	Diglycidyl ether bisphenol-A epoxy

LIST OF SYMBOLS

SYMBOLS

T_g	Glass transition temperature
G'	Storage modulus
G''	Loss modulus



CHAPTER 1

INTRODUCTION

Polybenzoxazines are a class of thermosetting phenolic resins that are connected by a Mannich bridge ($-\text{CH}_2-\text{N}(\text{R})-\text{CH}_2-$) instead of methylene ($-\text{CH}_2-$) bridge associated with the traditional phenolics. Polybenzoxazines have several advantages and overcome the problems of conventional phenolic resins such as being poor shelf life, need of acid or base catalyst for the preparation of resin and release byproducts during polymerization that may form micro voids. The benzoxazine monomer can easily be synthesized using amine and phenolic derivatives and formaldehyde/paraformaldehyde without requirement of a catalyst. Therefore, polybenzoxazines have great design flexibility and can be tailored considering the application requirements. They have additional advantages such as high char yield, dimensional stability, and low water absorption. However, as the polymers are brittle due to short molecular weight and relatively low crosslinking density, their use in practical applications are limited. Another problem is relatively high temperature requirement for ring opening curing reaction. In order to overcome these drawbacks and to improve performance characteristics extensive studies were performed [1]. These include preparation of polybenzoxazine polymer blends, and composites with organic/inorganic particles, synthesis of novel monomers, and preparation of fiber reinforced composites. As a consequence, lower curing temperatures were lowered, toughness was enhanced and better mechanical and thermal properties polybenzoxazine were achieved.

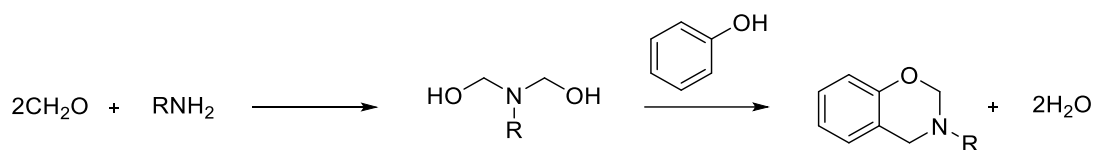
In general, polymerization of benzoxazine monomer is through ring opening polymerization without catalyst and producing no toxic by-products.

1.1. Benzoxazine Chemistry in Solution and Melt

Benzoxazine monomer is a molecule including oxazine ring (a heterocyclic six-membered ring with oxygen and nitrogen atom) attached to the benzene ring. Benzoxazine can be easily synthesized by the Mannich reaction between phenolic derivative ($\text{RC}_6\text{H}_4\text{OH}$), amine (RNH_2) and formaldehyde/paraformaldehyde in solution or melt state. Using solution state has many drawbacks such as slow reaction time and poor solubility of precursor. Moreover, synthesis in solution system leads to increases in the cost and environmental problems. In order to overcome these problems solventless synthesis in the melt state is proposed by Ishida [2]. Solventless synthesis method starts with preparation of a mixture of the precursors of benzoxazine, after stirring physically the mixture heat at the melting temperature. Then, the reactants are mixed for an adequate time to obtain desired benzoxazine monomer. The main advantage of solventless method is formation of less amount of unwanted intermediates and by-products. Moreover, the amount of formation oligomers are related to the basicity of the nitrogen and oxygen atoms on the oxazine ring. This is affected the ring opening and so oligomer formation [2,3]. Hence, several studies were showed that selection of phenols and amine is important for the benzoxazine monomer and its polymer properties such as thermal stability and char yield [4-8].

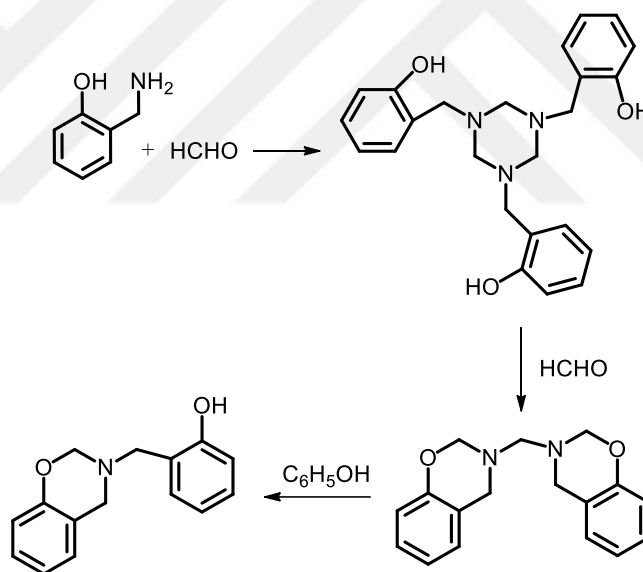
1.2. Monofunctional Benzoxazine Monomer

In 1944, Holly and Cope synthesized the first aromatic oxazine in solution by reaction of primary amine, formaldehyde and phenol as shown in Scheme 1.1 [9]. This reaction is completed in solvent in two-steps. In the first step, condensation reaction of formaldehyde and primary amine takes place at low temperatures then the product reacts with phenol and forms benzoxazine molecule.



Scheme 1.1. Synthesis of 3,4-dihydro-2H-1,3-benzoxazines

In 1950s, Burke prepared benzoxazine molecule by rapid polymerization of phenol with formaldehyde and methylamine (mole ratio of 1:2:1) in high yield. He also found that phenolic derivatives react preferentially at free *ortho* and then *para*-positions to form a Mannich Bridge [11]. Moreover, the reaction between 2-hydroxybenzylamine and 2 moles of formaldehyde yield bis-(3,4-dihydro-2H-1,3-benzoxazine-3-yl)-methylene. This molecule may give further reaction with phenol and produce 3,4-dihydro-3(2-hydroxy)benzyl-2H-1,3-benzoxazine shown in Scheme 1.2 [12].



Scheme 1.2. The synthetic method of 3,4-dihydro-3(2-hydroxy)benzyl-2H-1,3-benzoxazine

Several monofunctional benzoxazine monomers were prepared by using unsubstituted phenol, formaldehyde and primary aromatic amines shown in Scheme 1.3. The ring opening polymerization of these resins was also achieved [13]. Synthesis of benzoxazine and polybenzoxazine having low viscosity were studied due to for their potential for high performance applications. The liquid benzoxazines

are suitable for wide range of processes and polymerizations may be faster than their solid counterparts. It was stated that amines used as precursor determine the viscosity of the final product. Therefore, the aromatic amine based benzoxazines displayed higher viscosities than the aliphatic amine-based counterparts. On the other hand, the viscosity of benzoxazine monomer directly related with the size of amine moiety whether it is aliphatic or aromatic.



Scheme 1.3. Monomer synthesis based on various amines.

It has been revealed that the reaction sites of polymerization of monofunctional aromatic amine-based benzoxazines is the *ortho* position to the hydroxyl group. The reaction of *meta* position of hydroxyl group requires long polymerization periods and/or high temperatures. The regioselectivity was studied for the polymerization of several monofunctional benzoxazines based on alkylated phenols and aryl amines [14]. The position of alkyl group affects the basicity of arylamine ring, steric hindrance and so ring opening polymerization. For example, presence of methyl group at *ortho* position of arylamine decreases basicity and increases steric hindrance. This leads to large amount of rings fragmenting upon polymerization that releases free amine. Furthermore, alkyl substituents at *meta* position of arylamine facilitate ring opening/degradation at lower temperatures. This leads to a secondary reaction generating bisphenolic methylene linkages.

1.3. Difunctional and Multifunctional Monomer

Polybenzoxazines display lower crosslinking densities compared to common thermosetting epoxy and phenolic resins [15]. In some studies, difunctional or multifunctional reactants were used and increase in crosslinking density yielding higher molecular weights were achieved. One of these studies on difunctional benzoxazines was related to benzoxazine monomer based on bisphenol-A produced highly cross-linked structures during polymerization [16]. In addition, an infinite

network structure upon polymerization may be achieved by using a multifunctional phenolic resin and/or a multifunctional amine. However, the application of bisphenol-A based benzoxazine is limited due to brittle nature of its polymer. Therefore, several benzoxazines monomers based on aliphatic diamines were prepared to increase toughness by flexible aliphatic chains (Figure 1.1). Moreover, these polybenzoxazines have relatively high glass transition temperatures. Kinetic studies showed that polymerization rate was conversely related to aliphatic chain length of diamine. [17]. The reaction rates of benzoxazines based on aliphatic diamines and several types of substituents phenols were studied. It was observed that unsubstituted benzoxazines show the highest reaction rate and crosslinking density. The reaction rate decreases by substitution, in the order, *para*, *meta* and *ortho* position due to less favored reaction site [18].

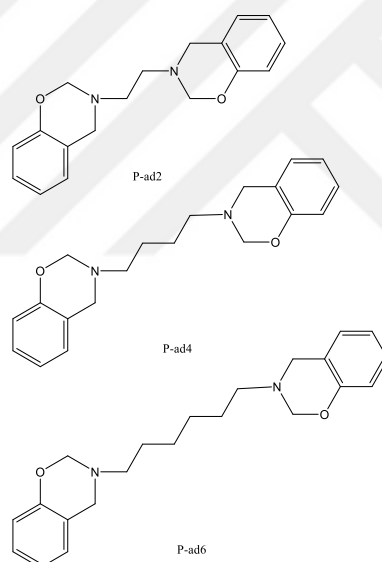
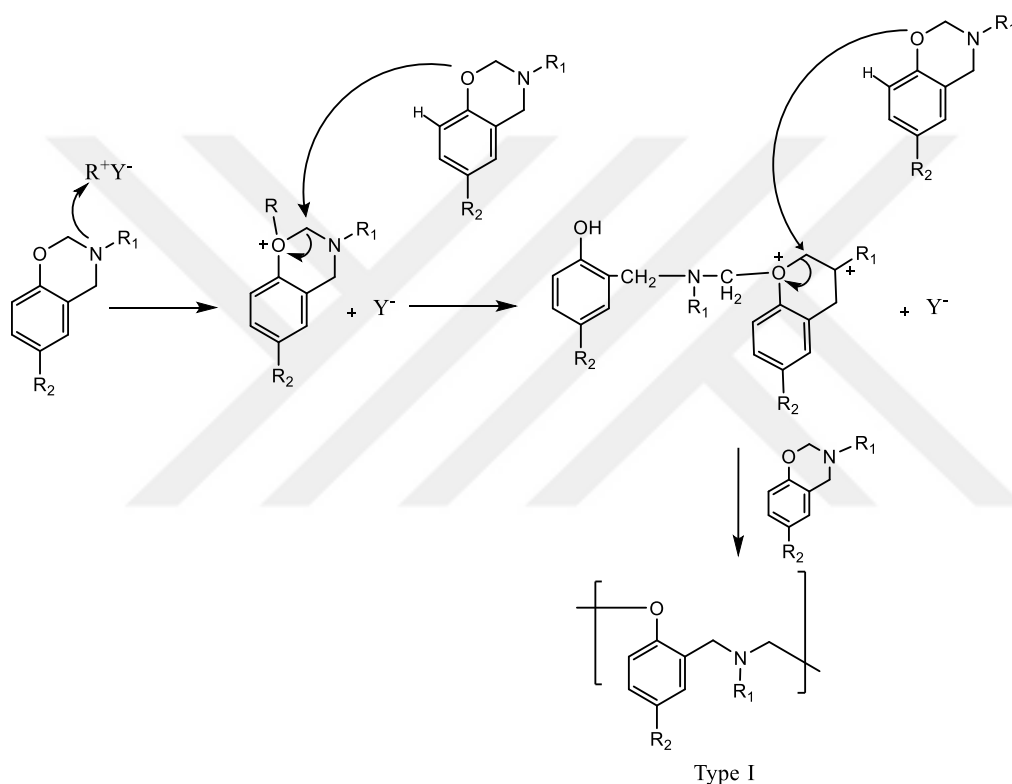


Figure 1.1. Structures of linear aliphatic diamine-based benzoxazine monomers.

1.4. Polymerization Mechanism

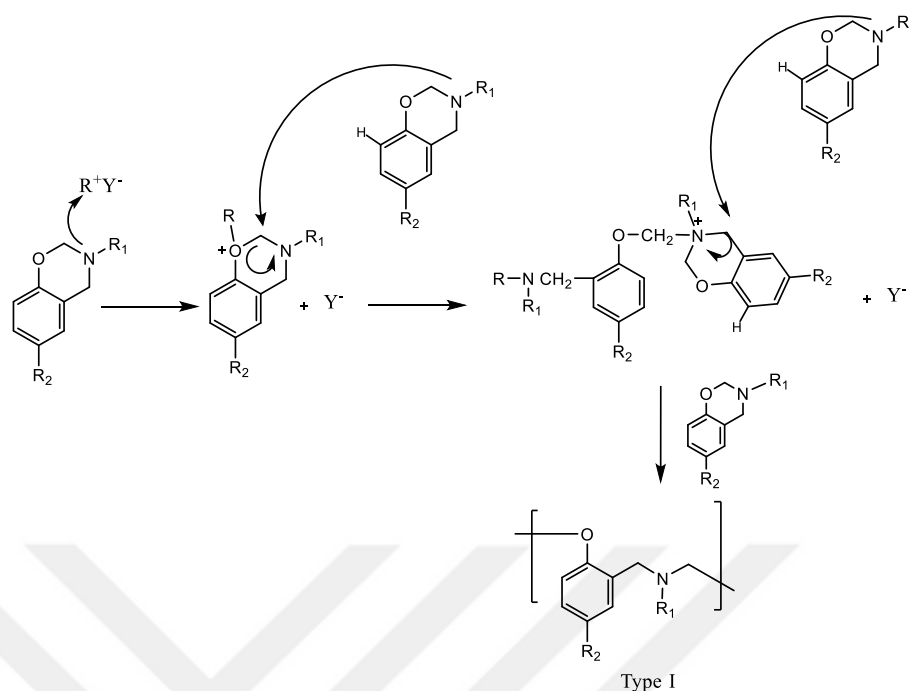
In general, polybenzoxazine is obtained by ring opening polymerization at elevated temperatures without catalyst. However, in some applications low temperatures and/or reduction in curing period is required. Hence, a suitable catalyst may be used to assist the polymerization. Oxazine ring is a six-membered heterocyclic ring consisting nitrogen (N) and oxygen (O). Therefore, this cyclic structure has irregular

chair conformation and the ring strain provides a driving force for ring opening polymerization via cationic mechanism. Moreover, oxygen in the oxazine ring behaves as an initiator because of its high negative charge distribution (O, - 0.311; N, - 0.27). If the polymerization is initiated at oxygen site by cationic catalyst, then a cyclic tertiary oxonium ion is formed. This structure undergoes reaction with monomers and yield a Mannich base phenoxy-type (Type I) polybenzoxazine structure as shown in scheme 1.4 [19].



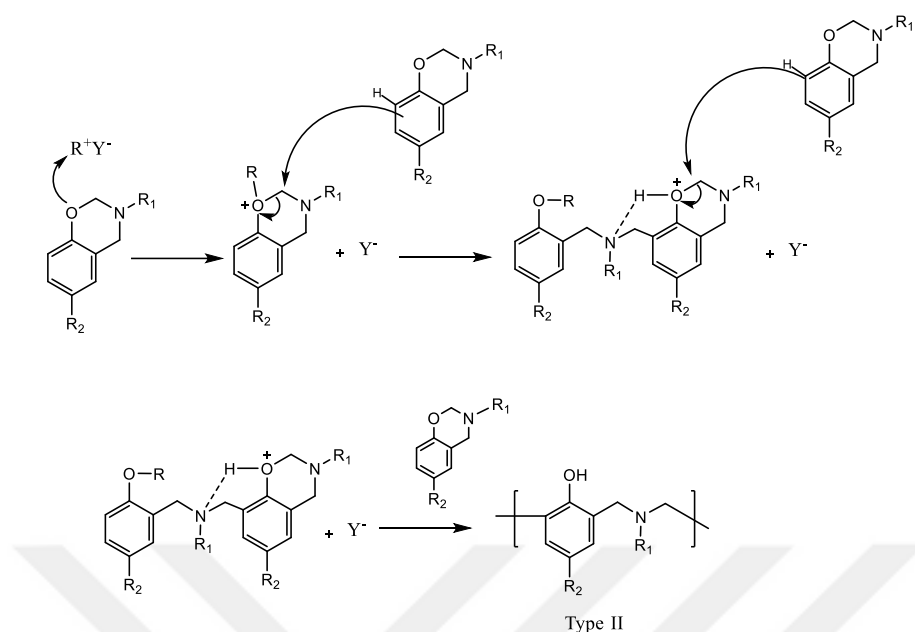
Scheme 1.4. Polymerization mechanism A

Moreover, nitrogen atom also propagate the polymerization by cationic initiator. In this case, an alternative polymerization mechanism can be observed and as a result, Mannich base phenoxy-type (Type I) polybenzoxazine structure is formed (Scheme 1.5).



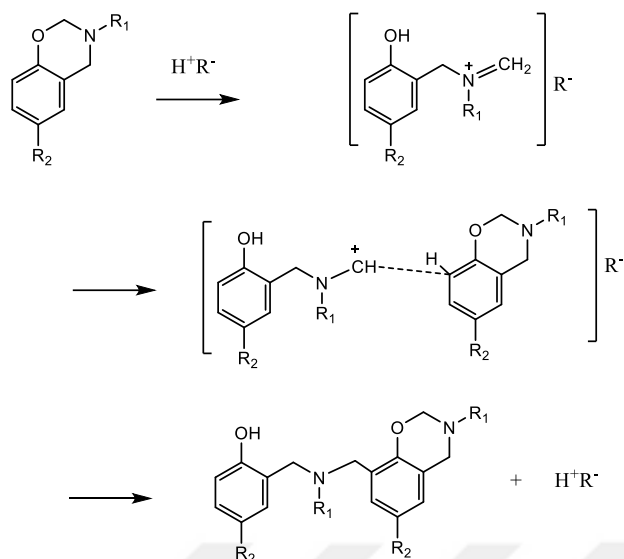
Scheme 1.5. Phenoxypy type polybenzoxazine by alternative of polymerization mechanism A

The benzene ring in the presence of benzoxazine molecule has also high reactivity for the thermal polymerization. Mannich base phenolic type (Type II) polymer is formed by the reaction of electron rich benzene ring. It can be explained as the attack of *ortho* position of benzene to carbocation which formed by cationic initiator. In this case, carbocations is more stable due to intramolecular hydrogen bonding. Therefore, higher molecular weight polymers can be obtained by phenolic type polymerization mechanism.



Scheme 1.6. Phenolic type polybenzoxazine by polymerization mechanism B

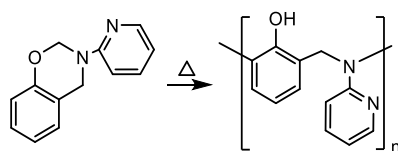
Mannich bridge formation as polymerization of phenols containing both free *ortho* and *para* positions was studied. It was reported that *ortho* position to the hydroxyl group shows high reactivity and react preferentially [20]. McDonagh and Smith achieved that iminium ion is formed when the nitrogen atom protonated. Then, carbocation and iminium ions tautomerism were observed [21]. Ring opening mechanism by protonation of the oxygen atom to form an iminium ion, followed by electrophilic aromatic substitution, as shown in Scheme 1.7 was proposed by Dunkers and Ishida [22].



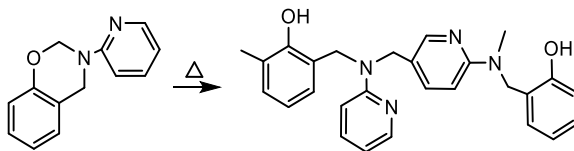
Scheme 1.7. Formation of iminium ions

The polymerization mechanism of polybenzoxazine was also studied in our group by DP-MS technique in detail. According to the results, polymerization can be explained several pathways. The first probability is the heterocyclic ring opening may be followed by attack of $-NCH_2$ groups to *ortho* and *para* positions of phenol and pyridine as shown in Scheme 1.8.

a) by attack to phenyl ring



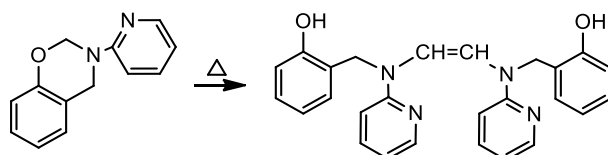
b) by attack to pyridyl ring



Scheme 1.8. Ring opening polymerization of benzoxazines

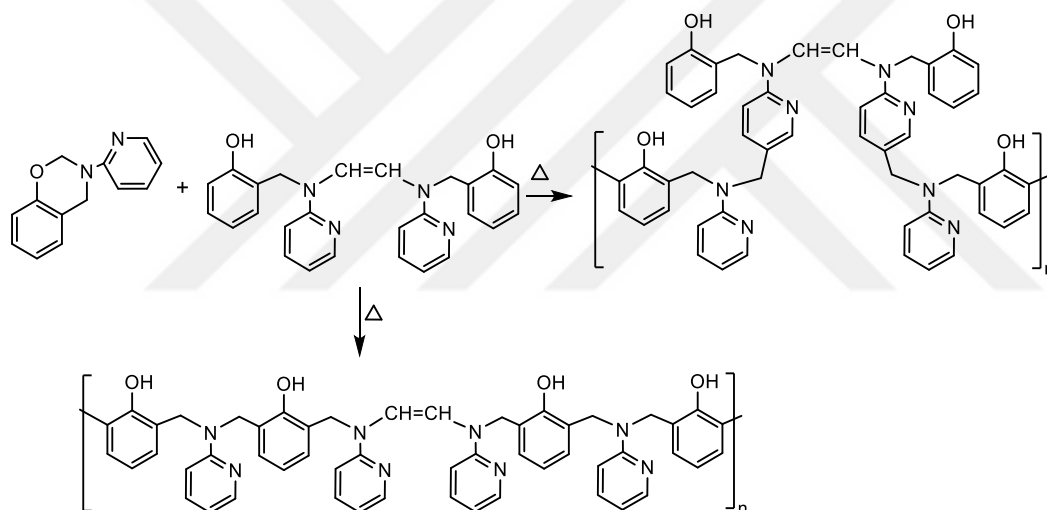
Another possible pathway is the dimer formation by the coupling of $-NCH_2$ groups and dimer polymerization via attack of $-NCH_2$ groups to phenol and/or pyridine rings or vinyl polymerization (Scheme 1.9).

a) Generation of the dimer by coupling of $-NCH_2$ groups

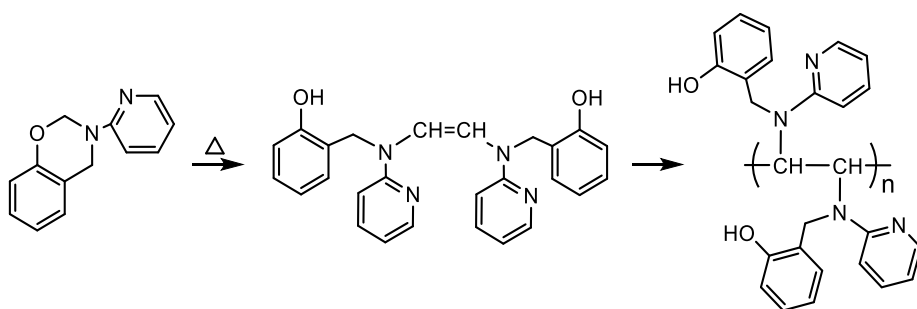


b) polymerization of the dimer

i) by attack of NCH_2 groups



ii) by vinyl polymerization



Scheme 1.9. Polymerization of benzoxazines based on dimer formation

1.5. Unique Properties of Benzoxazine and Polybenzoxazine

1.5.1. High Char Yield

The flammability of polymer has important role for wide range of applications. Char is one of the effective way to decrease burning by reducing the diffusion rate of decomposed, flammable gases toward the flame front. Therefore, polymers with high char yield are high flame retardant materials. Char yield is measured as remaining weight of polymer under nitrogen atmosphere and in some cases under air atmosphere. In general, one of the common resins, epoxy, has low char yield in the ranges 5-15% (at 800 °C under nitrogen). Phenolic resins exhibit higher char yields in the ranges 30-55% (at 800 °C under nitrogen). According to Walter and Lyon's method, polybenzoxazines are inherently good flame-retardant materials as molar group contribution of hydroxyl groups, tertiary amine, and benzene groups are high [23]. In general, polybenzoxazines exhibit high char yield in the range 35-75%. The thermal degradation of polybenzoxazines based on bisphenol A and monofunctional amine consists of three main steps.

1.5.2. High Glass Transition Temperature

The polymerization of local motion segments of polymer chain allows structural rearrangement or/and additional crosslinking, yielding higher glass transition temperature (T_g). Polybenzoxazine has available active sites and benzene ring to react. Thus, polymerization reaction results in higher crosslinking density and exhibit high glass transition temperatures ranging from 140 to 400 °C. Another point may be ring opening chain polymerization of polybenzoxazine rather than the condensation polymerization.

1.5.3. Near Zero Volume Changes

Thermosetting resins shrink during polymerization by about 2-10% even for low shrinkage materials, and this is an important property in terms of applications [24]. Polybenzoxazines exhibit near zero shrinkage and volume change is about $\pm 1\%$

upon polymerization [26, 27]. The volume change decreased slightly during isothermal polymerization at high temperature. Nevertheless, volume change is observed during curing at room temperature with small changes in density.

1.5.4. Low Water Absorption

One of the problems of common resins is the high water absorption as 3-20% by weight upon saturation [27–29]. This is directly related to presence of polar groups in the structure of resins. Polybenzoxazine has also polar groups such as phenolic hydroxyl group and Mannich linkages ($-\text{CH}_2\text{-N-CH}_2-$). However, polybenzoxazine exhibits surprisingly low water uptake property, for example polybenzoxazine based on bisphenol-A and aniline saturated 1.9% by weight in water [30]. Moreover, water absorption level can be minimized by using amines and phenols involving hydrophobic radicals. This property is important for applications that require little difference between T_g and wet T_g .

1.5.5. Fast Physical and Mechanical Property Development

In order to have good mechanical and physical properties for condensation polymers such as epoxy, high degree of conversion is required. Therefore, small changes in conversion at the end of polymerization display significant changes in mechanical properties. Conversely, addition polymerization shows high conversion rate at early stages of polymerization. Polybenzoxazine obtained by the ring opening addition polymerization improved physical and mechanical properties rapidly while curing proceeds. For Biphenol A and aniline based benzoxazine (BA-a), 80% of T_g development takes place at 50% conversion of benzoxazine monomer polymerization [31].

1.6. Polybenzoxazine Composites and Blends

1.6.1. Polybenzoxazine/Clay Composites

Clay is widely used as reinforcing agent for the preparation of polymer nanocomposites by dispersing layered silicates at nanometer scale in the matrix.

Clay, low-cost filler, has great ability to enhance both mechanical and thermal properties of the neat polymer. Immiscible, intercalated or exfoliated nanocomposites may be obtained depending on the interactions between the clay and the polymer matrix (Figure 1.2) [32]. Montmorillonite, MMT, has a hydrophilic character and surface modification required in order to increase the diffusion of monomer, oligomer or polymer into clay layers. Two common methods; solution mixing and melt blending can achieve dispersion of nano-sized clay in the polymer matrix.

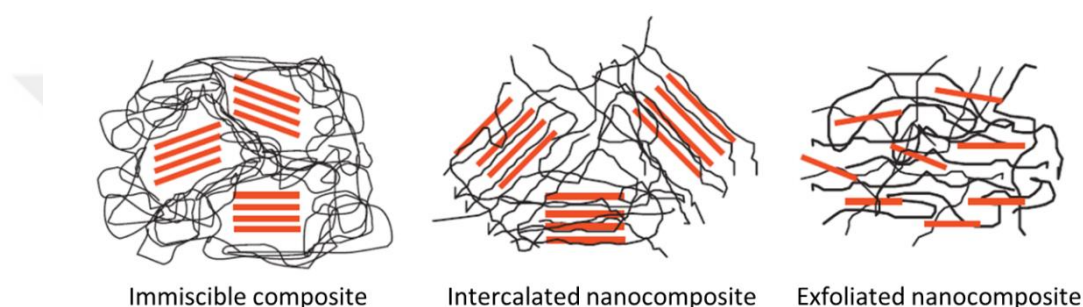


Figure 1.2. Dispersion modes of polymer-clay nanocomposites

Agag and Takeichi first prepared polybenzoxazine-clay nanocomposites with bisphenol A/aniline type benzoxazine monomer (BA-a) and organically modified montmorillonite (OMMT) by melt mixing method [33]. OMMT were obtained by surface treatment of montmorillonite (MMT) by octyl, dodecyl or stearyl ammonium chloride. The blends of benzoxazine monomer and OMMT showed lower exothermic polymerization peak by inclusion of different kinds of OMMTs. This represents the catalytic effect of OMMT on ring opening polymerization. Moreover, OMMTs enhanced thermal stability of nanocomposites by minimization of permeability to volatile degraded products due to barrier effect of clay.

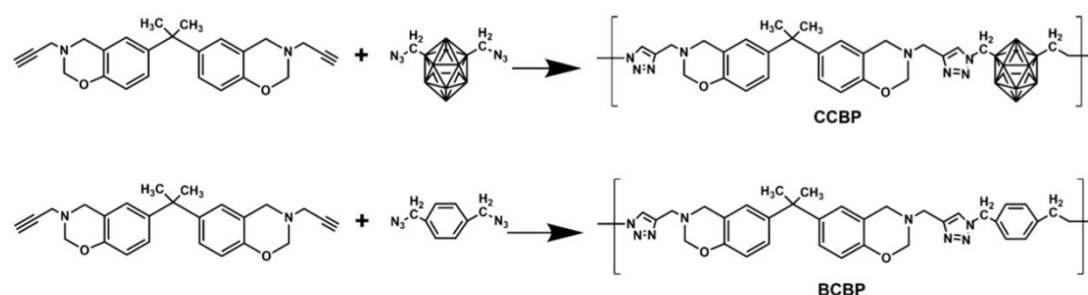
Phiriyawirut et al. prepared various types of immiscible polybenzoxazine organically modified montmorillonite nanocomposites by different types of OMMT and using various solvent, binary solvent or solventless systems [34]. They observed that exfoliation of OMMT strongly depends on the compatibility of monomer and

modifying agent. It was also reported that solvent and melt methods show no significant difference when a proper solvent for OMMT swelling was used.

1.6.2. Polybenzoxazine/Boron Containing Compounds Composites

The use of boronic compounds in polybenzoxazine resins was first studied by Huang and Ishida [35]. In this study, hexagonal boron nitrides were selected as reinforcing agent for polybenzoxazine composites. It was reported that thermal conductivity of composites was increased in the presence of boron nitrides, but they acted as an inhibitor for polymerization. Nanocomposites of polybenzoxazines based on bisphenol A and aniline involving boron carbide nanoparticles were also prepared. It was reported that stiffness and glass transition temperatures were improved. Moreover, thermal conductivity was improved significantly by the addition of nano-sized boron carbide [36].

Huang et. al. prepared polybenzoxazine composites with icosahedral carborane consisting stable cage structure and high boron content (Scheme 1.10). It was found that composites showed higher modulus and excellent thermal stability [37].



Scheme 1.10. Use of icosahedral carborane with benzoxazine

Jing and Xu used hyperbranched polyborate (Figure 1.3), boron containing hyperbranched polymer, to modify the thermal properties of benzoxazine. Polybenzoxazine prepared, showed excellent thermal resistance and improved mechanical properties. It was also concluded that hyperbranched polyborate can initiate the ring opening polymerization due to the presence of phenolic groups [38].

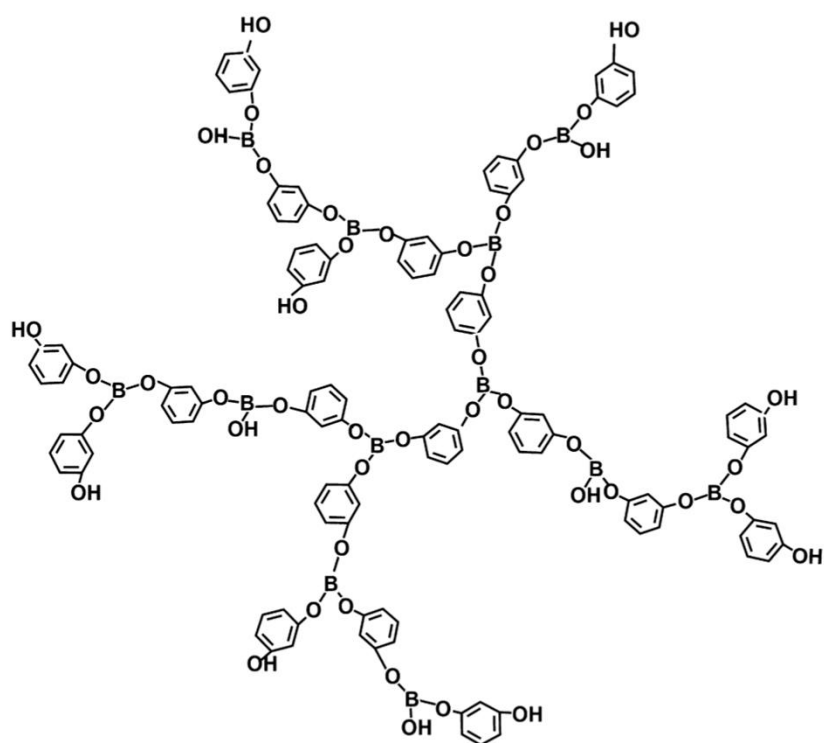


Figure 1.3. Structure of hyperbranched polyborate (HBPB)

Liu et. al. synthesized hyperbranched polyborazines (Figure 1.4) using boron trichloride and p-phenylene diamine to improve thermal properties. Polyborazines employed as catalyst for the curing reactions of benzoxazine. Increase in thermal stability and improvement in oxidation resistance due to high content of boron and nitrogen were detected [39].

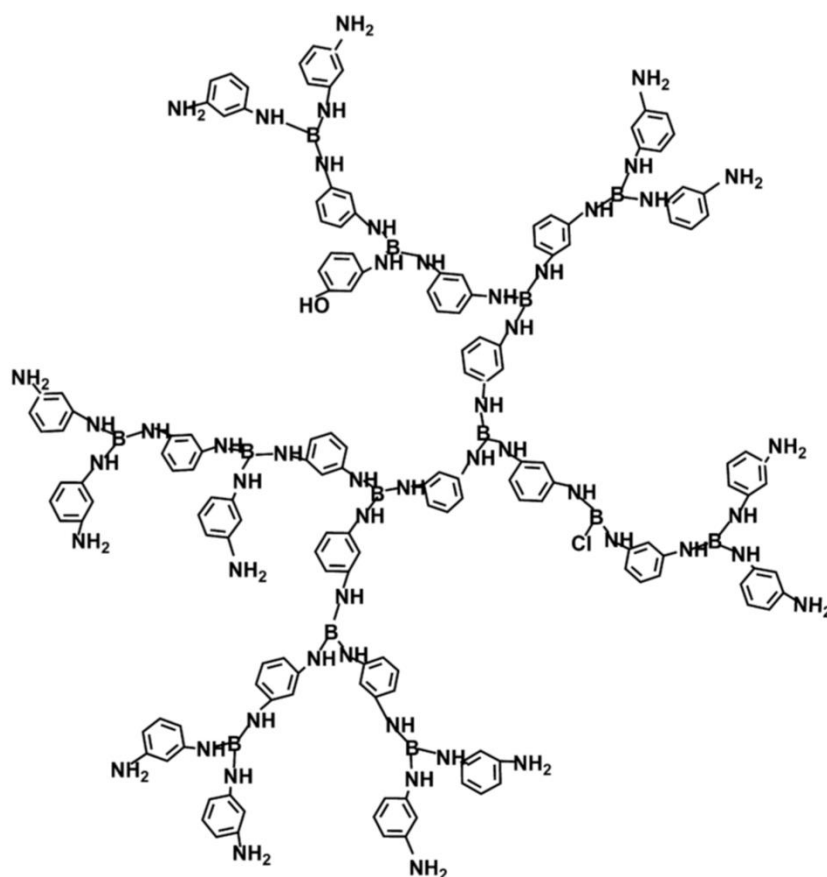


Figure 1.4. Structure of hyperbranched polyborazine

1.6.3. Polybenzoxazine/POSS Composites

Polyhedral oligomeric silsesquioxane (POSS) is an inorganic Si_8O_{12} core and is surrounded by eight hydrocarbon substituents, or functional groups, which are polymerizable and crosslinkable (Figure 1.5). The rigid Si-O-Si framework provides excellent thermal and mechanical improvements for the polymer composites. Polybenzoxazine composites involving POSS structure were prepared by physical blending and chemical modification of benzoxazine monomer with POSS.

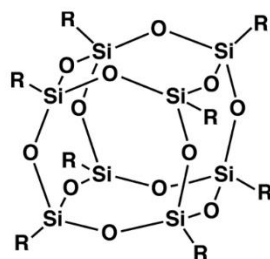
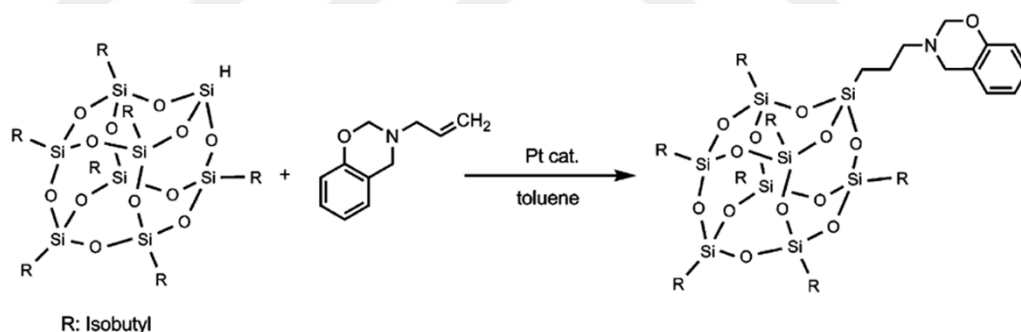


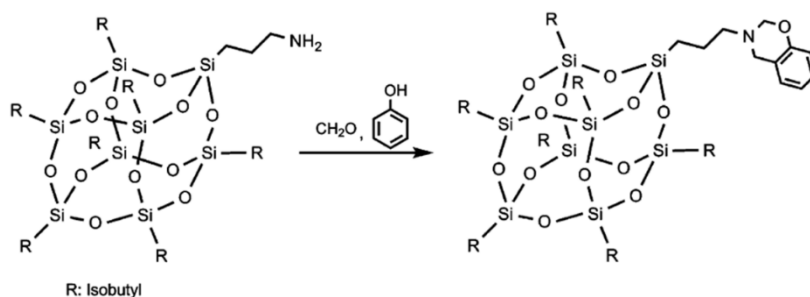
Figure 1.5. Structure of Polyhedral oligomeric silsesquioxane (POSS)

The distribution of POSS particles (nanometer scale) is challenge for nanocomposite preparation. Hence, modification of POSS with benzoxazine moieties as polymerizable group and copolymerized it with benzoxazine monomer is the most efficient way to get high distribution level. The ring-opening polymerization is occurred at the conditions similar to those used to polymerize pure benzoxazines to form hybrid materials. Benzoxazine-functional POSS was synthesized by the hydrosilylation reaction of vinyl-terminated benzoxazine with hydrosilane-functional POSS (H-POSS) shown in Scheme1.11 [40].



Scheme 1.11. Synthesis of benzoxazine functional polyhedral oligomeric silsesquioxane by hydrosilylation.

The second route for modification of POSS with benzoxazine is the reaction of a primary amine terminated POSS (Amine-POSS) with phenol and formaldehyde/paraformaldehyde as shown in Scheme 1.12 [41].



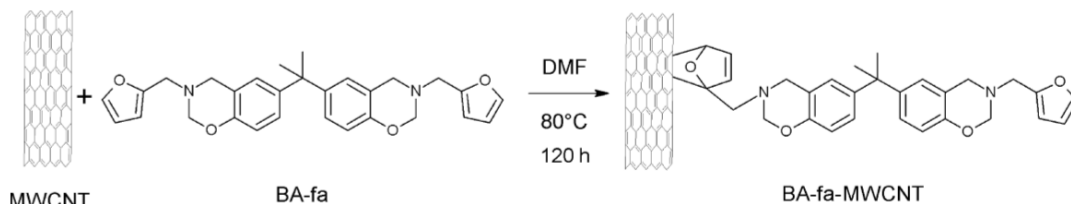
Scheme 1.12. Synthesis of benzoxazine functional polyhedral oligomeric silsesquioxane by oxazine ring formation.

Polybenzoxazine/POSS nanocomposite prepared by using monofunctional benzoxazine-substituted POSS (MBz-POSS) showed enhanced thermal stability compared to those of neat polybenzoxazine. Then, eight benzoxazine groups were introduced into the POSS and multifunctional POSS was polymerized with benzoxazine monomers. The dispersion at a nanometer scale was obtained at low POSS content and the improvement in thermal properties (i.e. glass transition temperature and thermal decomposition) was higher relative to MBz-POSS content [42].

1.6.4. Polybenzoxazine/CNT Composites

Carbon nanotubes (CNTs), either single-walled (SWCNT) or multiwalled (MWCNT), have attracted great attention of researchers due to their remarkable physical and mechanical properties. However, the main drawback of the preparation of CNT reinforced polybenzoxazine composite was the poor dispersion of CNTs in polybenzoxazine matrix [43]. In order to overcome this problem, chemical modification of the surface of CNT was achieved with functional groups. Consequently, homogeneous dispersion and control the de-aggregation of CNTs in the polybenzoxazine matrix were obtained. Two main approaches involve use of oxidized groups at CNT surfaces as reactive sites and functionalization of CNTs with benzoxazine moieties. Chen et al. one of the pioneer groups studied modification of MWCNT surface by nitric acid, followed by toluene-2,4-diisocyanate (TDI) treatment with the aim of introducing oxidized functional groups

such as hydroxyl, carboxyl and isocyanate groups [44]. Bisphenol-A and aniline based benzoxazine monomer (B-a) was used as polybenzoxazine precursor. The phenolic hydroxyl groups of benzoxazine and isocyanate groups of CNTs reacted and improved adhesion between B-a and MWNT. Therefore, well-dispersed polybenzoxazine/CNT nanocomposite showed high storage modulus as well as high T_g values by addition of 0.2-1.5% of MWCNT. The second and most effective approach is the use of benzoxazine moieties as functional group on CNT surface. Wang et al. studied for the first time preparation of benzoxazine functionalized (namely bisphenol A and furfuryl amine based benzoxazine; BA-fa) MWCNTs nanohybrids (Scheme 1.13) and nanocomposites. Modification by benzoxazine moieties effectively improved the compatibility between benzoxazine-based resins with MWCNTs, enhancing the dispersion of MWCNTs in the polymer matrix. The polybenzoxazine/CNT nanocomposites provide a great opportunity to improve the electrical and mechanical properties of polybenzoxazine [45].



Scheme 1.13. Preparation of benzoxazine functionalized MWCNT by Diels Alder reaction

1.6.5. Polybenzoxazine/Glass Fiber Composites

Glass Fiber (GF) reinforced polymer composites provide excellent thermal properties for flame retardant applications. Low et. al. synthesized silane coupling agent functionalized benzoxazine monomer and prepared glass fiber reinforced polybenzoxazine composites. The composites showed excellent interlaminar short beam shear (ILSS) strength due to silane coupling [46]. Kimura et al. studied benzoxazine monomer with bisoxazoline as the curing agent. Polybenzoxazine/GF composites were prepared in molten state of benzoxazine resin with curing agent. It

was observed that composites exhibited great improvement in heat and flame resistances, and mechanical properties [47].

The mechanical and thermal properties depend on the amount of SiO₂ in of GFs. Several GF reinforced polybenzoxazine composites prepared with different grades (such as F-grade or H-grade) are widely used for high performance structural and insulating applications. All GF composites have excellent physical and mechanical properties, higher heat resistance, good dielectric properties, and low water absorption [1].

1.6.6. Polybenzoxazine/Carbon Fiber Composites

Carbon Fiber (CF) reinforced polymer composites showed high thermal properties, excellent mechanical properties and suitable to light weight usage. According to applications, fiber diameter, fiber length, volume fraction of fibers and orientation of fibers has to be considered. Shen and Ishida prepared high-performance carbon fiber composites using two new kinds of benzoxazine monomers with good mechanical and thermal properties (Figure 1.6). The result of this study revealed that both of CF/44Oa and CF/22Pa composites have particularly high T_g values up to 260 °C and also high char yield (up to 85%) [48].

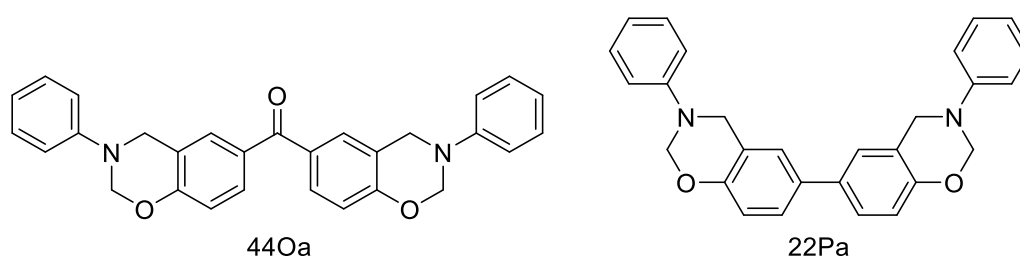


Figure 1.6. Structure of 2,2'-dihydroxybiphenyl (22P) and 4,4'-dihydroxybenzophenone (44O)

The effect of fiber lengths of chopped carbon fibers on mechanical properties of CF-reinforced polybenzoxazine composites was also investigated. Benzoxazine monomer based on bisphenol A and aniline was used with various fiber lengths. [49]. The mechanical properties such as tensile and flexural strengths were increased with increased fiber length and optimized when the length of the fiber was 17 mm.

On the other hand, the compressive strength was decreased with the increase in fiber length and fiber concentration. The polybenzoxazine CF composites with good strength, ductility, and modulus may be successfully developed using CFs of proper length and composition.

1.6.7. Polybenzoxazine/Epoxy Blends

Epoxy is widely used resin in industrial applications. Blending of polybenzoxazine with epoxy showed great enhancements in the crosslinking density and especially in mechanical properties. Ishida and Allen were reported copolymerized Bisphenol-A and aniline based benzoxazine (B-a) monomer with diglycidyl ether of bisphenol-A (DGEBA) based epoxy resin in order to adjust these properties. It was proposed that copolymerization was occurred as a consequence of reaction of the phenolic hydroxyl group of benzoxazine with epoxide group. Additional reaction was observed between hydroxyl group of epoxy resin and benzoxazine as ring opening reaction. Therefore, the final products have improvements in thermal and mechanical properties such as higher glass transition temperature and higher flexural stress [50]. Benzoxazine and epoxy blends were also studied in order to analyze the effect of molecular weight epoxy resin (Rao et. al.). In order to control molecular weight of epoxy resin, tetrabromobisphenol A was used as chain extender. In general blending of epoxy and benzoxazine yielded higher crosslinking density and higher glass transition temperature. However, copolymerization of benzoxazine with epoxy was slightly decreased char yields [51].

1.7. Characterization of Benzoxazine

Numerous techniques are used for characterization of benzoxazine and its polymers.

1.7.1. Nuclear Magnetic Resonance Spectroscopy (NMR)

Nuclear magnetic resonance (NMR) spectroscopy is one of the most common technique to confirm the formation benzoxazine structure. Oxazine ring typically show ^1H resonances frequency ranges of two different CH_2 groups in the

benzoxazine structure, Ph-CH₂-N(R) and O-CH₂-N(R)-. The protons attached to carbon atom between phenyl and amine group are seen in the range 3.8-4.8 ppm and the other protons attached to the carbon between oxygen and amine group has resonance in the region 4.7-5.7 ppm. Moreover, the characteristic ¹³C resonances of oxazine ring has frequencies in the range of 79-84 ppm for Ph-CH₂-N(R) and 49-59 ppm for O-CH₂-N(R)- groups [52]. Cross-linked polybenzoxazines are insoluble and solid state NMR has to be used [53].

1.7.2. Fourier Transform Infrared Spectroscopy (FTIR)

Fourier transform infrared spectroscopy (FTIR) is a useful technique for the characterization of benzoxazine monomer and polymerization of monomer. The trisubstituted benzene shows a characteristic peak at around 1500 cm⁻¹. Another characteristic band of oxazine ring structure is observed in the range of 960-910 cm⁻¹. Disappearance of this peak can be considered as an indication for polymerization, but this peak is not a direct evidence of polymerization. In addition to this, reduction in the intensity of peaks at around 1230 cm⁻¹ related with C-O-C asymmetric stretching vibration and at around 1030 cm⁻¹ related to symmetric stretching vibration band of C-O-C, also indicates the ring opening polymerization of benzoxazine [54].

1.7.3. Thermal Characterization

1.7.3.1. Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) is used to determine ring opening polymerization. Benzoxazine monomers display symmetric and sharp exotherm peak in the range of 200-250 °C in the case of pure samples. This peak shifts to lower temperature ranges and show asymmetric broad shape if the sample involve impurities such as raw materials and oligomers. These materials behave as a catalyst and initiate the ring opening polymerization at the lower temperatures [55].

1.7.3.2. Thermal Gravimetric Analysis (TGA)

Thermal gravimetric analysis is used for the study of thermal characteristics of materials such as rate of degradation, char yield and thermal stability. Polybenzoxazines have high char yield in the range of 35-75% and show multiple decomposition stages.

1.7.3.3. Direct Pyrolysis Mass Spectrometry (DP-MS)

Pyrolysis is thermal degradation of materials by cleavage at their weakest point to produce smaller volatile fragments in an inert atmosphere and/or vacuum. Direct pyrolysis mass spectrometry (DP-MS) is an effective method to study thermal stability, degradation behavior and decomposition mechanism. As, the secondary reactions can be prevented by removal of degradation products from the heating region immediately, unstable thermal degradation products and thermal decomposition mechanism can be determined. Furthermore, DP-MS has high sensitivity, high reproducibility, and requires only small amount of sample [56].

1.8. Aim of Study

In this study, our aim was to investigate the effect of various additives on thermal characteristics of polybenzoxazines composites. For this purpose, novel benzoxazine polymers and composites containing aromatic diboronic acid, boric acid, zirconium diboride, Cloisite 10A and diglycidyl ether bisphenol-A were prepared and characterized. Improved thermal characteristics were expected due to the contribution of interaction between additive and polybenzoxazine to the crosslinking. In the first part, phenol and aniline based benzoxazine monomer, in the second part difunctional benzoxazine monomer were synthesized and composites were prepared.

Structural characterization studies were performed by Fourier Transform Infrared Spectroscopy (FTIR) and Nuclear Magnetic Resonance Spectroscopy (NMR).

Thermal characteristics were investigated by Differential Scanning Calorimetry (DSC), Thermal Gravimetric Analysis (TGA) and Direct Pyrolysis Mass Spectrometry (DP-MS) techniques



CHAPTER 2

EXPERIMENTAL

2.1. Materials

Phenol (99.5%), paraformaldehyde, ethylenediamine, benzene-1,4-diboronic acid, boric acid, sodium hydroxide, and chloroform were supplied by Sigma Aldrich Co. Aniline, hexane, ethyl acetate, n-methyl pyrrolidone, and MgSO_4 were purchased from Merck. Cloisite 10A obtained from Southern Clay Products Inc. Zirconium diboride supplied from Nanografi. Epoxy resin received from Duratek. All chemicals were used as received without further purification.

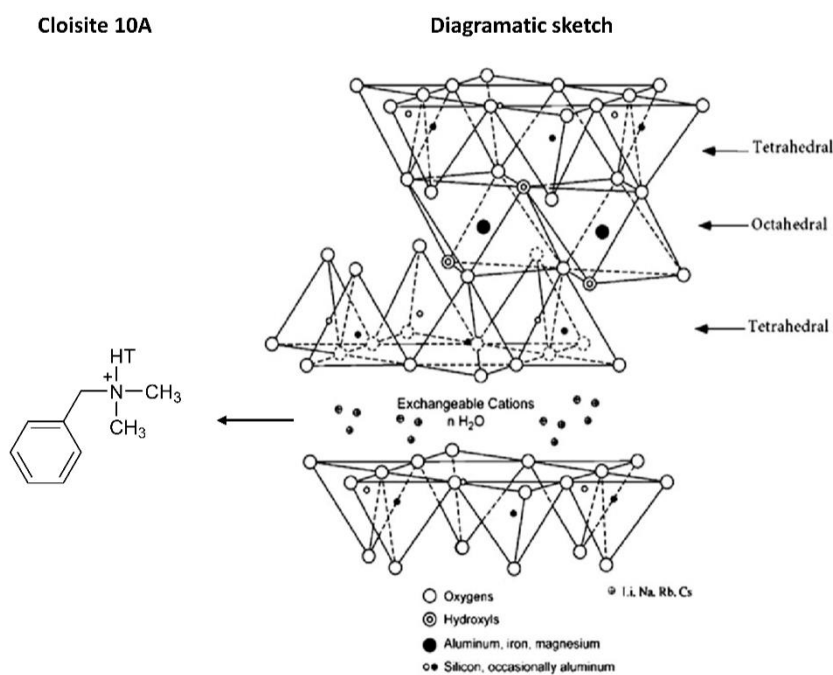


Figure 2.1. Schematic representation of organically modified clay, C10A

2.2. Characterization Techniques

2.2.1. Nuclear magnetic resonance spectroscopy (NMR)

Proton NMR spectra were acquired with a Bruker AC250 (250.133 MHz) spectrometer using CDCl_3 as the solvent and tetramethylsilane (TMS) as the internal standard.

2.2.2. Infrared spectrophotometer (ATR-FT-IR)

ATR-FT-IR analysis of the samples was performed by direct insertion of the solid sample using Bruker Vertex 70 Spectrophotometer with 0.4 cm^{-1} resolution.

2.2.3. X-Ray Diffraction (XRD)

XRD measurement of the samples was carried out by Rigaku, Mini-Flex X-ray powder diffractometer using $\text{Cu-K}\alpha$ radiation line ($\lambda=1.54056\text{ \AA}$).

2.2.4. Thermogravimetry (TGA) and Differential Scanning Calorimetry (DSC)

TGA and DSC analyses were performed on a Perkin Elmer Instrument STA6000 under the nitrogen atmosphere at a flow rate of 20 mL/min and a heating rate of $10\text{ }^\circ\text{C/min}$.

2.2.5. Direct pyrolysis mass spectrometry (DP-MS)

Direct pyrolysis mass spectrometry (DP-MS) analyses of the samples (0.010 mg) in flared quartz sample vials were performed on a Waters Micromass Quattro Micro GC Mass Spectrometer with a mass range of $15\text{--}1500\text{ Da}$ coupled to a direct insertion probe. The samples were heated to $650\text{ }^\circ\text{C}$ at a rate of $10\text{ }^\circ\text{C/min}$ while recording 70 eV EI mass spectra, at a rate of 1 scan/s . The step-wise curing of the monomers and the pyrolysis of the polymers, if generated any, during the curing process were also utilized inside the mass spectrometer while recording the mass spectra continuously at a rate of 1 scan/s . All the analyses were repeated at least twice to ensure reproducibility.

Collision induced dissociation experiments were conducted using argon as the collision gas and 40, 30 and 20 eV EI ionization. The daughter spectra of the precursor ions were recorded at the temperatures at which the yield of the selected precursor ion was maximized. Interpretation of the pyrolysis mass spectra was achieved by analyses of the trends in single ion evolution profiles and precursor-ion spectra.

2.2.6. Dynamic Mechanical Analysis (DMA)

Dynamic viscoelastic measurements were conducted on TA Instruments ARES-G2 rotational rheometer. The test was performed with the rectangular specimens (40 mm*10 mm* 3 mm) in a rectangular torsion fixture. A frequency of 1 Hz was applied during each temperature sweep experiment. Measurements were carried out in the temperature interval from 30 °C to 200 °C by a heating rate of 5 °C/min.

2.3. Synthesis

2.3.1. Synthesis of benzoxazine monomer based on aniline and phenol, aBz and pBz

Benzoxazine monomer was synthesized according to the literature method from phenol, aniline, and paraformaldehyde via solventless method as shown in Scheme 1 [2]. The mixture of phenol (5 mmol), aniline (5 mmol), and paraformaldehyde (10 mmol) was stirred at 110 °C for 1.5 h. Subsequently, the viscous liquid was cooled to about 50 °C, and about 30 mL chloroform was gradually introduced into the flask. Then, the chloroform solution was poured into a separatory funnel and washed three times with NaOH aqueous solution (3 mol/L) and deionized water, respectively. The chloroform solution was dried over anhydrous MgSO₄ and the solvent was removed under reduced pressure. The obtained product divide into two portions. One of them was heated at 80 °C for 1 hour and the light orange residue was named as-synthesized benzoxazine monomer, aBz. The second portion of the residue was purified by silica-gel column chromatography using hexane/ethyl acetate mixture as eluent. Pure benzoxazine monomer, pBz, was obtained as a yellow solid.

2.3.2. Synthesis of benzoxazine monomer based on phenol and aniline, Pa

The mixture of phenol (0,5 mol), paraformaldehyde (1 mol) and aniline (0,5 mol) were mixed at room temperature. The reaction temperature was adjusted for 110 °C and the mixture stirred at this temperature for 1.5 h. Subsequently, the viscous orange liquid was cooled to about 50 °C, and about 200 mL chloroform was gradually introduced into the flask. Then, the chloroform solution was poured into a separatory funnel and washed three times with NaOH aqueous solution (3 mol/L) and deionized water, respectively. The chloroform solution was dried over anhydrous MgSO_4 and the solvent was removed under reduced pressure. Benzoxazine monomer, Pa was obtained as yellow semi-solid residue.

2.3.3. Synthesis of benzoxazine monomer based on phenol and ethylene diamine, Peda

The benzoxazine monomer based on phenol and ethylene diamine synthesized according to the literature method. Phenol (33 mmol), paraformaldehyde (66 mmol) and ethylenediamine (16.5 mmol) were dry mixed in a reaction flask. Approximately 30 ml of chloroform was added to the flask and stirred at 60 °C for 1.5 h. After the mixture was cooled to room temperature, the crude residue was washed several times with 1N NaOH solution and distilled water until neutral by using a separatory funnel. The product was dried over MgSO_4 and filtered. Then the solvent was removed under vacuum. The obtained powder was washed with methanol and dried under a vacuum oven at room temperature for 24 h. Benzoxazine monomer based on phenol and ethylene diamine was obtained as a white colored powder.

2.4. Preparation of Polymers

2.4.1. Polymerization of benzoxazine monomer based on aniline and phenol

Three curing temperature program were applied in order to obtain polymers from benzoxazine monomer based on phenol and aniline.

2.4.1.1. Curing Program 1

Benzoxazine monomers based on phenol and aniline were cured at 150, 175 and 200 °C for 1 hour each in the vented oven. Reddish Brown colored polymers (PaBz and PpBz) were obtained.

2.4.1.2. Curing Program 2

Benzoxazine monomer (Pa) based on phenol and aniline was cured step-wise at 175, 200 and 225 °C for 1h each in the vented oven. Transparent reddish-brown colored polymer (PPa) was obtained.

2.4.1.3. Curing program 3

Benzoxazine monomer (Pa) based on phenol and aniline was cured step-wise at 100, 150, 175 and 200 °C for 1h each in the vented oven. transparent reddish-brown colored polymer (PePa) was obtained.

2.4.2. Polymerization of benzoxazine monomer based on phenol and ethylene diamine

Benzoxazine monomer based on phenol and ethylenediamine was cured step-wise at 140, 160, 180 and 185 °C for 1h each in the vented oven. Yellow-colored polymer (PPeda) was obtained.

2.5. Preparation of Composites

2.5.1. Preparation of Polybenzoxazine Composites PaBz/BDBA and PpBz/BDBA

For the preparation of polybenzoxazine composites involving different weight ratios (5, 15 and 20 wt%) benzene diboronic acid (BDBA), firstly, BDBA was dispersed in 3 mL of N-methyl pyrrolidone (NMP) and refluxed at 80 °C for 1–2 h. Then as-synthesized or pure benzoxazine monomer is dispersed in the solution. The blends were cast on the glass plate. After drying at 80 °C for 2 h under vacuum, the films were cured step-wise temperature program at 150, 175 and 200 °C for 1 h each in the

vented oven. The transparent reddish-brown colored polybenzoxazine/BDBA (PaBz/BDBA and PpBz/BDBA) composites were obtained.

2.5.2. Preparation of Polybenzoxazine Composites PPa/BA

Benzoxazine monomer (Pa) and boric acid (BA) were blended in different weight ratios (5, 10, 15 and 20wt%) at 60 °C. The mixture was stirred for 2 hours and a small amount of chloroform was added to assist the dispersion of the boric acid for high ratio loading by decreasing the viscosity of medium. The blends were cast on aluminum plate and dried under vacuum oven at 60 °C for 2 hours. The films were cured step-wise at 175, 200 and 225 °C for 1 h each in the vented oven. The reddish-brown polybenzoxazine/boric acid (PPa/5BA, PPa/10BA, PPa/15BA, and PPa/20BA) composites were obtained.

2.5.3. Preparation of polybenzoxazine Composites PPa/C10A

Benzoxazine monomer (Pa) and Cloisite 10A were blended in different weight ratios (1, 3, 5 and 7 wt%) at 60 °C. The mixture was stirred for 4 hours and chloroform was added to assist the dispersion of the C10A for high ratio loading by decreasing the mixture viscosity. The blends were cast on aluminum plate and dried under vacuum oven at 60 °C for 2 hours. The films were cured step-wise at 175, 200 and 225 °C for 1 h each in the vented oven. The reddish-brown polybenzoxazine/Cloisite 10A (PPa/1C10A, PPa/3C10A, PPa/5C10A, and PPa/7C10A) composites were obtained.

2.5.4. Preparation of polybenzoxazine Composites PPa/ZrB₂

Benzoxazine monomer (Pa) and zirconium diboride were blended in different weight ratios (5, 10, 15 and 20wt%) at 60 °C. The mixture was stirred for 2 hours and chloroform was added to assist the dispersion of the ZrB₂ for high ratio loading by decreasing the mixture viscosity. The blends were cast on aluminum plate and dried under vacuum oven at 60 °C for 2 hours. The films were cured step-wise temperature program at 175, 200 and 225 °C for 1 h each in the vented oven. The black

polybenzoxazine composites (PPa/5ZrB₂, PPa/10ZrB₂, PPa/15ZrB₂, and PPa/20ZrB₂) composites were obtained.

2.5.5. Preparation of polybenzoxazine Composites PePa/EP

Semisolid benzoxazine monomer (Pa) was melted at 40 °C and the viscous liquid was obtained. The blends of benzoxazine monomer and epoxy with different weight ratios (10, 20 and 30 wt%) were prepared. The mixture was stirred for 30 minutes at room temperature. The mixtures were cast on the aluminum plate. The samples were cured step-wise by heating for 1 hour at 100, 150, 175 and 200 °C in a vented oven. The transparent reddish-brown polybenzoxazine composites (PePa/10EP, PePa/20EP, and PePa/30EP) were obtained.

2.5.6. Preparation of polybenzoxazine composites PPeda/BDBA

Benzoxazine monomer based on phenol and ethylenediamine was dissolved in chloroform. The mixtures of benzoxazine monomer (Peda) and BDBA with different ratios (5, 10, 15 and 20 wt%) were prepared and stirred at room temperature for 5 hours. The blends were cast on aluminum plates and dried under vacuum oven at 60 °C. The samples were cured at 140, 160, 180 and 185 °C for 1h each in the vented oven. The light yellow polybenzoxazine composites (PPeda/5BDBA, PPeda/10BDBA, PPeda/15BDBA, and PPeda/20BDBA) were prepared. |



CHAPTER 3

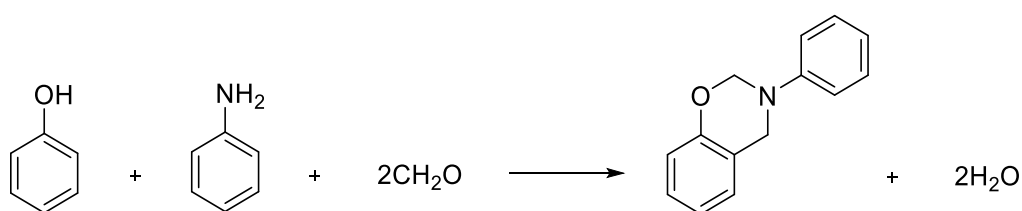
RESULTS AND DISCUSSION

3.1. Polybenzoxazine Composites PaBz/BDBA and PpBz/BDBA

Polybenzoxazines based on phenol and aniline were prepared by curing as-synthesized and purified monomers in the presence of (5, 15 and 20 wt%) aromatic diboronic acid, BDBA. Condensation reactions between BOH groups of diboronic acid and phenolic OH groups of benzoxazine took place during curing only when unreacted phenol or low mass oligomers were present in the medium. Generation of fragments involving B-O-C groups and significant improvement in thermal characteristics were detected upon curing the as-synthesized monomer in the presence of even 5wt% BDBA. On the other hand, enhancement in thermal characteristics was not detected for the polybenzoxazine prepared by curing the purified monomer, when the wt% of BDBA was lower than 15%.

3.1.1. Synthesis of Benzoxazine Monomer Based on Phenol and Aniline

Benzoxazine monomer based on phenol and aniline was synthesized by the reaction between aniline, phenol, and paraformaldehyde according to literature methods with a solventless method as shown in Scheme 3.1[57].



Scheme 3.1. Synthesis of benzoxazine monomer based on aniline and phenol

The benzoxazine monomer obtained was named as-synthesized benzoxazine monomer, aBz. This monomer may contain very small amount of oligomeric

structures and starting materials. Hence, in order to purify the product was isolated by silica gel column chromatography using hexane/ethyl acetate mixture as eluent. The yield was named as pure benzoxazine monomer, pBz. Both monomers aBz and pBz have similar NMR spectrum. The proton NMR spectrum of the monomer based on phenol and aniline shows strong resonances at 4.64 and 5.30 ppm corresponding to the characteristic methylene protons (H1 and H2) of Ar-CH₂-N and O-CH₂-N of the oxazine ring, respectively. The resonance signals at 6.71 (1H, H9), 6.84 (1H, H6), 6.86 (1H, H7), 6.91 (1H, H5) 7.08 (2H, H10 and H14), 7.52 (1H, H4), and 8.24 (2H, H11 and H13) are associated with the aromatic protons (Figure 3.1).

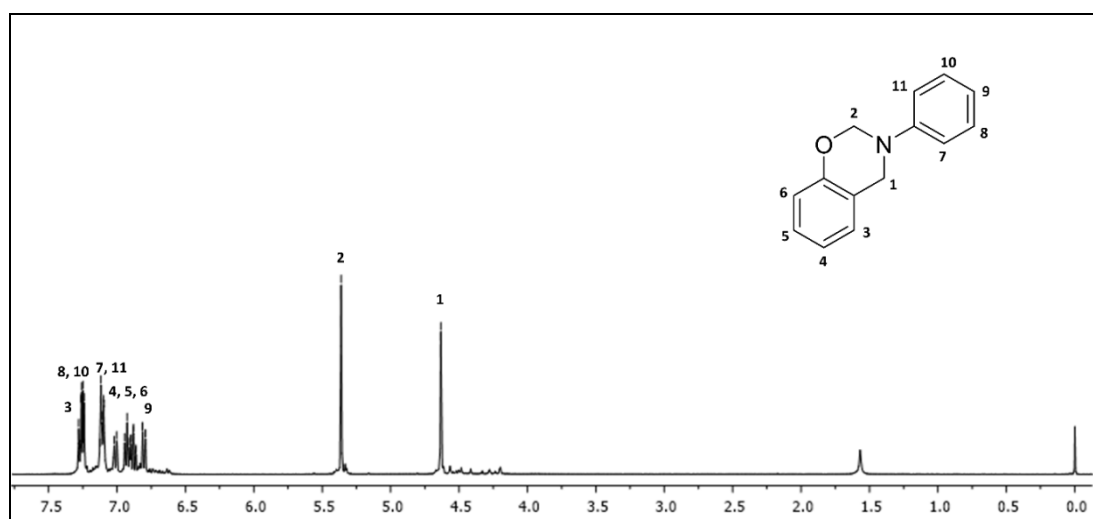


Figure 3.1. ¹H-NMR spectra of benzoxazine monomer based on phenol and aniline

Although the NMR spectra of both as-synthesized and purified monomers are almost identical, mass spectrum of as-synthesized benzoxazine monomer shows a very weak peak at $m/z = 422$ Da and 316 Da that may be associated with dimer. The fragment generated by loss of CH₂NHC₆H₅ from dimer indicating presence of dimer and most probably low mass oligomers as by-products (Fig. 3.2). On the other hand, the mass spectrum of the purified monomer is in accordance with the expected fragmentation pattern for benzoxazine monomer based on phenol and aniline, showing molecular ion peak at 211 Da and intense peaks due to CH₂NC₆H₅ (105 Da), C₆H₅ (77 Da) and C₅H₅ (51 Da).

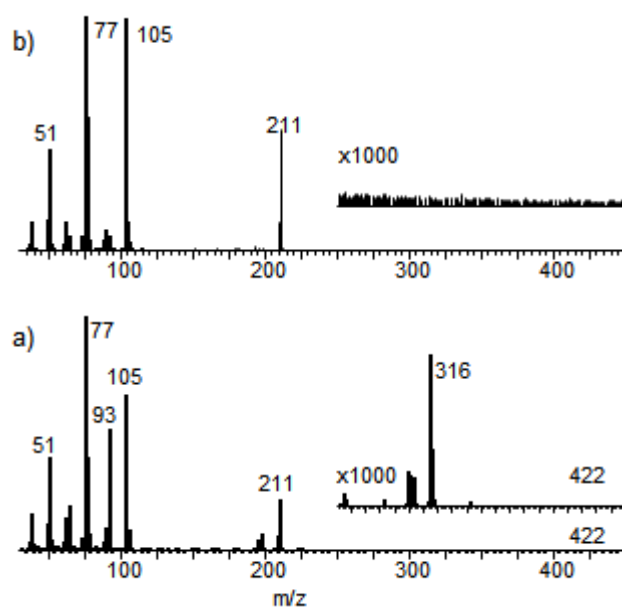
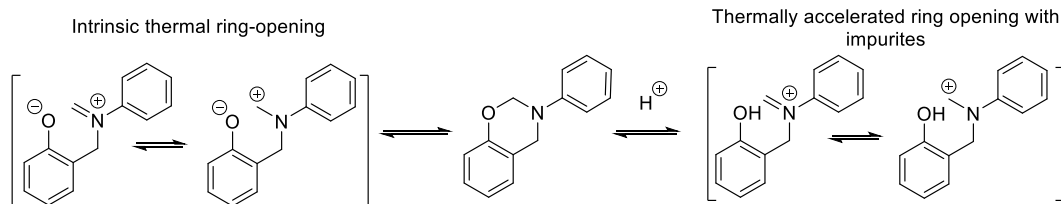


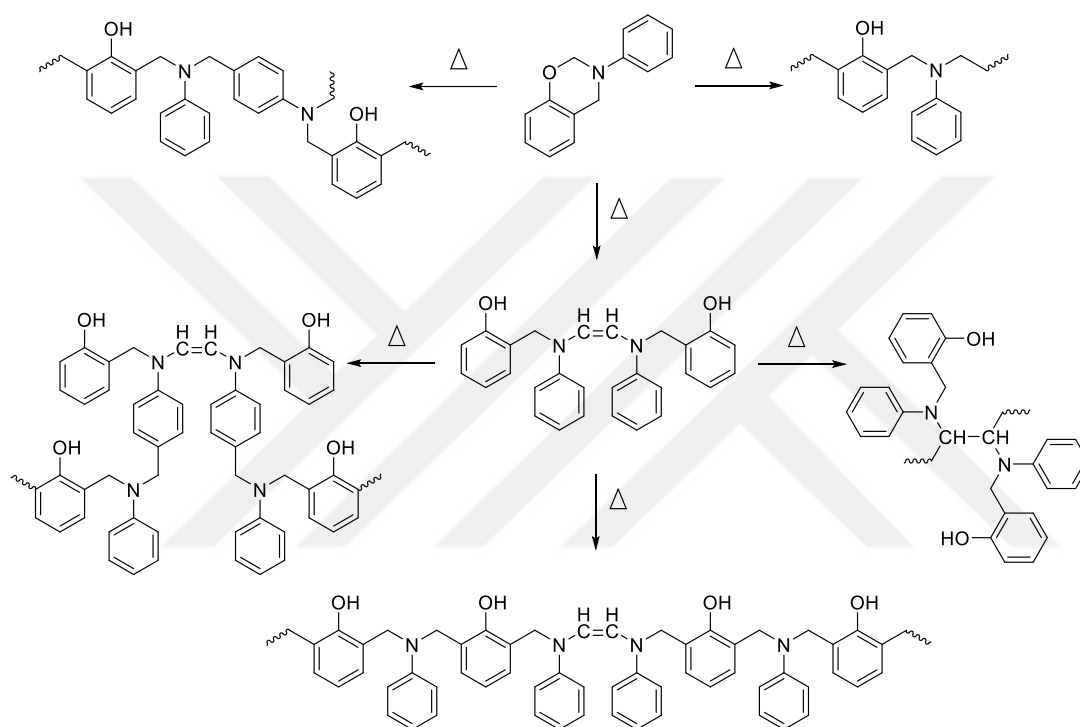
Figure 3.2. Mass spectra of a) as-synthesized and b) purified benzoxazine monomers based on phenol and aniline.

Benzoxazine monomer based on phenol and aniline was heated step-wise curing temperature program in a vented oven. The monomers the ring opening polymerization occurred in two ways namely thermally accelerated polymerization mechanism presence of impurities and intrinsic thermal ring-opening polymerization mechanism while applying curing program [58]. These possible polymerization mechanisms of various polymer chains formed during the ring opening polymerization shown in Scheme 3.2 [57].

a) Ring opening mechanisms



b) Polymerization mechanisms after ring opening



Scheme 3.2. Possible ring opening polymerization pathways

3.1.2. Preparation of polybenzoxazines and polybenzoxazine/BDBA composites (PaBz/BDBA and PpBz/BDBA)

Benzoxazine monomers based on phenol and aniline were cured at 150, 175 and 200°C for 1h each in the vented oven. Reddish-brown colored as-synthesized polymer (PaBz) and pure polymer (PpBz) were obtained. For the preparation of polybenzoxazine composites involving 5, 15 or 20wt% BDBA, firstly, BDBA was dispersed in 3mL of N-methylpyrrolidone (NMP) and refluxed at 80 °C for 1–2h. Then crude or pure benzoxazine monomer was dispersed in the solution. The blends

were casted on the glass plate. After drying at 80 °C for 2h under vacuum, the films were cured step-wise at 150, 175 and 200 °C for 1h each in the vented oven. The as-synthesized and pure products were named as PaBz/BDBA and PpBz/BDBA, respectively.

The DSC curve of the purified monomer showed a sharp exothermic peak starting at around 229 °C and maximizing at 240 °C, due to the typical thermal curing characteristic of oxazine ring-opening polymerization (Fig. 3.3). On the other hand, a broader peak starting at around 205 °C with a maximum at around 228 °C was observed in the DSC curve of the as-synthesized monomer. The significant shift of the exothermic ring opening polymerization peak is associated with the catalytic effect of dimer and higher oligomers present as by-products in the as-synthesized benzoxazine monomer sample as stated by Ishida and co-workers [58]. In this study, Ishida and coworkers studied the intrinsic thermal ring-opening polymerization of benzoxazines without the influence of any impurity. They determined that polybenzoxazines can be obtained by both the traditional thermally accelerated (or activated) polymerization, where impurities or purposefully added initiators are involved in the reaction; or, by the classic thermal polymerization, where only heat is enough to initiate the reaction. In the present study, the same step-wise curing program applied to all samples lead to the disappearance of the exothermic peak(s) in the DSC curves of polybenzoxazines prepared using as-synthesized and purified monomers and composites involving 5, 15 and 20wt% BDBA confirming polymerization of the monomers (Fig. 3.3).

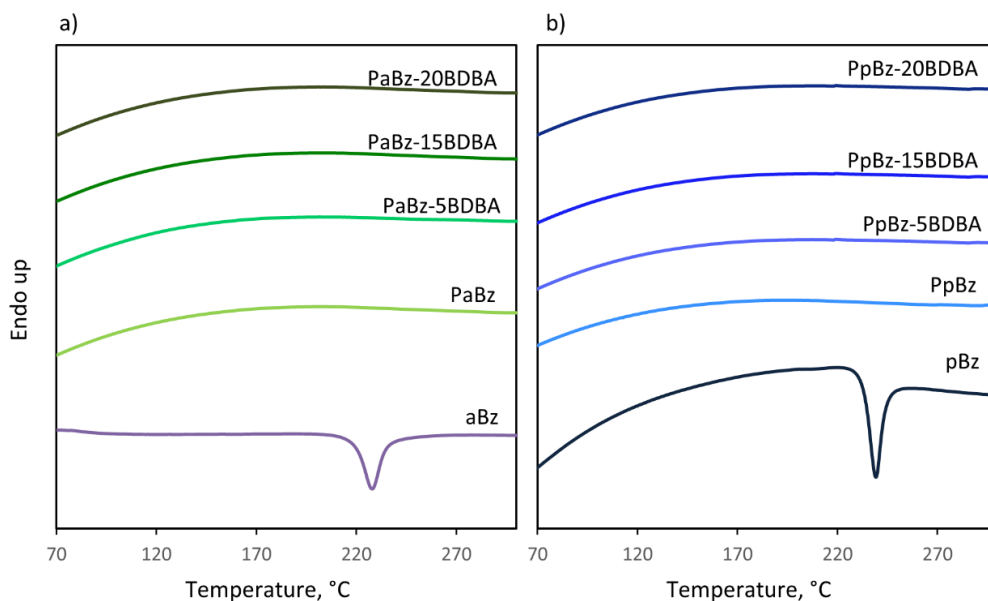


Figure 3.3. DSC profiles of (a) as-synthesized and (b) purified benzoxazine monomers and corresponding polymers and composites involving 5, 15 and 20wt% BDBA

The polymerization of the as-synthesized and purified monomers was also confirmed by FTIR analyses (Fig. 3.4). The characteristic mode of benzene with an attached oxazine ring appeared at around 933 cm^{-1} and peaks at around 1224 and 1034 cm^{-1} attributed to asymmetric and symmetric stretching peaks of C-O-C of oxazine ring, respectively disappeared upon polymerization. The decrease in the relative intensities of the peaks at around 1490 cm^{-1} and 1362 cm^{-1} associated with disubstituent benzene ring and CH_2 wagging respectively may be regarded as an indication for ring-opening polymerization of the oxazine ring. Appearance of tri-substituted benzene ring absorptions around 1620 cm^{-1} and 1502 cm^{-1} supported also the oxazine ring-opening reaction during curing at this stage. Unfortunately, absorption peak positions of BDBA and expected linkages with benzoxazine units such as B-O-C exhibit approximately the same positions; B-C stretching band between 1080 and 1110 cm^{-1} , out-of-plane deformation mode of BO_2 group around $620\text{--}680\text{ cm}^{-1}$, B-C-O stretching vibration at around 1350 cm^{-1} . Thus, we were unable, to identify the interaction of BDBA with benzoxazine units with acceptable certainty.

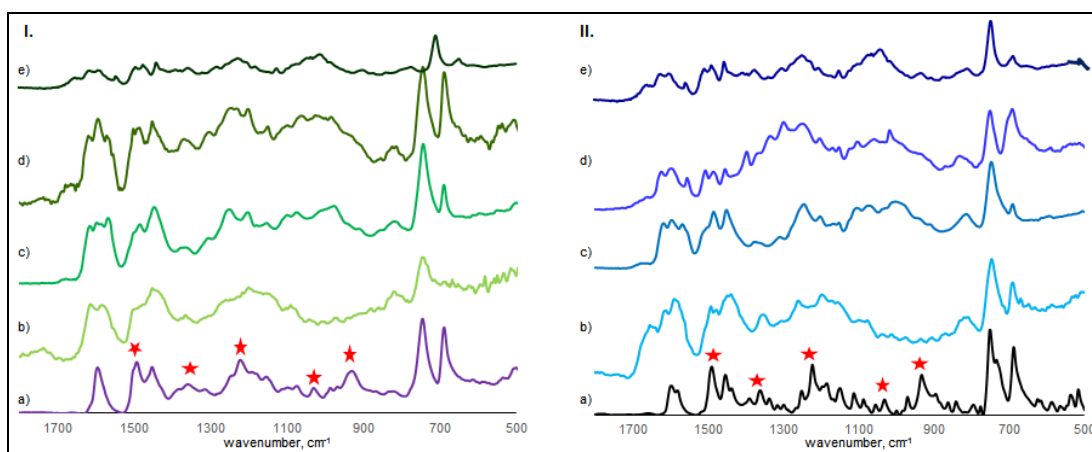


Figure 3.4. FTIR spectra of I. a)aBz, b)PaBz, c)PaBz-5BDBA, d)PaBz-15BDBA and e)PaBz-20BDBA and II. a)pBz, b)PpBz, c)PpBz-5BDBA, d)PpBz-15BDBA and e)PpBz-20BDBA

In order to investigate the loss of any substance during the curing process, TGA analyses were performed while the aBz and pBz monomers were cured at 150, 175 and 200°C for 1h. During the curing processes, although only about 6.0 wt% loss was detected for aBz, about 19.1 wt% of the purified monomer was lost (Fig. 3.5). The curing experiments performed inside the mass spectrometer indicated that the weight loss was mainly due to the elimination of monomer. Thus, it may be concluded that presence of dimer and/or low mass oligomers limits the amount of monomer that can be evaporated during the curing process, and consequently, the use of as-synthesized monomer may be preferential.

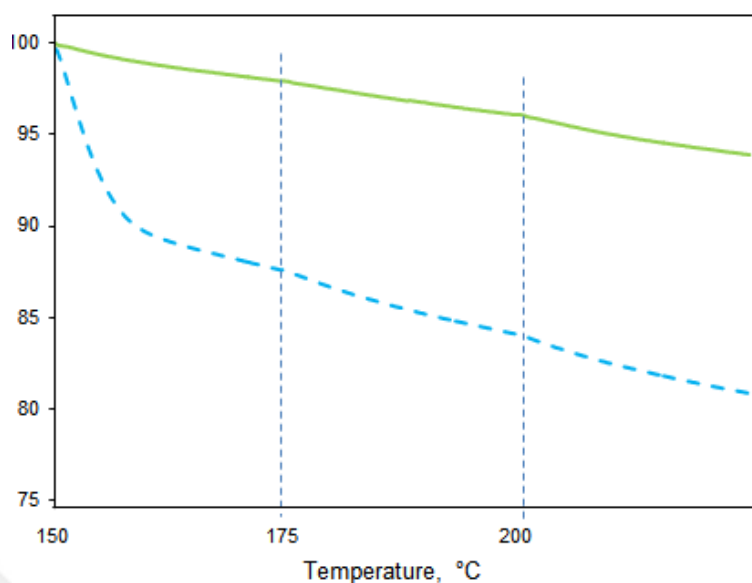


Figure 3.5. % weight loss during the curing of aBz (green line) and pBz (blue dashed line)

3.1.3. Thermal Analysis of PaBz/BDBA and PpBz/BDBA Composites

The TGA curves of polybenzoxazines, PaBz and PpBz and the corresponding composites involving 5, 15 and 20 wt% BDBA are shown in Fig. 3.6 and the relevant data are listed in Table 3.1. TGA results revealed that thermal degradation of polybenzoxazines occurred in three steps, below 300°C, around 400°C and finally around 500°C. Yet, the second and third thermal degradation steps of the polymer obtained by curing the purified monomer, PpBz, took place at significantly higher temperatures. Besides, noticeably greater % char yield was detected for this sample. Upon addition of BDBA, variations in the temperature regions of the three thermal decomposition steps were detected. The most significant effect was observed in the last stage of decomposition and % char yield of PaBz. On the other hand, although a significant increase in the % char yield was detected for PaBz even with the addition of 15wt% BDBA, the effect of BDBA on % char yield of PpBz was almost negligible.

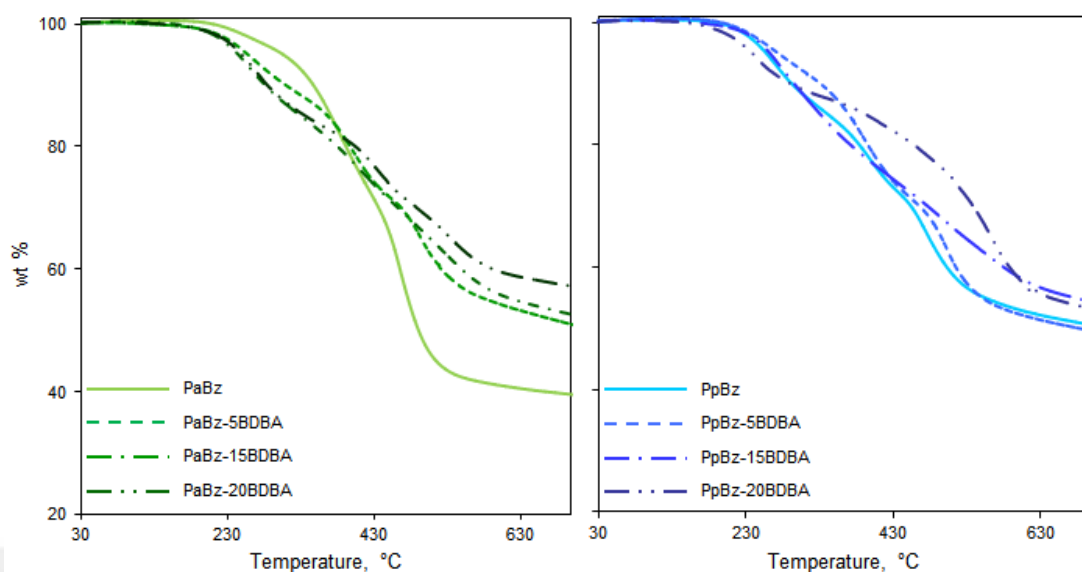


Figure 3.6. TGA curves of polybenzoxazines and polybenzoxazines involving 5, 15 and 20wt% BDBA prepared using as-synthesized and purified benzoxazine monomers.

Table 3.1. TGA data of polybenzoxazines and polybenzoxazines involving 5, 15 and 20wt% BDBA prepared using as-synthesized and purified benzoxazine monomers.

Sample	T _{5%}	T _{max}			% char yield, at 650 °C
		Step 1	Step 2	Step 3	
PaBz	306	263	389	471	40.1
PaBz-5BDBA	258	299	392	482	52.5
PaBz-15BDBA	245	268	414	537	54.0
PaBz-20BDBA	250	278	424	551	58.2
PpBz	258	287	400	480	51.6
PpBz-5BDBA	273	279	397	490	50.8
PpBz-15BDBA	284	245	481	573	55.8
PpBz-20BDBA	239	249	428	567	54.7

In Fig. 3.7, total ion current, TIC, curves, the variation of total ion yield as a function of temperature, of polybenzoxazines prepared using as-synthesized and purified monomers are shown. Both of the TIC curves showed three broad overlapping

peaks. Yet, maxima and relative intensities of the peaks showed differences, especially in low-temperature regions. The pyrolysis mass spectra recorded at low temperatures showed noticeable differences. On the other hand, high-temperature pyrolysis mass spectra were quite similar. The pyrolysis mass spectra were dominated with peaks at 77 (C_6H_5), 91 (C_7H_7), 93 ($C_6H_5NH_2$), 94 (C_6H_5OH), 105 (C_8H_9), 107 ($HOC_6H_4CH_3$), 121 ($HOC_6H_4CH_2N$), 193 ($CH_2C_6H_4C_2H_2C_6H_4$), 199 ($HOC_6H_4CH_2NHC_6H_5$) due to characteristic fragments of monomer and dimer that can be generated during pyrolysis and/or dissociative ionization of the polymers during the DP-MS analyses.

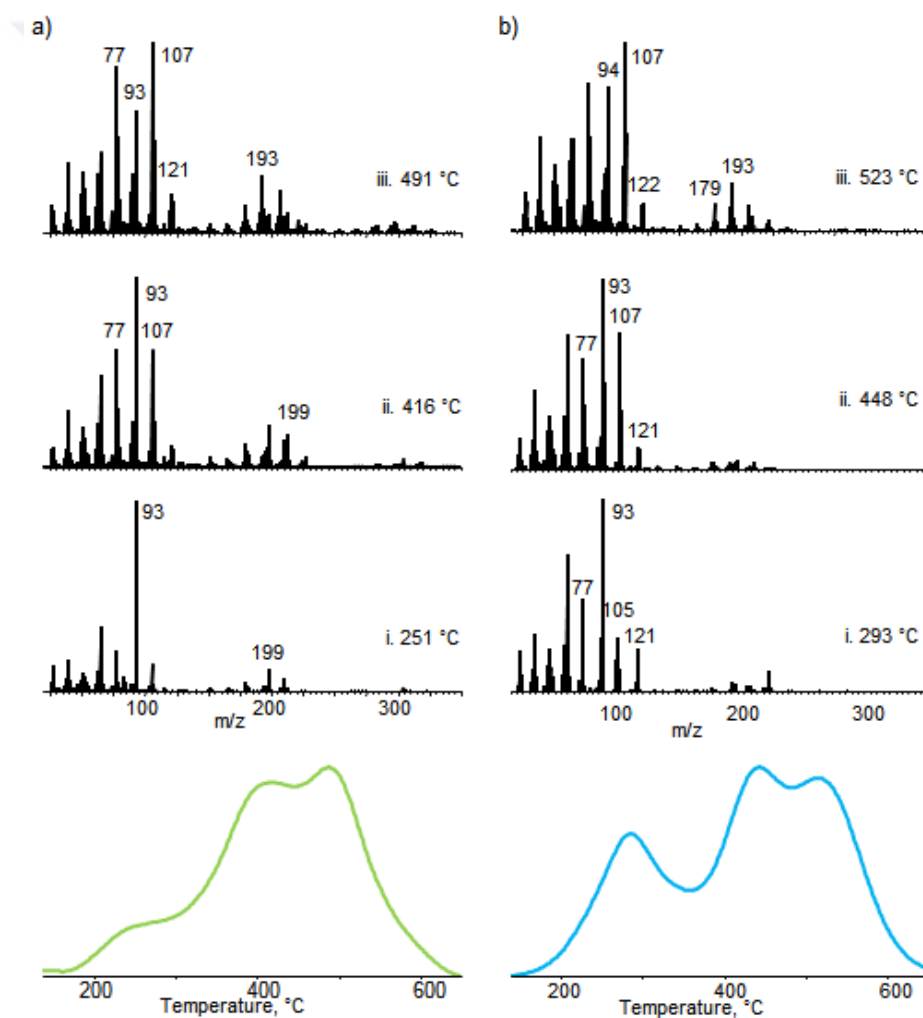


Figure 3.7. TIC curves and pyrolysis mass spectra recorded at peak maxima recorded during the pyrolysis of a) PaBz and b) PpBz.

In order to get a better insight, single ion evolution profiles of intense and/or characteristic products were analyzed and grouped considering the similarities in the trends observed. In Fig. 3.8, single ion evolution profiles of monomer (211 Da), dimer, (422 Da), $\text{C}_6\text{H}_5\text{NH}_2$ or HOC_6H_4 (93 Da) HOC_6H_5 (94 Da), $\text{C}_6\text{H}_5\text{CH}_2$ (91 Da) and $\text{C}_6\text{H}_5\text{C}_2\text{H}_2\text{C}_6\text{H}_5$ (179 Da) are shown as representative examples. Three main degradation stages were recorded for both samples in accordance to TGA results. The degradation of PaBz was started at lower temperatures. At temperatures below 300°C , low mass species, aniline being the most abundant, were eliminated. At moderate temperatures above 400°C loss of monomer and dimer were detected. Loss of phenol and fragments that can be associated with degradation of cross-linked units were observed in the final stages of pyrolysis. One of the main differences between polymers prepared by curing the as-synthesized and purified monomers was the significant amount of dimer lost during the pyrolysis of PaBz, although loss of dimer from PpBz was almost negligible. The decomposition of the cross-linked structures at around 496 and 571°C during the pyrolysis of PaBz and PpBz respectively was the second point that should be noticed. It maybe thought that the increase in the rate of reaction due to the presence of dimers and low mass oligomers in the as-synthesized monomer generated low molecular mass chains with limited cross-linked units.

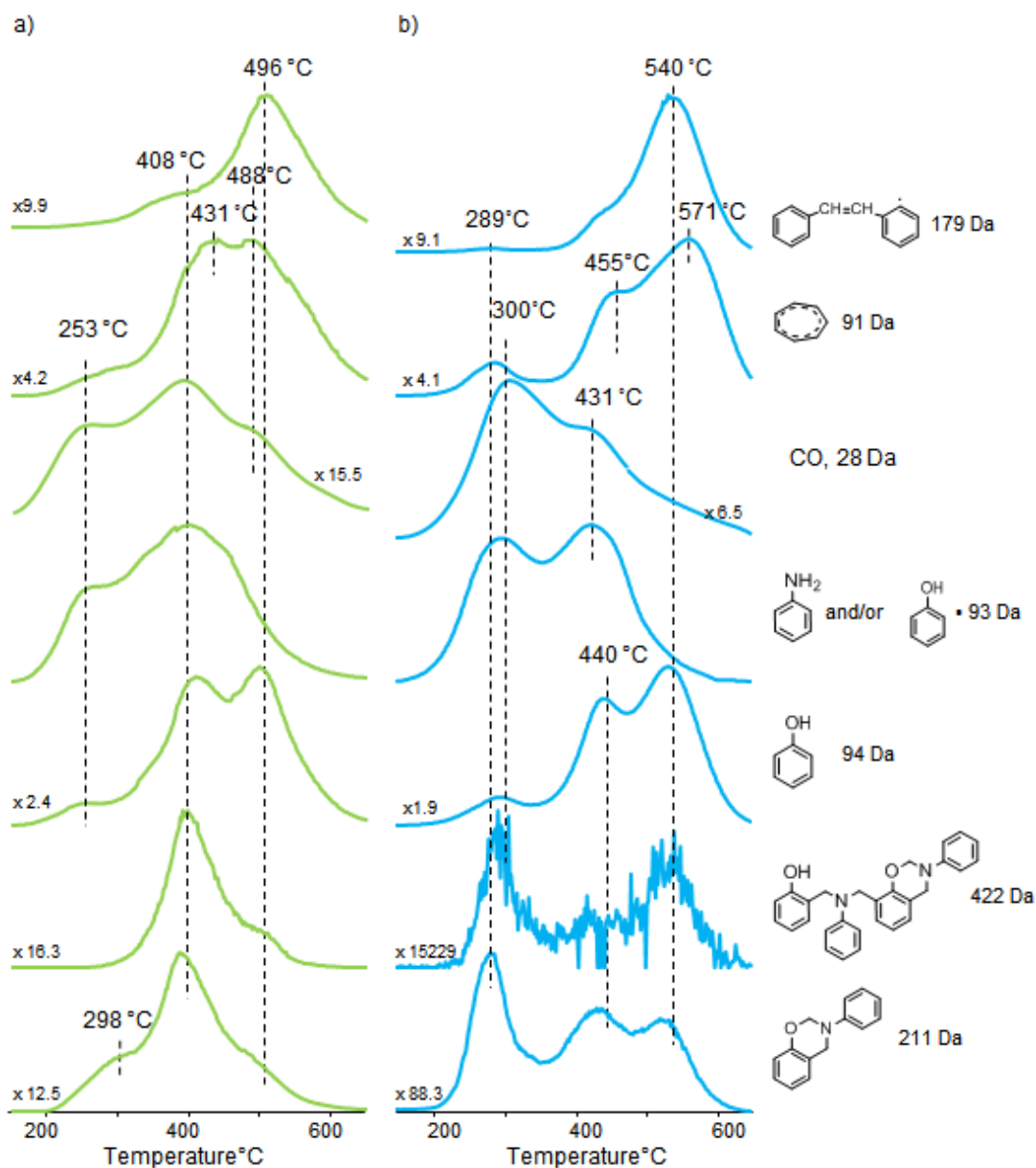


Figure 3.8. Single ion evolution profiles of selected products recorded during the pyrolysis of (a) PaBz and (b) PpBz.

Upon addition of 5wt% BDBA, the thermal stability and the char yield of PaBz were increased noticeably, whereas, no significant effect was detected for PpBz. An increase in thermal properties was detected for PpBz only after increasing wt% of BDBA to 15%. In Fig. 3.9, single ion evolution profiles of monomer (211 Da), dimer, (422 Da), $C_6H_5NH_2$ or HOC_6H_4 (93 Da) HOC_6H_5 (94 Da), $C_6H_5CH_2$ (91 Da)

and $\text{C}_6\text{H}_5\text{C}_2\text{H}_2\text{C}_6\text{H}_5$ (179 Da) recorded during the pyrolysis of PaBz involving 5, 15 and 20wt% BDBA and PpBz involving 20wt% BDBA are shown. The relative yield of the dimer lost during the pyrolysis of PaBz was decreased significantly upon the addition of 5wt% BDBA and almost totally disappeared for the sample involving 15wt% BDBA. Also, the loss of fragments associated with the degradation of cross-linked units shifted drastically to high temperature regions and the relative yields of these products increased noticeably as the wt% of BDBA was increased. The loss of units associated with degradation of cross-linked structures was detected mainly at around 612°C during the pyrolysis of PaBz involving 15wt% BDBA. Increasing BDBA content to 20wt% further increased thermal stability.

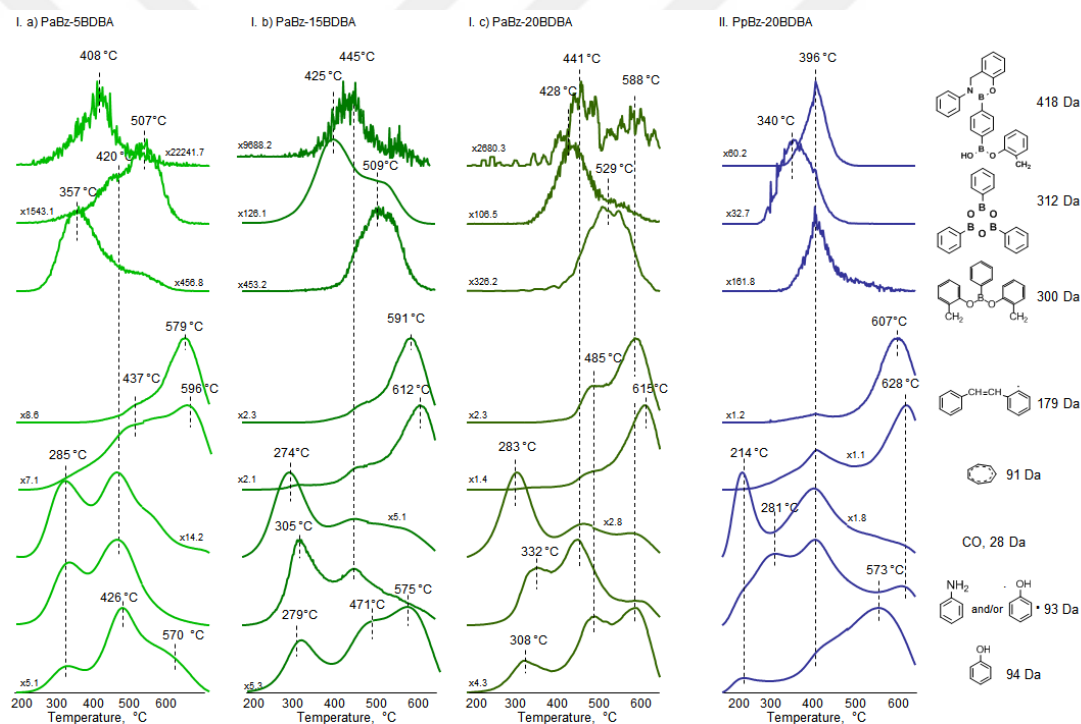
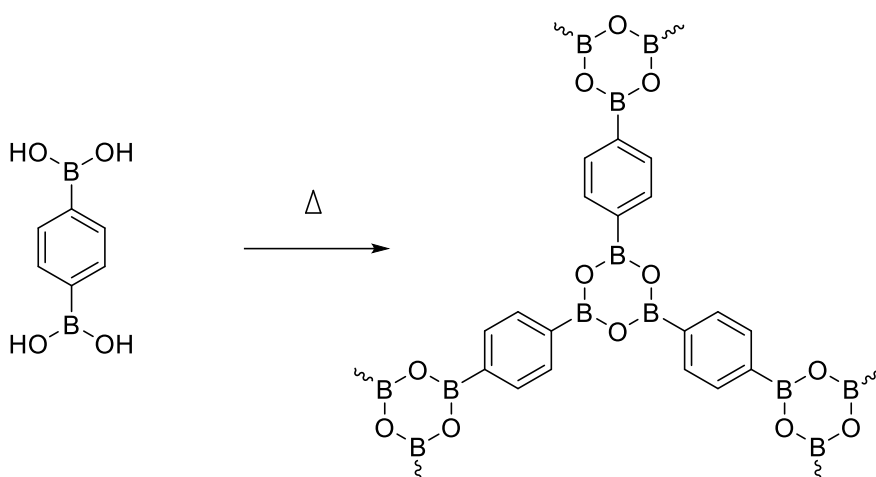


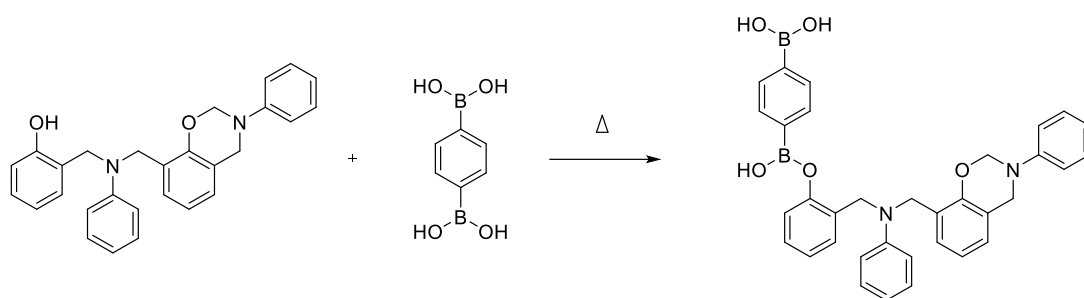
Figure 3.9. Single ion evolution profiles of selected products recorded during the pyrolysis of PaBz involving 5, 15 and 20 wt % BDBA and PpBz involving 20 wt % BDBA.

Another point that should be noticed was the elimination of boraxine and fragments indicating reactions between BDBA and OH groups of benzoxazines. Related reactions are given in Scheme 3.3 and Scheme 3.4. The yield of these products increased noticeably with the increase in wt% of BDBA.



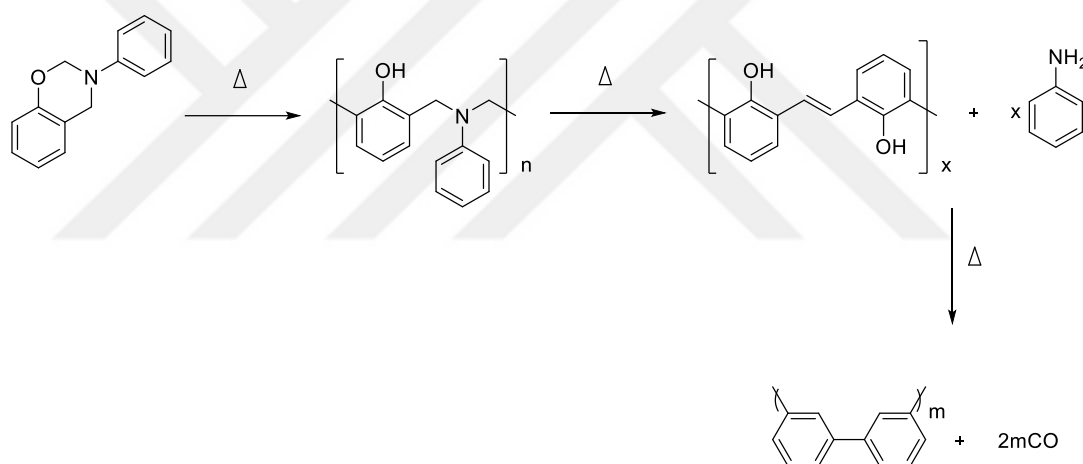
Scheme 3.3. Generation of boraxine net-work

On the other hand, no noticeable change in the thermal characteristics of PpBz was recorded upon addition of 5wt% BDBA during the curing process and only a slight increase in the thermal stability was detected for the samples involving 15 and 20wt% BDBA. Although the generation of boron network and fragments that can be associated with units generated by the interaction of BDBA and OH groups of benzoxazine was also observed for PpBz, these products were detected at relatively lower temperature regions. It may be thought that the dimers present as by-products in the as-synthesized benzoxazine sample interacted with BDBA units more readily, increasing the thermal stability and the char yield of the polymer generated. The BDBA units linked to OH group of the dimer may form a cross linked structure. On the other hand, during the curing process of the pure monomer, BDBA molecules reacted by each other generating mainly low molecular weight boron net-work. The relative yield of products indicating interactions of BDBA with Bz units was significantly higher for purified samples. However, these products were eliminated at relatively lower temperatures than the corresponding ones lost during the pyrolysis of the as-synthesized sample.



Scheme 3.4. Interaction of aromatic diboronic acid with benzoxazine dimer

Another point that should be noticed was the significant increase in the relative amount of CO (28 Da) and $C_6H_5C_2H_2C_6H_5$ (179 Da) lost during the pyrolysis as the content of BDDBA added was increased. It may be thought that due to the interactions between the OH group of the polymer and BDDBA, elimination of aniline occurs more readily generating unsaturated linkages as shown in Scheme 3.5.



Scheme 3.5. Loss of aniline and CO during the thermal degradation of polybenzoxazine

In conclusion, the significant improvement in thermal characteristics of the polybenzoxazine prepared by curing as-synthesized monomer was detected upon incorporation of 5% BDDBA whereas no significant effect was detected for purified benzoxazine when the BDDBA was lower than 15%. Condensation reactions between B-OH groups and OH groups of phenol were only effective during the curing of the as-synthesized monomer sample involving also some dimer with available OH groups.

3.2. Polybenzoxazine/Boric Acid Composites

Different amounts of boric acid (5, 10, 15 and 20%) were mixed with benzoxazine monomer and polymerized to achieve PPa/BA composites. Condensation reactions between boric acid and phenolic OH groups of phenol and/or benzoxazine took place during the curing process. The generation of B-O-C groups, boraxine network and hydrogen bonding lead to enhancement in thermal characteristics. It has been determined thermal properties were improved as the amount of boric acid added was increased. Structural and thermal characterizations were performed by FTIR, DSC, TGA, and DP-MS techniques.

3.2.1. Preparation of Polybenzoxazine, PPa

Benzoxazine monomer, Pa, based on phenol and aniline was cured step-wise at 175, 200 and 225 °C for 1h each in vented oven. Reddish brown colored polymer (PPa) was obtained. The polymerization process may follow various reaction pathways resulting in different polymer chains.

3.2.2. Preparation and Characterization of PPa/BA Composites

Benzoxazine monomer and boric acid were blended in different weight ratios (5, 10, 15 and 20%) at 60 °C. The mixture was stirred for 2 hours and a small amount of chloroform was added to assist the dispersion of the boric acid for high ratio loading by decreasing the mixture viscosity. The blends were casted on aluminum plate and dried under vacuum. The films were cured step-wise at 175, 200 and 225 °C for 1 h each in the vented oven. The reddish brown polybenzoxazine/boric acid (PPa/5BA, PPa/10BA, PPa/15BA, and PPa/20BA) composites were obtained.

FTIR analysis also supported the polymerization of the benzoxazine and the samples involving the monomer and various amounts of BA (Fig. 3.10). The characteristic mode of benzene with an attached oxazine ring appeared at around 933 cm^{-1} and peaks at around 1224 and 1034 cm^{-1} attributed to asymmetric and symmetric stretching peaks of C-O-C of oxazine ring, respectively disappeared upon

polymerization. The decrease in the relative intensities of the peaks at around 1490 cm^{-1} and 1362 cm^{-1} associated with the disubstituted benzene ring and CH_2 wagging respectively may be regarded as an indication for ring-opening polymerization of the oxazine ring. Furthermore, new peaks at around 3200 and 645 cm^{-1} may be associated with out-of-plane deformation mode of B-OH and BO_2 group stretching vibration, respectively. Moreover, vibration at 1310 cm^{-1} may be attributed to B-CO stretching indicating an interaction between the filler and the monomer.

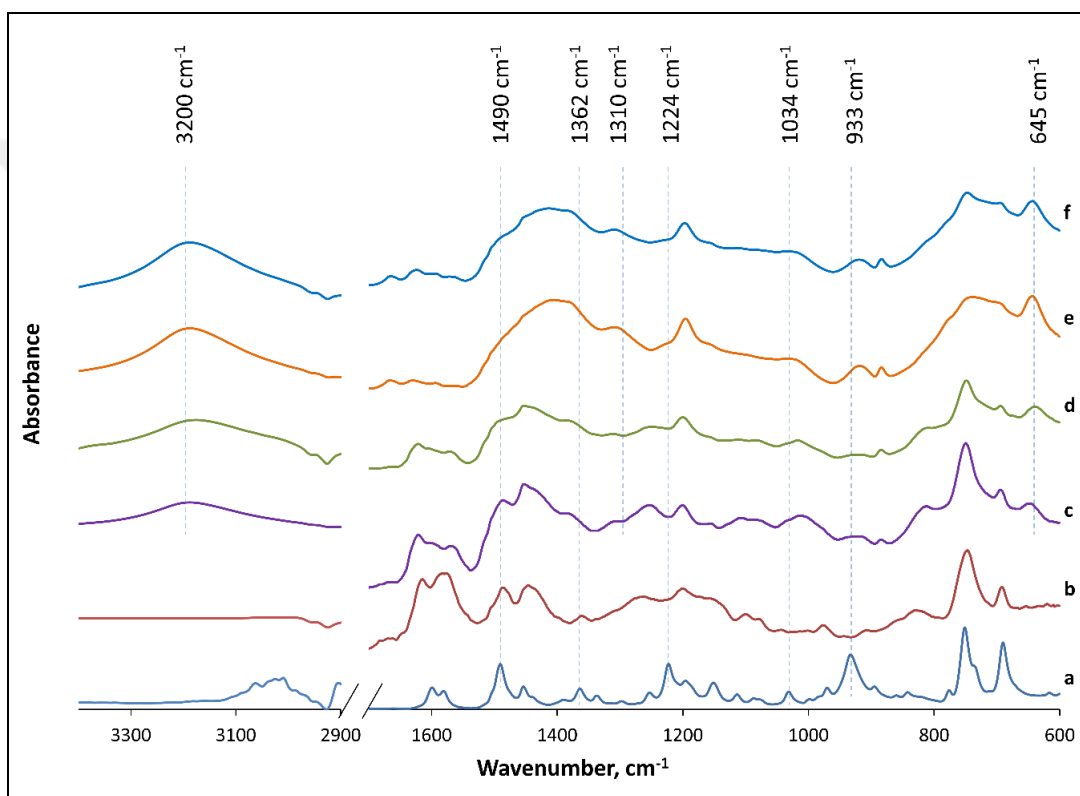


Figure 3.10. FTIR spectras of a)Pa monomer, b)PPa polymer and c)PPa/5BA, d)PPa/10BA, e)PPa/15BA and f)PPa/20BA composites

3.2.3. Thermal Analysis of PPa/BA Composites

The DSC curve of the monomer showed a sharp exothermic maximizing at around $228\text{ }^{\circ}\text{C}$, due to ring-opening polymerization of oxazine ring (Fig. 3.11). The disappearance of the exothermic peak in the DSC curve of polybenzoxazines and

polybenzoxazine composites involving 5, 10, 15 and 20wt% BA may be regarded as an evidence for the polymerization of the monomer by the applied curing program.

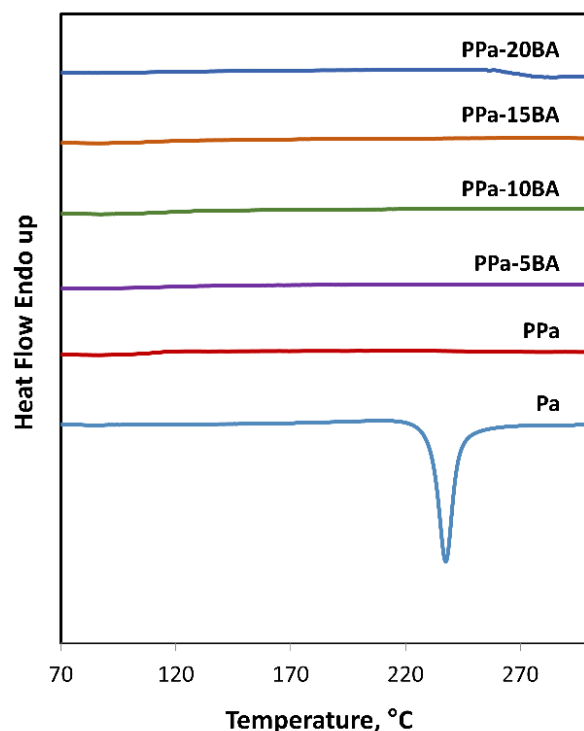


Figure 3.11. DSC curves of Pa monomer, PPa polymer, and PPa-BA composites

The TGA curves of polybenzoxazine and the composites involving 5, 10, 15 and 20 wt% BA are shown in Fig. 3.12 and the relevant data are listed in Table 3.2. TGA results revealed a multi-step thermal decomposition. The first step in the TGA curve was associated with the decomposition of aniline linkages. In our previous studies, the second step the weight loss in the temperature region 300 - 450 °C was related to degradation of polymer chains involving Mannich bridges, and the weight loss at around 500 °C was associated with decomposition of phenolic network generated upon loss of aniline units and unsaturated polymer backbone [23]. The addition of boric acid affected temperature regions of these steps. The most significant effect was observed for the last step related to the decomposition of phenolic and unsaturated chains. The increase in the char yield was considered as an evidence for the interaction of boric acid with hydroxyl groups present in the structure especially

phenolic derivatives. As the amount of boric acid added increased, low temperature peak in the TGA curve of the composite was shifted to high temperature regions. Thus, it is related to degradation and/or evaporation of low mass fragments such as boric acid and its low mass derivatives.

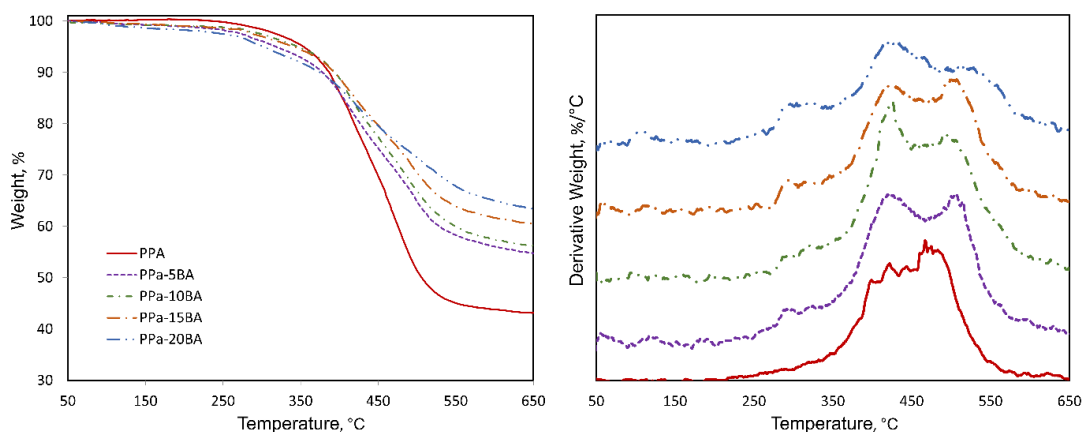


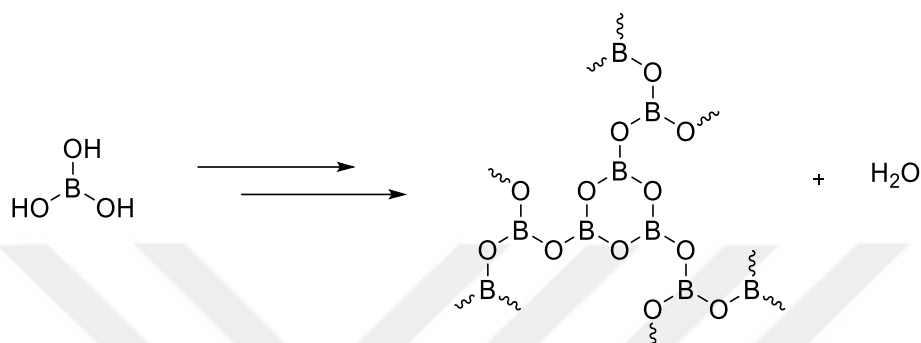
Figure 3.12. TGA curves and derivatives of PPA polymer and PPA/BA composites

The most significant improvement in the char yields was detected with PPA/5BA composite compared to other boric acid composites. It can be thought that the distribution of boric acid with low amounts is more efficient than a higher level inclusion of boric acids.

Table 3.2. TGA data for PPA polymer and PPA/BA composites involving 5, 10, 15 and 20 wt% BA

Sample	T _{5%} (°C)	T _{max} (°C)			Char yield % at 650 °C
		Step 1	Step 2	Step 3	
PPa	354	-	411	465	43
PPa/5BA	318	277	412	485	55
PPa/10BA	346	275	406	478	57
PPa/15BA	340	271	405	487	60
PPa/20BA	302	294	408	512	63

Thermal stability and % char yield of the polybenzoxazine/boric acid composites increased as the boric acid content was increased. This behavior may be related not only to the interaction of boric acid with the monomer but also to self-condensation reactions of boric acid forming boraxine with six-membered B_3O_3 ring structures as shown in Scheme 3.6.



Scheme 3.6. The boric acid condensation reaction

In order to get better understand the effect of BA on the thermal stability pyrolysis mass spectrometry analyses were also performed. Total ion current (the variation of total ion yield as a function of temperature) TIC, curves of polybenzoxazine and its composites are given in Fig. 3.13. The TIC curves of all the samples showed more than one peak indicating either a multi-step degradation mechanism and/or presence of chains with different thermal stabilities in accordance to TGA results. The relative yields of the products lost at initial stages of pyrolysis were decreased while those evolved at elevated temperatures were increased, as the amount of boric acid added was increased. The pyrolysis mass spectra were dominated with peaks at 91 (C_7H_7), 93 ($C_6H_5NH_2$ or $HO-C_6H_4$), 94 ($HO-C_6H_5$), 105 (C_8H_9), 107 ($HO-C_6H_4CH_3$), 121 ($HO-C_6H_4CH_2N$), 179 ($C_6H_5C_2H_2C_6H_4$ and/or $C_6H_4CHNC_6H_4$), 193 ($CH_2C_6H_4C_2H_2C_6H_4$ and/or $C_6H_4CH_2NC_6H_4CH$), due to characteristic fragments of monomer and dimer that can be generated during pyrolysis and/or dissociative ionization of the polymers during the DP-MS analyses.

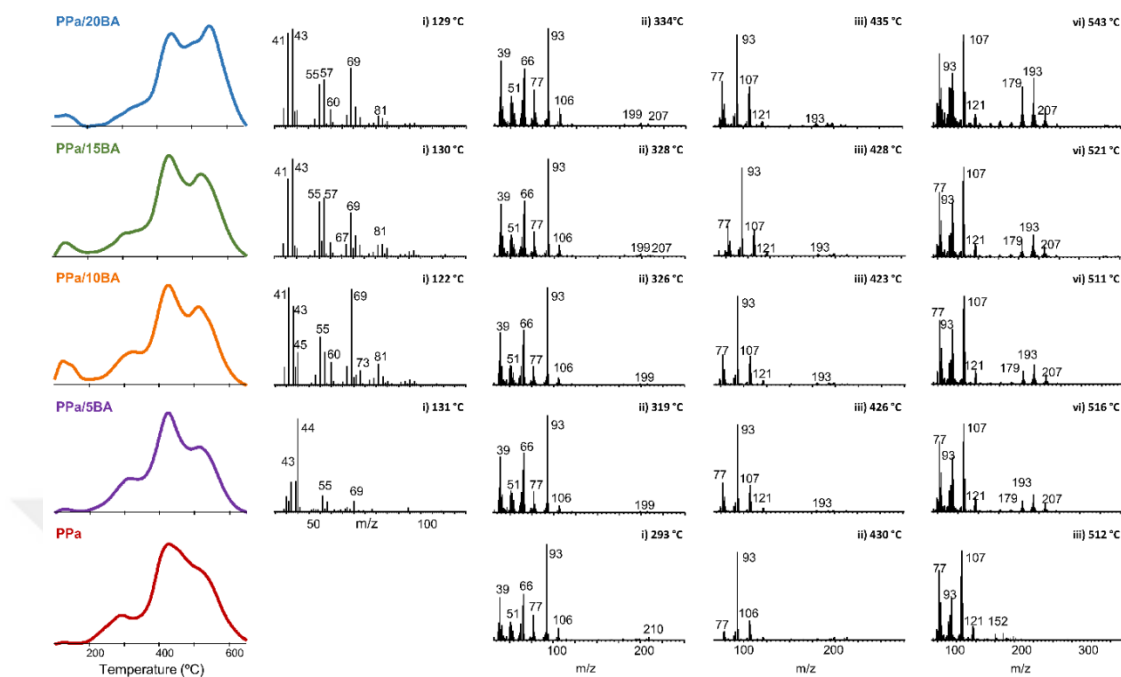


Figure 3.13. Total Ion Curves of PPa polymer and PPa/BA composites

In order to get a better insight, single ion evolution profiles of intense and/or characteristic products were analyzed and grouped considering the similarities in the trends observed. Single ion evolution profiles of $C_6H_5NH_2$ or HOC_6H_4 (93 Da), HOC_6H_5 (94 Da), monomer (211 Da), C_7H_7 (91 Da), $C_6H_5C_2H_2C_6H_5$ and/or $C_6H_4CHNC_6H_4$ (179 Da) and $C_6H_5C_2H_2C_6H_5CH_2$ and/or $C_6H_4CH_2NC_6H_4CH$ (193 Da) recorded during the pyrolysis of PPa and involving 5, 10, 15 and 20 wt% boric acid are shown in Figure 3.14. Besides, single-ion pyrograms of 179 Da and 193 Da fragments, may be $(OH)_2BOC_6H_4CH_2NHCH$ and $(OH)_2BOC_6H_4CH_2NHC_2H_3$, respectively are also included in the Figure 3.14. It may be thought that these fragments are generated by reactions between boric acid and hydroxyl groups present in the structure of polybenzoxazine (Scheme 3.7). Significant increases in their abundances with the increase in the amount of boric acid (mixed with the monomer just before curing) supported these proposals.

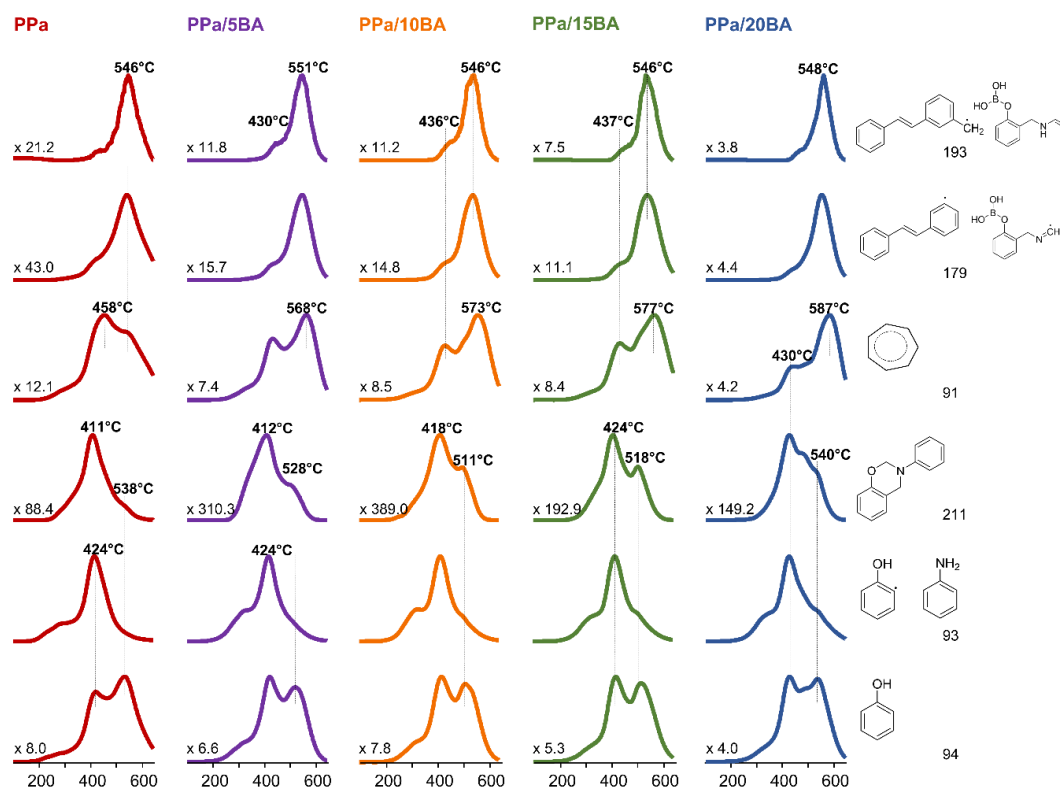
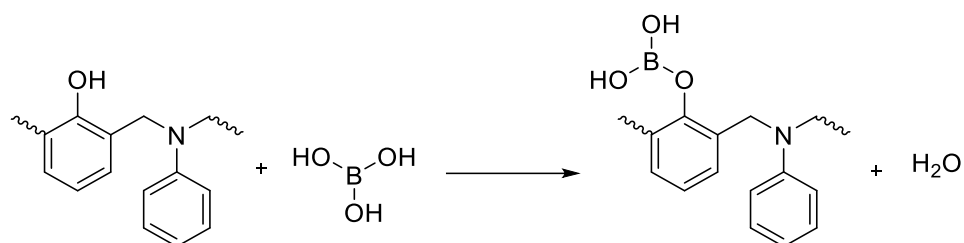


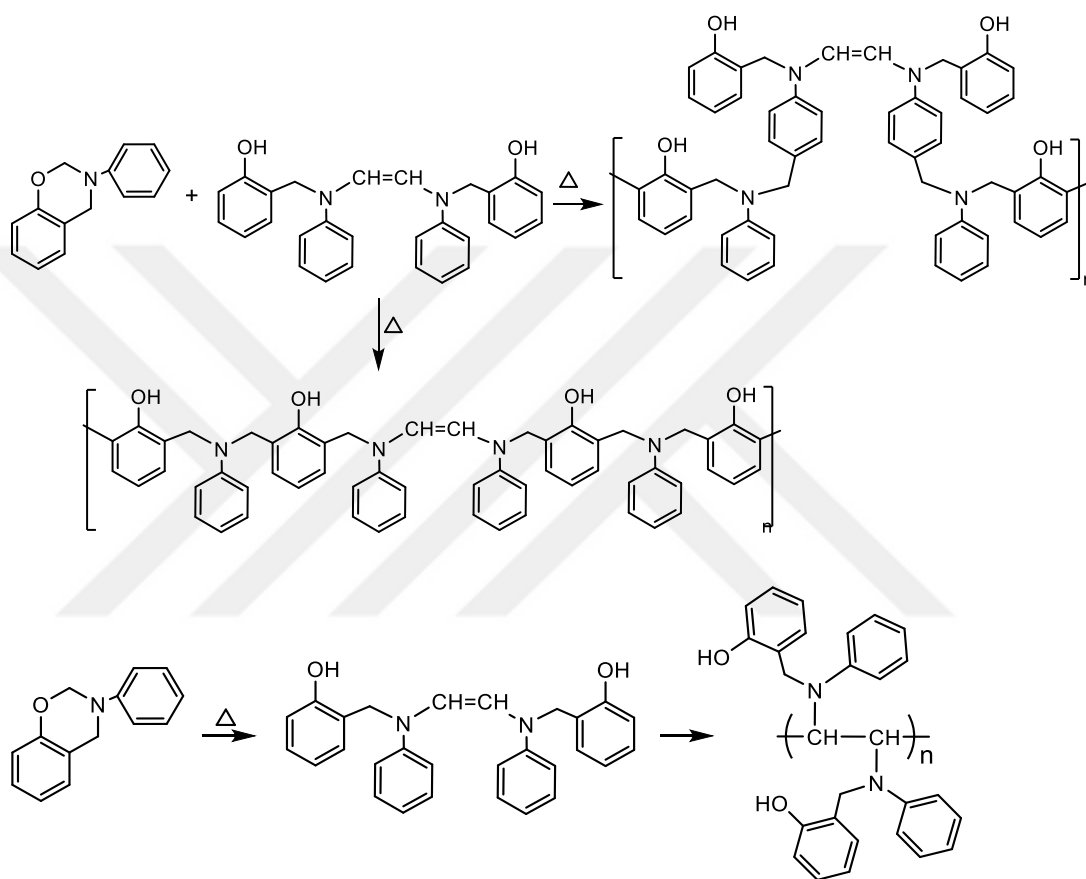
Figure 3.14. Single Ion Curves of PPa polymer and PPa/BA composites



Scheme 3.7. The reaction between benzoxazine fragment and boric acid

Moreover, upon addition of boric acid single ion evolution profiles of characteristic fragments of C_7H_7 (91 Da) showed noticeable differences. The peak at around 540 °C detected in the single ion curve of C_7H_7 generated during the pyrolysis of the neat polybenzoxazine shifted to higher temperature regions. In our previous studies, we proposed decomposition of the units generated by vinyl polymerization of the dimer formed upon loss of aniline units (shown in Scheme 3.8) of the dimer formed in the

final stages of pyrolysis, at elevated temperatures [23,58]. It may be thought that the interaction of boric acid and its fragments with the hydroxyl group of phenol promoted the generation of dimer by coupling of $-NCH_2$. Hence, boric acid loading results in thermally more stable unsaturated and cross-linked chains and higher char yield.



Scheme 3.8. Polymerization pathways by dimer by coupling of $-NCH_2$ groups

It may further be proposed that the significant improvement in thermal stability of polybenzoxazine is also due to the stabilization of the Mannich bridges by the very stable intramolecular hydrogen bonding between the phenolic OH and the nitrogen atom of the Mannich Bridge. Hence, the hydrogen bonding between not only OH groups of benzoxazine and boric acid (Fig 3.15) and also boric acid itself caused improvement in thermal stability.

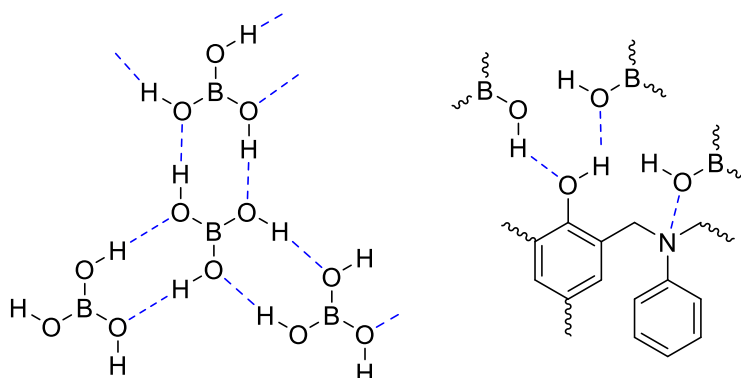


Figure 3.15. Possible hydrogen bondings

In summary, the effect of boric acid on thermal characteristics of polybenzoxazine based on phenol and aniline was investigated. In general, improvement in thermal stability was detected upon the addition of boric acid. Condensation reactions between B-OH groups and OH groups of phenol or/and monomer took place during the ring-opening polymerization. Boraxine was also generated by self-condensation reactions. As a consequence of these interactions and barrier effect of boroxine network, thermal stability and char yield were increased.

3.3. Polybenzoxazine/Clay (C10A) Composites

Organically modified clay Cloisite 10A (C10A) was mixed (1, 3, 5 and 7%) with benzoxazine monomer Pa, to obtain Polybenzoxazine/C10A composites improved thermal stability and char yield due to nanoscale dispersion of silicate layers. Organically modified clay enhances the dispersion and penetration of monomers and/or polymers into the silicate layers. XRD method was used to determine the mode of dispersion of clay. FTIR, DSC, TGA and DP-MS analyses were applied for the characterization of the polybenzoxazine composites.

3.3.1. Preparation and Characterization of PPa/Clay (C10A) Nanocomposites

Benzoxazine monomer and Cloisite 10A (C10A) were mixed in different weight ratios (1, 3, 5 and 7%). The films were cured step-wise at 175, 200 and 225 °C for 1

h each in the vented oven. The reddish-brown polybenzoxazine/C10A (PPa/1C10A, PPa/3C10A, PPa/5C10A, and PPa/7C10A) nanocomposites were obtained.

FTIR analyses were achieved for the characterization of the PPa/C10A nanocomposites. FTIR spectra of Pa monomer, PPa polymer, and PPa/7C10A nanocomposite are given in Fig 3.16. The characteristic peaks of oxazine ring observed at 1034 and 1224 cm^{-1} were disappeared. Moreover, the peaks associated with benzoxazine monomer were disappeared for PPa and PPa/C10A nanocomposites indicating that the polymerization was completed. The absorbance peak at 1097 cm^{-1} of PPa/7C10A represents the Si-O-Si groups of the clay.

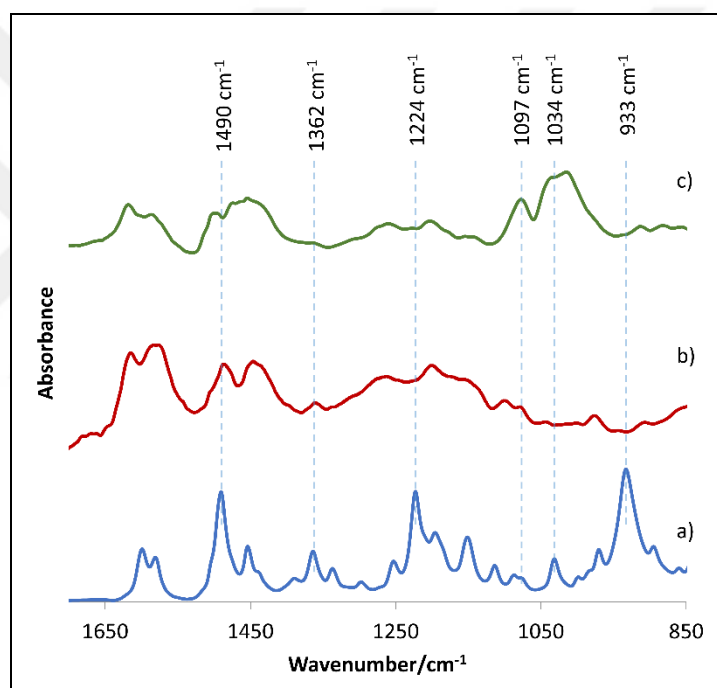


Figure 3.16. FTIR spectra of a) Pa monomer, b) PPa polymer and c) PPa/7C10A composite

The dispersion of the organically modified clay was characterized by XRD in order to determine the change in interlayer spacing of the silicate layers. When the benzoxazine monomer migrates and polymerizes into the layers of organoclay, the expansion of the interlayer spacing was observed. Thus, organoclay disperses into the polymer matrix as polymerization of benzoxazine monomers into layers of organoclay and intercalating and/or exfoliated structure was obtained. If the peak of

organoclay shifted to a lower 2θ angle value, the intercalated nanocomposite was obtained. Moreover, the absence of any diffraction peaks was correspond to exfoliated nanocomposite. The XRD patterns of C10A and PPa/C10A nanocomposites are shown in Fig 3.17. The absence of diffractions in XRD patterns of PPa/1C10A, PPa/3C10A and PPa/5C10A nanocomposites were proved that the silicate sheets were homogeneously dispersed into polybenzoxazine network and exfoliated nanocomposites were obtained. The inclusion of 7% of C10A polybenzoxazine nanocomposite showed an intercalating and exfoliated dispersion due to the shift of diffraction peak.

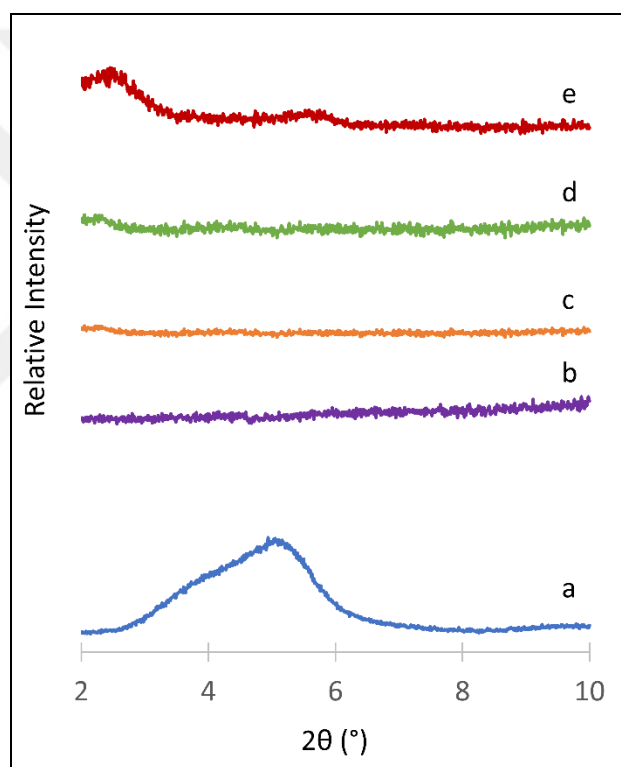


Figure 3.17. XRD patterns of a) C10A, b)PPa/1C10A, c)PPa/3C10A, d)PPa/5C10A and , d)PPa/7C10A

3.3.2. Thermal Analysis of PPa/C10A Nanocomposites

The exothermic ring opening polymerization peak in the DSC curve of Pa monomer peak maximizing at around 228 °C. The polymerization was completed; the exothermic peak was disappeared in the DSC curves of the polymer and its

composites involving 1, 3, 5 and 7 wt% C10A by the applied curing program (Figure 3.18).

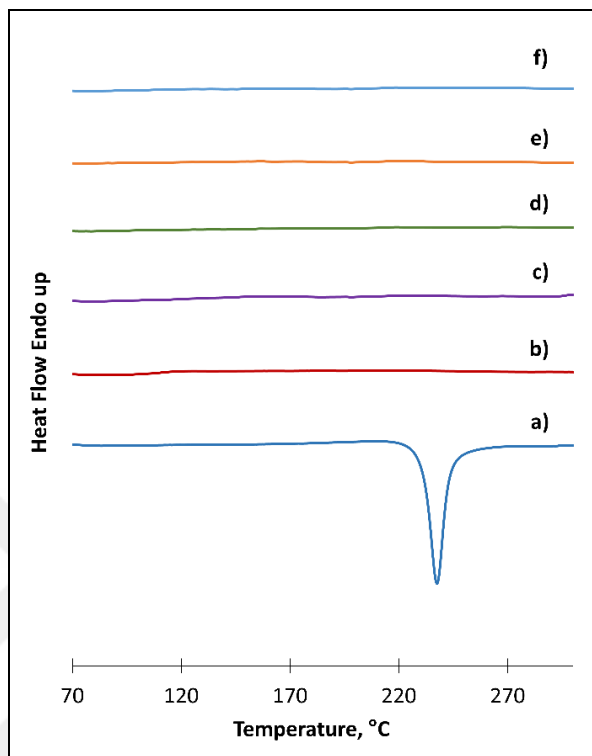


Figure 3.18. DSC curves of a) Pa monomer, b) PPa polymer and c) PPa/1C10A, d) PPa/3C10A, e) PPa/5C10A and f) PPa/7C10A composites

The TGA curve of PPa revealed a two-step thermal decomposition with $T_{5\%}$ and char yield values 354 °C and 43% respectively. PPa/C10A nanocomposites also displayed two-step degradation mechanism and improved thermal characteristics (Figure 3.19).

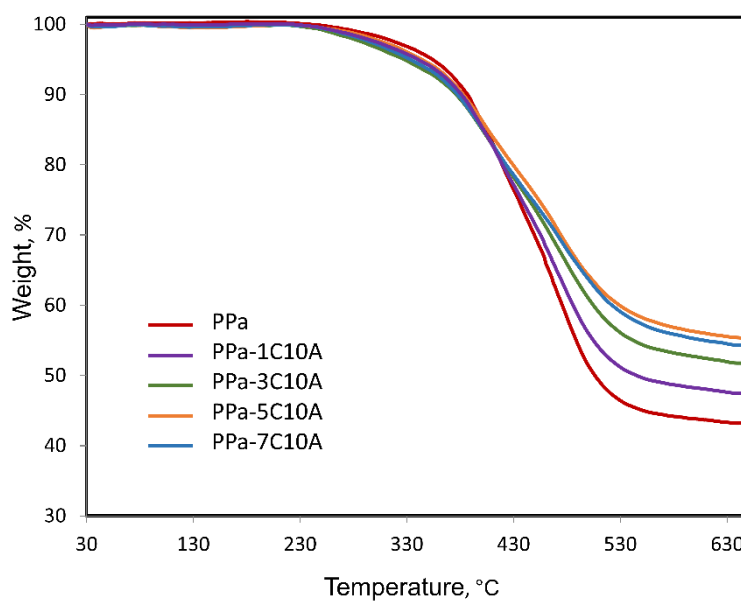


Figure 3.19. TGA curves of PPa polymer and PPa/C10A composites

Thermal stabilities and char yields of PPa and PPa/C10A nanocomposites were investigated by TGA analyses. It was concluded that PPa/C10A nanocomposites showed enhanced thermal properties. The char yields of the composites involving 1, 3, 5 and 7 % C10A were 47, 52, 55 and 54 % respectively at 650°C (Table 3.3).

Table 3.3. TGA data for PPa polymer and PPa/C10A composites involving 1, 3, 5 and 7wt% C10A

Sample	T _{5%} (°C)	T _{max} (°C)		Charyield % at 650 °C
		Step 1	Step 2	
PPa	354	411	465	43
PPa/1C10A	340	408	467	47
PPa/3C10A	326	397	470	52
PPa/5C10A	343	405	473	55
PPa/7C10A	332	409	475	54

The total ion current, TIC, curves and the pyrolysis mass spectra at the maximum of the peaks present in the TIC curves of the PPa polybenzoxazine and PPa/C10A composites are given in Figure 3.20. The TIC curves of PPa and PPa/C10A composites exhibited more than one peak indicating either a multi-step degradation mechanism and/or presence of chains with different thermal stabilities.

The TIC curves of all samples showed two intense peaks with maxima at around 420 and 470 °C. The base peak at 93 Da was readily associated with $C_6H_5NH_2$ and other intense peaks obtained at 107, 77 and 63 Da were attributed to $H_2NC_6H_4O$ and/or $HOC_6H_4CH_2$, C_6H_5 , and C_5H_3 , respectively. Generation of these peaks displays that thermal decomposition of PPa started by the loss of aniline. It can be concluded that the PPa/C10A composites showed similar behavior. Moreover, peaks at elevated temperatures point out the elimination of phenol and unsaturated hydrocarbons for all samples.

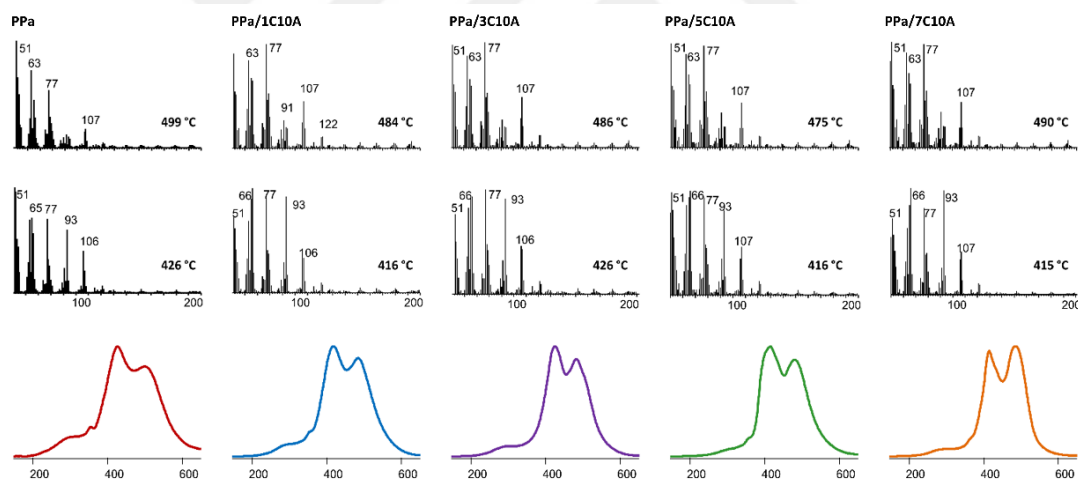


Figure 3.20. Total ion current curves and mass spectra of PPa, PPa/1C10A, PPa/3C10A, PPa/5C10A, and PPa/7C10A

To get more information for thermal degradation single ion evolution profiles of typical fragments were obtained. These fragments are $C_6H_5NH_2$ (93 Da), C_6H_5OH (94 Da), C_7H_7 (91 Da), $H_2NC_6H_4O$ and/or $HOC_6H_4CH_2$ (107 Da) and $C_6H_5CH=CHC_6H_4CH_2$ (193 Da) are shown in Fig 3.21. In general, abundances of all fragments are increased with the inclusion of C10A. The relative intensity of 91,

94 and 107 Da peaks which were related to phenolic fragments were increased at elevated temperature. It may be thought that loss of evolution of products were suppressed. This behaviour may be related to the barrier effect of clay. The monomer diffused into clay sheets during the mixing process was polymerized and chains grown in the clay sheets. Hence, the silicate layer of C10A inhibited the elimination of small molecules formed by the thermal degradation.

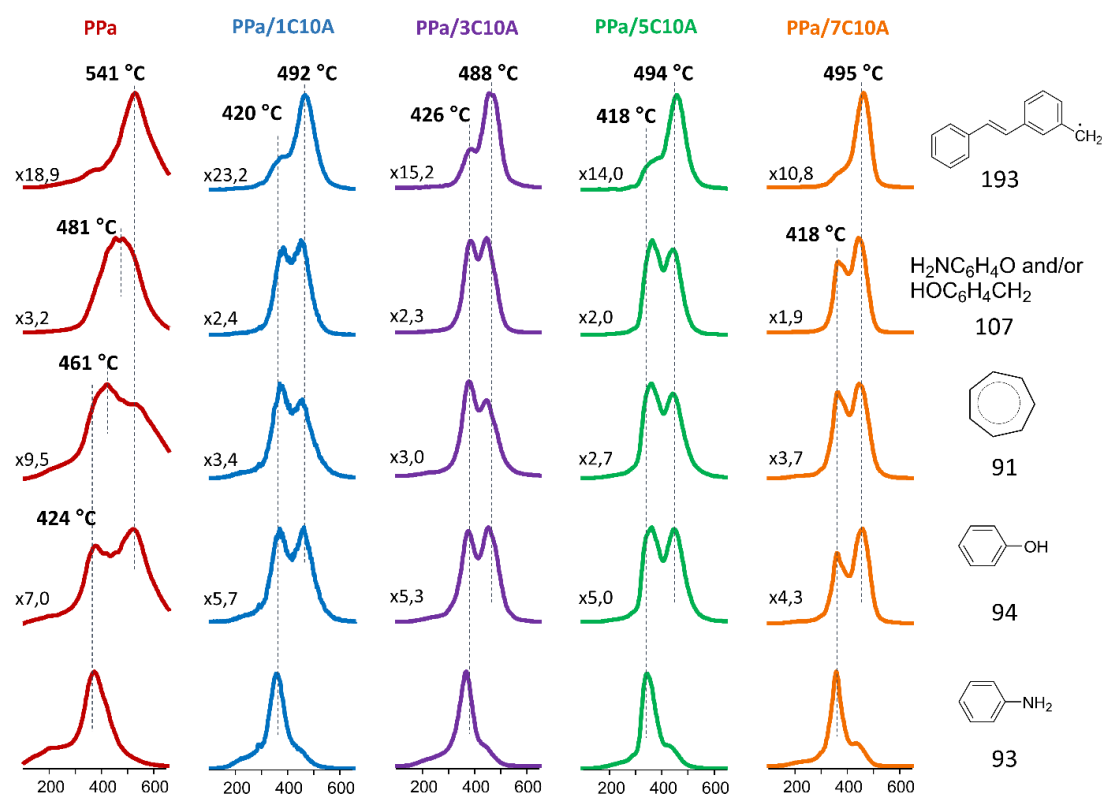


Figure 3.21. Single ion evolution profiles of PPa polymer and PPa/C10A composites

In conclusion, exfoliated and/or intercalated dispersion modes of polybenzoxazine nanocomposites were prepared with higher thermal stability and higher char yield by inclusion of Cloisite 10A as a result of barrier effect of organically modified clay (C10A).

3.4. Polybenzoxazine/Zirconium diboride (ZrB₂) Composites

Zirconium diboride (ZrB₂) was mixed (5, 10, 15 and 20%) a with benzoxazine monomer Pa, to obtain polybenzoxazines to improve thermal stability and char yield. FTIR, DSC, TGA and DP-MS analyses were applied for the characterization of the polybenzoxazine composites.

3.4.1. Preparation and Characterization of Polybenzoxazine/ZrB₂ Composites

Blends of benzoxazine monomer (Pa) and 5, 10, 15 and 20 wt% zirconium diboride (ZrB₂) were prepared and polymerized with step-wise curing temperature program at 175, 200 and 225 °C for 1 h each in a vented oven. Black color polybenzoxazine/ZrB₂ composites (PPa/5ZrB₂, PPa/10ZrB₂, PPa/15ZrB₂, and PPa/20ZrB₂) were obtained.

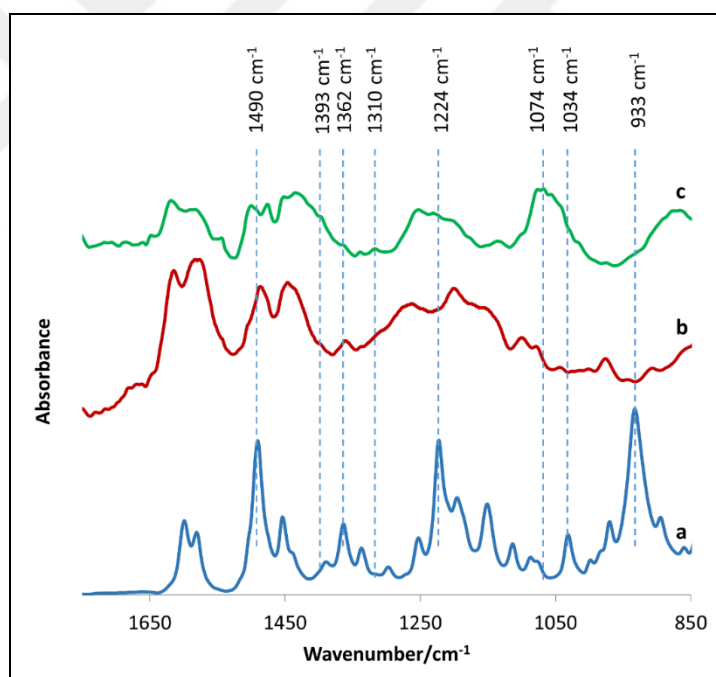


Figure 3.22. FTIR spectra of a) Pa monomer, b) PPa polymer and c) PPa/20ZrB₂ composite

FTIR analyses of monomer, polybenzoxazine, and composites were performed for characterization. FTIR spectra of Pa monomer, PPa polymer, and PPa/20ZrB₂ polymer composite are shown in Figure 3.22. The disappearance of the characteristic

peaks of oxazine ring obtained at 933, 1034 and 1224 cm^{-1} in FTIR spectra of PPa and PPab/ ZrB_2 composite supported the ring opening polymerization. The appearance of peaks at 1074 and 1310 cm^{-1} supported the presence of Zr-B structure [62]. Moreover, the peak in the FTIR spectrum of PPa/ ZrB_2 composite at around 1393 cm^{-1} was observed due to B-O stretching vibrations in the B-O-C structure of the composite network obtained by an interaction between ZrB_2 and hydroxyl groups of Pa during curing.

3.4.2. Thermal Analysis of PPa/ ZrB_2 Composites

The, exothermic peak maximizing at 228 $^{\circ}\text{C}$ was disappeared in the DSC curves of the polymer and its composites involving 5, 10, 15 and 20 wt% ZrB_2 by the applied curing program indicated that the polymerization was completed (Figure 3.23).

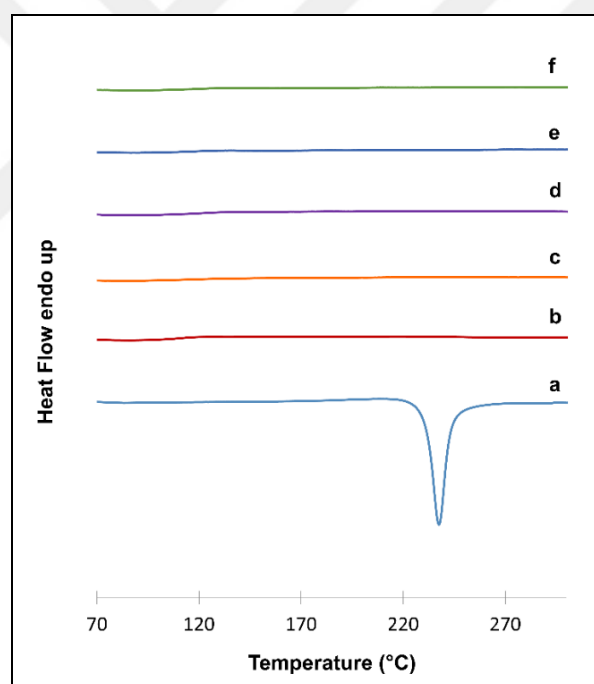


Figure 3.23. DSC curves of a) Pa monomer, b) PPa polymer and c) PPa/5 ZrB_2 d) PPa/10 ZrB_2 , e) PPa/15 ZrB_2 and f) PPa/20 ZrB_2 composites

TGA showed that thermal stability and char yield remarkably improved due to the addition of ZrB_2 particles (Fig 3.24). The ZrB_2 particles combined with zirconium

and boron particles by ionic bonding and boron atoms connected by covalent bonding. Moreover, ZrB_2 particle has an extremely high melting point at 3050 °C.

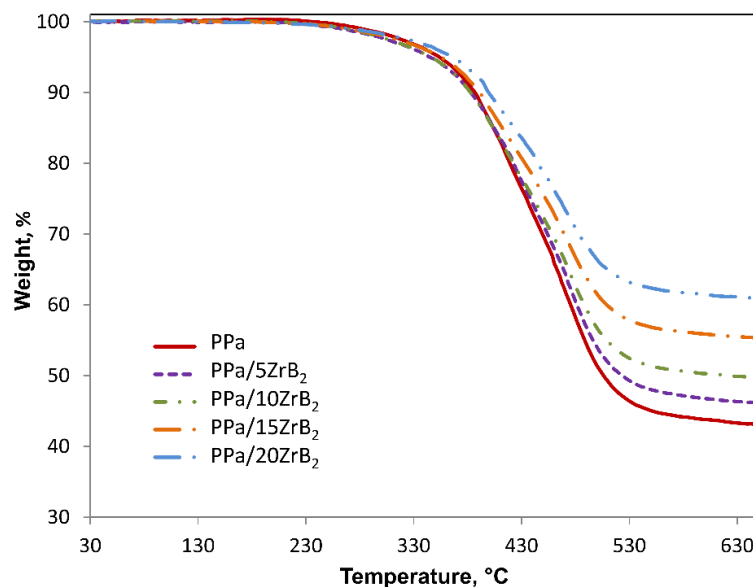


Figure 3.24. TGA curves of PPa polymer and PPa/ ZrB_2 composites

Char yields of composites involving 5, 10, 15 and 20 % ZrB_2 were 46, 50, 55 and 61%, respectively. Moreover, $T_{5\%}$ of composites drastically increased by the addition of ZrB_2 particles. It may be concluded that ZrB_2 particles delayed the evaporation of small molecules by serving as crosslinking spots.

Table 3.4. TGA data for PPa polymer and PPa/ZrB₂ composites involving 5, 10, 15 and 20wt% ZrB₂

Sample	T _{5%} (°C)	T _{max} (°C)		Char yield % at 650 °C
		Step 1	Step 2	
PPa	354	411	465	43
PPa/5ZrB₂	344	420	481	46
PPa/10ZrB₂	345	423	485	50
PPa/15ZrB₂	355	424	483	55
PPa/20ZrB₂	366	425	487	61

According to the total ion current curves, the base peak was at 93 Da conforming to the evolution of H₂NC₆H₅ for PPa. In the presence of ZrB₂, 107 Da was the base peak corresponding to the HOC₆H₄CH₂ and/or H₂NC₆H₄O fragments. Observation of these peaks may be associated with thermal degradation starting with the loss aniline for PPa and PPa/ZrB₂ composites. Yet, the peaks related to aniline were shifted to elevated temperatures indicating an increase in thermal stability. In addition, the evolution of phenol involving fragments and loss of unsaturated hydrocarbons were observed at higher temperatures by the inclusion of ZrB₂. The char yield was also enhanced.

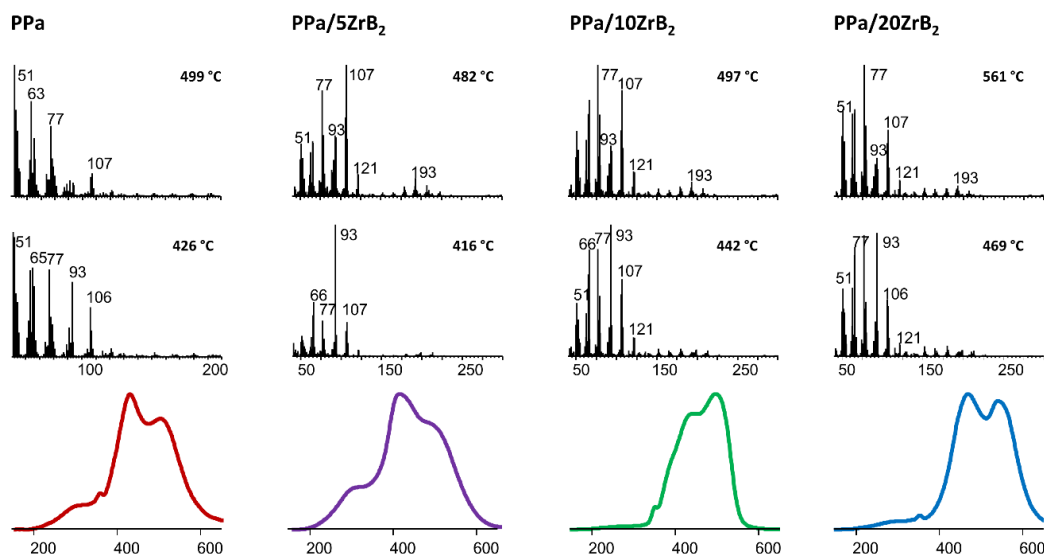


Figure 3.25. Total ion current curves of PPA polymer and PPA/ZrB₂ composites

Single ion evolution profiles of characteristics thermal degradation products of PPA and composites involving various amount of ZrB₂ are given in Fig 3.27. These products are C₆H₅NH₂ (93 Da), C₆H₅OH (94 Da), C₇H₇ (91 Da), H₂NC₆H₄O and/or HOC₆H₄CH₂ (107), C₆H₅CH=CHC₆H₄CH₂ (193 Da) and HOC₆H₅CH₂NC₆H₅ (198 Da). Moreover, an intense peak due to ZrB₂ (112 Da) is observed for PPA/ZrB₂ composites. Upon addition of ZrB₂, the thermal stability and char yield were improved drastically. In Fig 3.26, evolution profiles of NH₂C₆H₅ (93 Da) and HOC₆H₄CH₂NC₆H₅ (198 Da) related to aniline were shifted to high temperature regions noticeably. It may be thought that ZrB₂ particles inhibit the evolution and/or elimination of fragments from units involving the aromatic amine group. Moreover, loss of fragments associated with phenolic groups showed higher relative intensities and higher decomposition temperature. This behavior may be attributed to the linking effect of ZrB₂ particles.

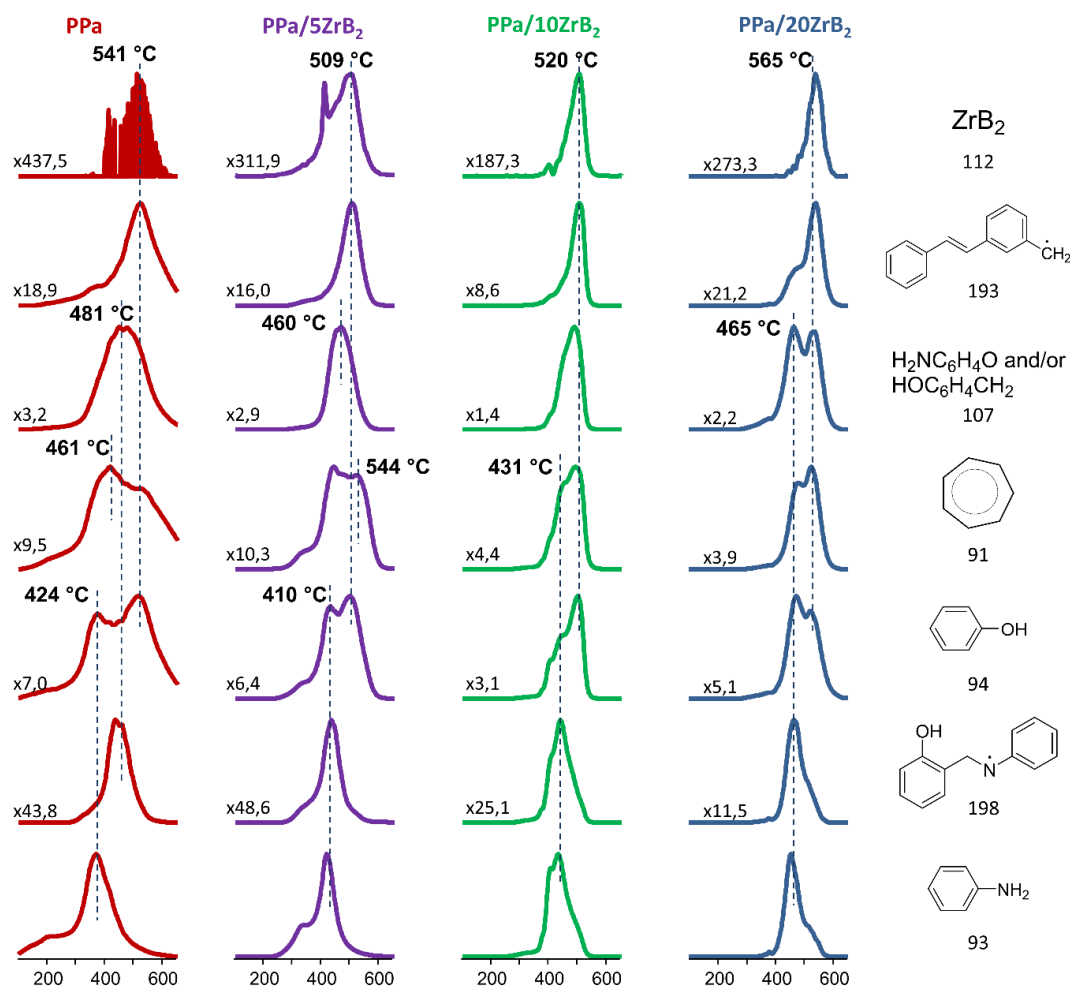


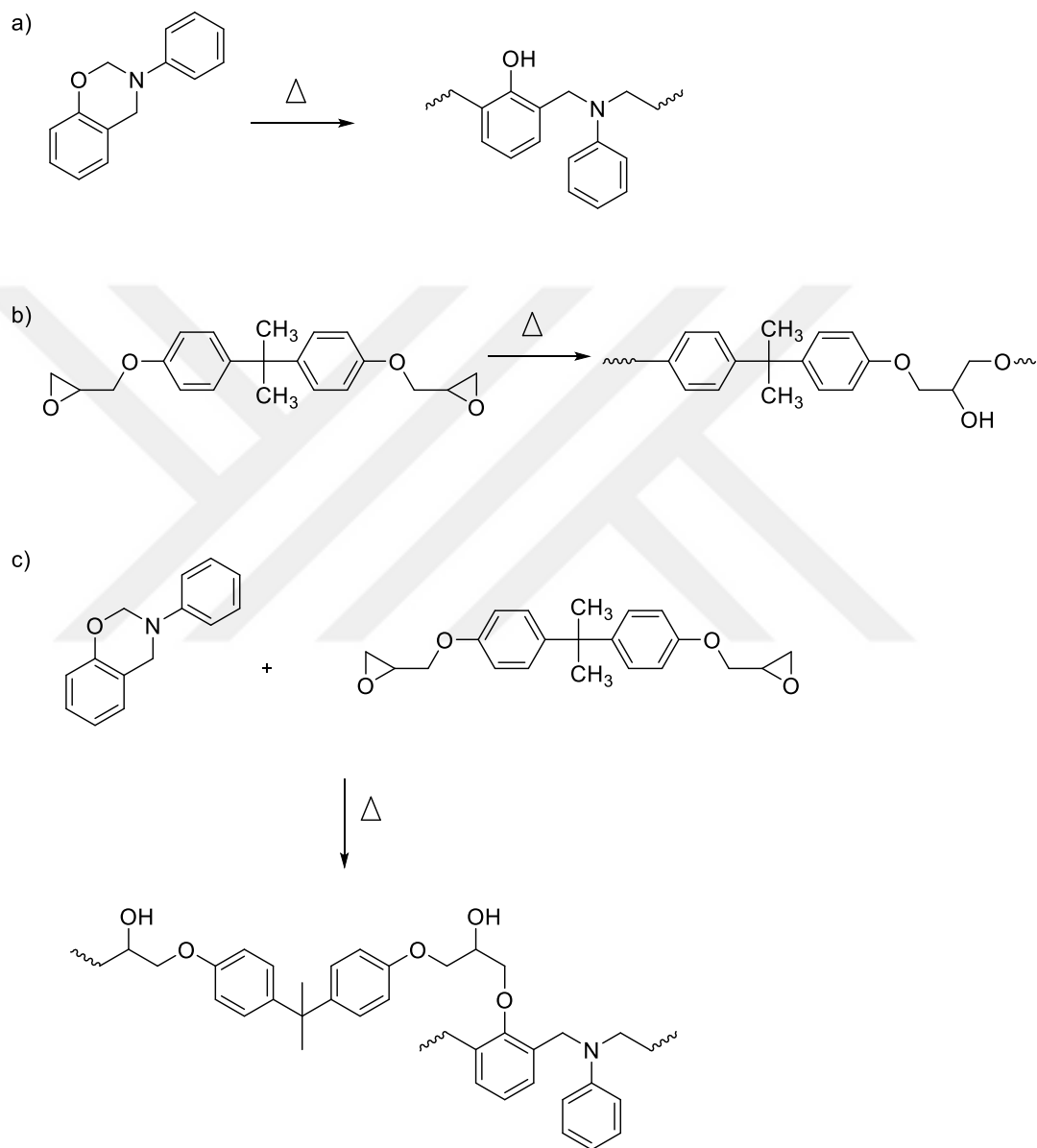
Figure 3.26. Single ion curves of PPa polymer and PPa/ZrB₂ composites

In summary, thermal stability and char yield were increased by addition of ZrB₂ particles. This behavior is explained by the linking effect and extremely high melting temperature of ZrB₂ particles.

3.5. Polybenzoxazine/Diglycidyl ether Bisphenol A epoxy (EP) Composites

Epoxy resin is a well-known material for industrial composite applications because of its high mechanical properties. Thus, diglycidyl ether bisphenol A based epoxy resin (EP) was mixed with benzoxazine monomer (Pa) with different weight ratios (10, 20 and 30 wt% of EP) and cured to obtain PePa/EP composites to produce composites with improved mechanical and thermal properties as a consequence of

the additional linkages that may be formed by the reaction between the epoxide and the phenolic hydroxyl groups. Structural, mechanical and thermal analysis of monomer (Pa), polymer (PePa) and composites (PePa/EP) were investigated by FTIR, DSC, DMA, TGA and DP-MS techniques.



Scheme 3.9. Possible reactions in the presence of polybenzoxazine composite preparation involving epoxy resin

3.5.1. Preparation and Characterization of PePa and PePa/EP Composites

Benzoxazine monomer (Pa) and epoxy resin (EP) were blended (10, 20 and 30 wt%) at room temperature. The mixtures were polymerized by stepwise curing program at 100, 150, 175 and 200 for 1 hour each in the vented oven. The transparent reddish brown polymer (PePa) and polybenzoxazine/EP (PePa/10EP, PePa/20EP, and PePa/30EP) composites were obtained.

FTIR analyses were performed for the characterization of PePa/EP composites. In Fig 3.27, FTIR spectra of Pa monomer, EP resin, PePa polymer, and PePa/30EP composite are presented. Characteristic peaks of Pa monomer related with oxazine ring at 933, 1034 and 1224 cm^{-1} disappeared in the FTIR spectra of PePa polymer and PePa/30EP composite. It can be concluded that the ring opening polymerization was completed. Moreover, the epoxide ring absorbance peaks at 858 and 908 cm^{-1} displayed at FTIR spectra of EP also disappeared for PePa/30EP composite. Hence, the reaction between the epoxide ring and benzoxazine monomer was supported by the consumption of epoxide ring absorbance peaks.

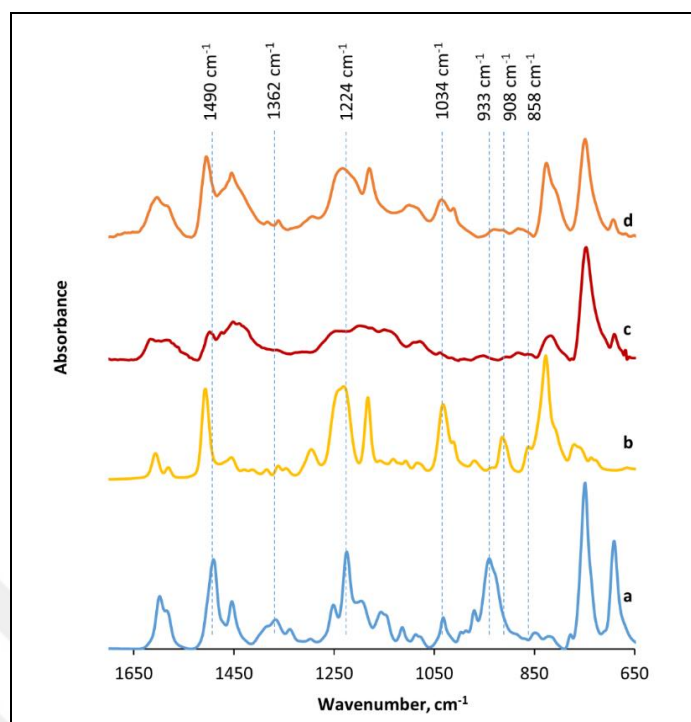


Figure 3.27. FTIR spectra of a) Pa monomer, b) Epoxy resin, c) PePa polymer and c) PePa/30EP composite

3.5.2. Thermal Analysis of PePa/EP Composites

DSC analyses of PePa/EP composites were performed and the curves are given in Fig 3.28. The exothermic peak of the monomer at around 228 °C disappeared in the DSC curves of polymer and composites pointing out that the polymerization of all samples was completed with the selected curing program.

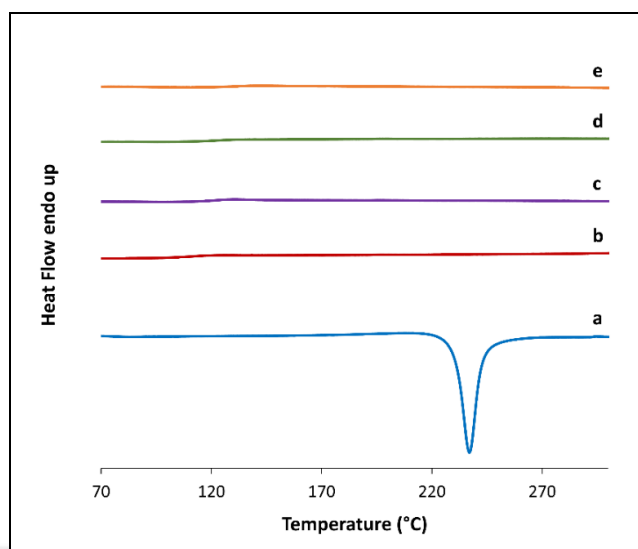


Figure 3.28. DSC curves of a) Pa monomer, b)PePa polymer, c) PePa/10EP, d) PePa/20EP and e)PePa/30EP

TGA traces of samples shown in Fig 3.29 and the decomposition temperatures and char yields were tabulated in Table 3.5. The decomposition temperature at 5% weight loss of the PePa/EP composites increased as the amount of epoxy was increased. PePa/30EP had higher $T_{5\%}$ (335 °C) compared to that of the neat polybenzoxazine (319°C). This behavior may be related to increased crosslinking density due to additional crosslinking reaction between the hydroxyl group of epoxy and oxazine ring.

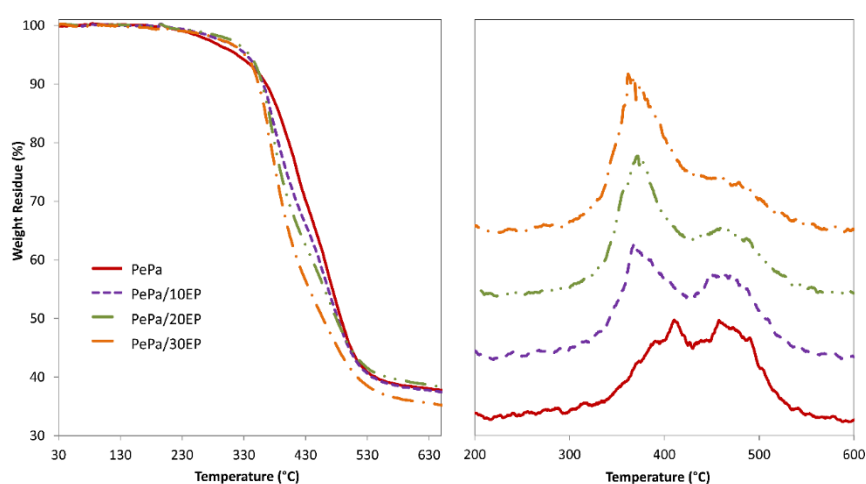


Figure 3.29. TGA curves and derivative curves of PePa and PePa/EP composites

The two degradation peaks were detected in the TGA derivative thermograms of neat polybenzoxazine and low ratio of epoxy loading composite (PePa/10EP). The degradation steps merged into a single peak for PePa/20EP and PePa/30EP, as the amount of epoxy polymer was increased. The char yields of the composites are almost the same; PePa/10EP and PePa/20EP composites had char yields as 37.5% and 38.4 %, respectively. However, the composite with highest epoxy content, PePa/30EP, has slightly lower char yield as 35.2% compared to pure polybenzoxazine, which has a char yield of 37.8 %. This behavior may be attributed to higher aromatic content of polybenzoxazine compared to that of epoxy polymer.

Table 3.5. TGA data of PePa and PePa/EP composites involving 10, 20 and 30% EP

Sample	T _{5%} (°C)	T _{max} (°C)		Char yield % at 650 °C
		Step 1	Step 2	
PePa	319	412	474	37.8
PePa/10EP	334	379	468	37.5
PePa/20EP	339	372	-	38.4
PePa/30EP	335	375	-	35.2

The rheological analysis was performed to investigate viscoelastic properties of polybenzoxazine and polybenzoxazine/epoxy composites and to evaluate glass transition temperatures. The storage modulus (G') and loss modulus (G'') of the samples were obtained as a function of temperature and the related plots are shown in Fig 3.30 and Fig 3.31, respectively. The storage modulus of the composites at the glassy state were decreased with increasing content as a result of softer molecular structure of epoxy resin. This may be related to the presence of ether linkages in the epoxy resin. It may be thought that these ether bonds increased the possibility of internal movement of molecules and decreased the stiffness of the structure. As can

be observed in Table 3.6, the storage modulus was 1.50 GPa for the neat polymer and 1.17 GPa for PePa/30EP the composite.

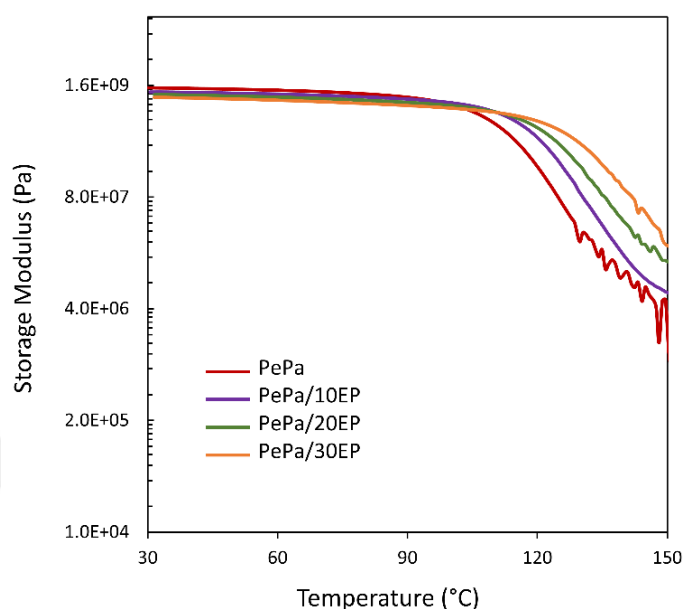


Figure 3.30. The storage modulus of PePa polymer and PePa/EP composites

The glass transition temperatures of the samples were determined by the maximum loss modulus and $\tan\delta$ values by rheology analysis as can be understood from the graphics given in Fig 3.31 and Fig 3.32, respectively. T_g temperatures increased significantly by introduction of the epoxy resin; the T_g of PePa/30EP composite was 133 °C and 149 °C determined by G'' and $\tan\delta$ measurements, respectively. Both measurements showed approximately 20 °C increase in these values compared to pristine polybenzoxazine.

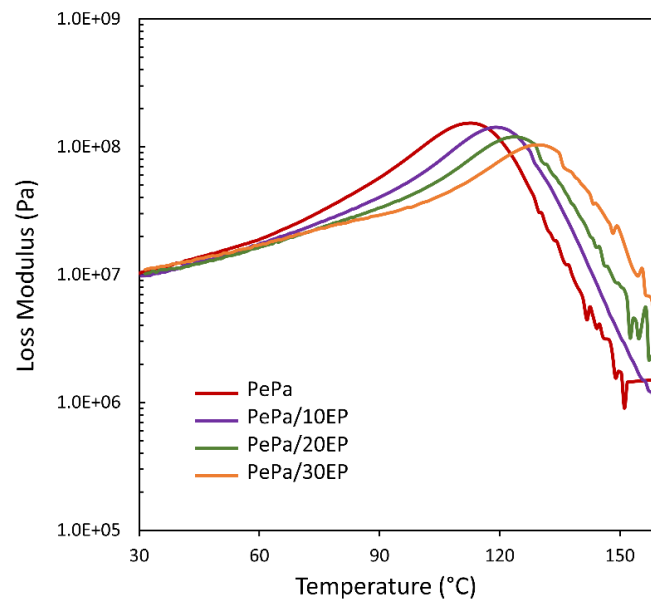


Figure 3.31. Loss Modulus of PePa and PePa/EP composites

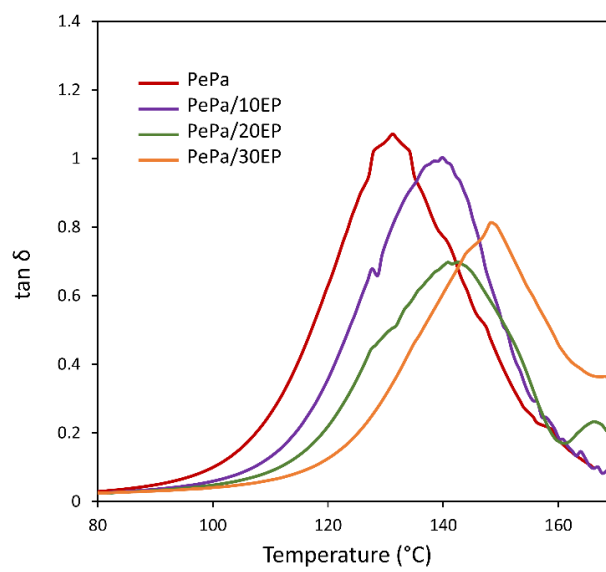


Figure 3.32. $\tan \delta$ values of PePa and PePa/EP composites

Table 3.6. Viscoelastic properties of PePa polymer and PePa/EP composites

Sample	G'_{rt} (GPa)	T_g (°C)	
		G''	$\tan\delta$
PePa	1.50	114	132
PePa/10EP	1.34	120	139
PePa/20EP	1.25	125	143
PePa/30EP	1.17	133	149

G'_{rt} : storage modulus at room temperature, G'' : loss modulus, T_g : glass transition temperature

In order to investigate the reason for the improvement of the glass transition temperature, FTIR analysis was applied to PePa and PePa/30EP composite. The curves of samples demonstrate the range from 2500 cm^{-1} to 4000 cm^{-1} that is the hydrogen-bonding region (Fig 3.33). The absorption peaks at almost 3200 cm^{-1} and 3400 cm^{-1} represented intramolecular and intermolecular hydrogen bonding, respectively. Intermolecular hydrogen bonding absorption peak of composite increased as compared to neat polymer. This can be confirmed that the hydroxyl group of epoxy resin caused the higher possibility of intermolecular hydrogen bonding. Therefore, the composites had higher T_g compared to the pristine polymer.

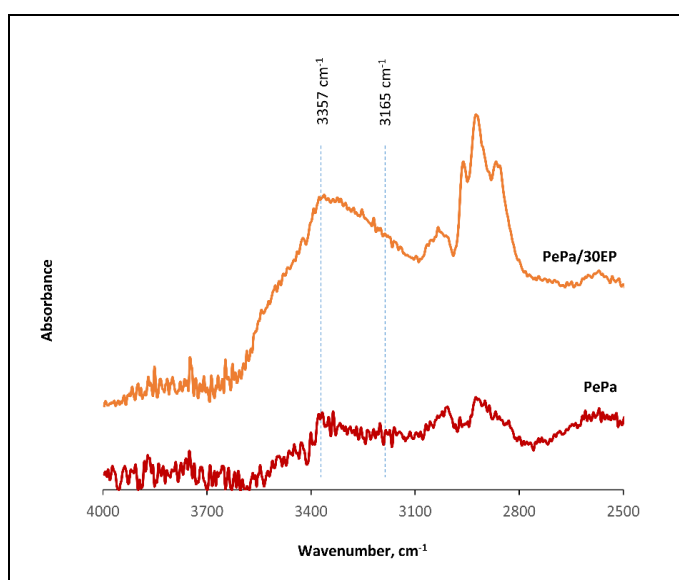


Figure 3.33. FTIR spectra of PePa and PePa/30EP

The total ion current curves (TIC) and the pyrolysis mass spectra at the maximum peaks of TIC curves of the PePa polymer and PePa/EP composites are depicted in Fig 3.34. The PePa polymer and PePa/10EP composite showed two overlapping peaks representing the more than one degradation mechanism and/or chains with various thermal stabilities. However, PePa polymer showed intense overlapping peaks with maxima at around 421 and 478 °C. The high temperature peak disappeared in the TIC curves of composites upon the addition of epoxy resin. As in case of composites involving higher amount of epoxy such as PePa/20EP and PePa/30EP showed a single decomposition peak. This may be related to the generation of thermally more homogenous polymer decomposing in narrower temperature range at around 410 °C.

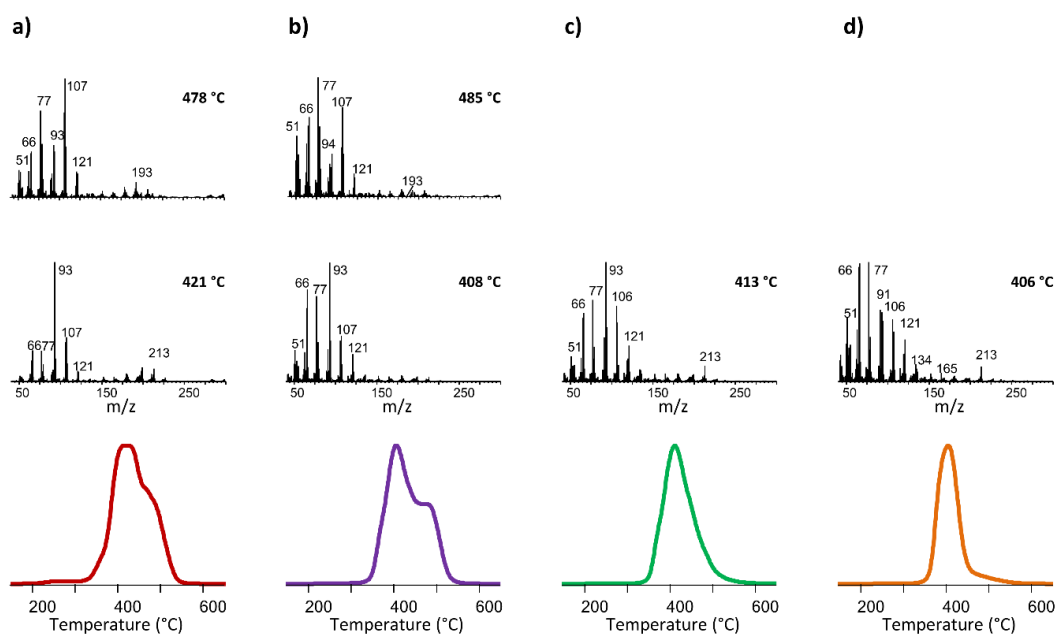
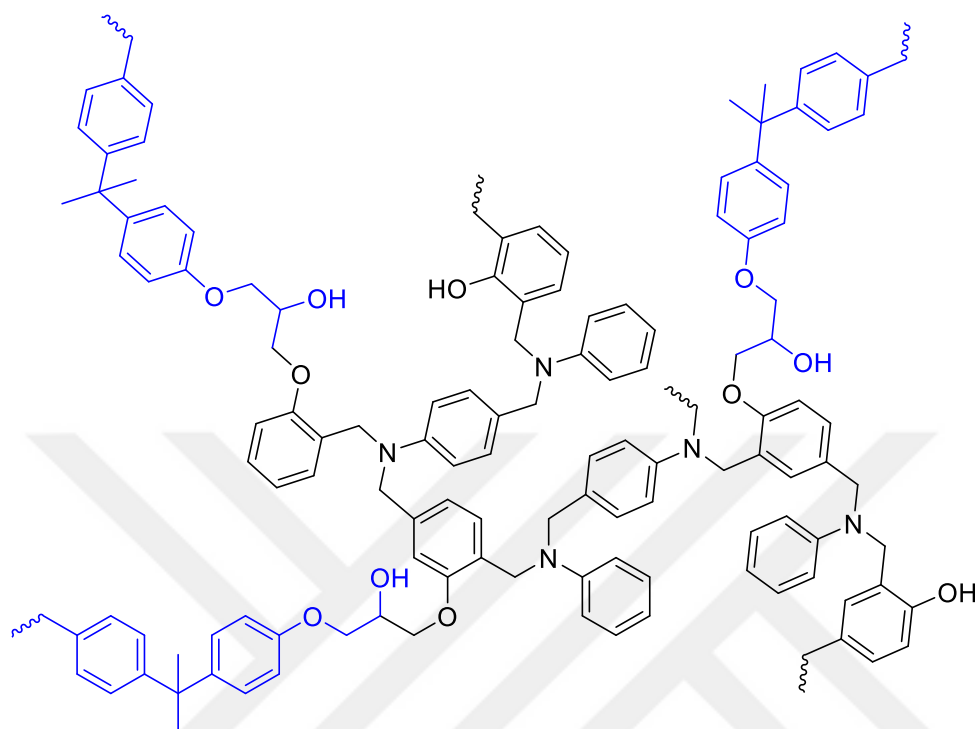


Figure 3.34. Total ion current curves of a) PePa polymer, b)PePa/10EP, c)PePa/20EP and d)PePa/30EP composites

It may be thought that addition of a higher amount of epoxy increased the possibility of the reaction between epoxide ring and hydroxyl group of benzoxazine monomer. The bulky group attached to the phenolic structure inhibited the formation of dimer by coupling of $-NCH_2$ group. Polymerization may take place mainly para position of

aniline and phenol. The possible cross-linked structure generated during curing process is shown in Scheme 3.10.



Scheme 3.10. Possible cross-linked structure

In order to obtain detailed information for the degradation processes of samples, single ion evolution profiles of intense and/or typical products were investigated. The single ion evolution profiles of some decomposition products established during the pyrolysis of polymer and composites are shown in Fig 3.35. The single ion profiles are classified according to the similarities in the trends. The selected fragments are C_7H_7 (91 Da), C_6H_5OH (94 Da), $C_6H_5NH_2$ (93 Da), $C_6H_5NHC_2H_2NHC_6H_5$ and/or $C_6H_4NHCH_2C_6H_4NHCH_2$ (210 Da), $C_6H_4CH=CHC_6H_4CH_2$ and/or $HOCH_2COC_2H_4NC_6H_5CH_3$ (193 Da), $C_6H_4CHNHC_6H_4$ and/or $C_6H_4C_2H_2C_6H_4$ (179 Da) and $OCHCH_2OC_6H_4CH_2NHC_6H_5$ (242 Da). The relative yields of product loss related to 91 Da and 94 Da increased upon addition of epoxy. This interaction was also supported by the increase in the relative yields of $HOCH_2COC_2H_4NC_6H_5CH_3$ (193 Da), and $OCHCH_2OC_6H_4CH_2NHC_6H_5$ (242 Da) fragments by the inclusion of epoxy resin.

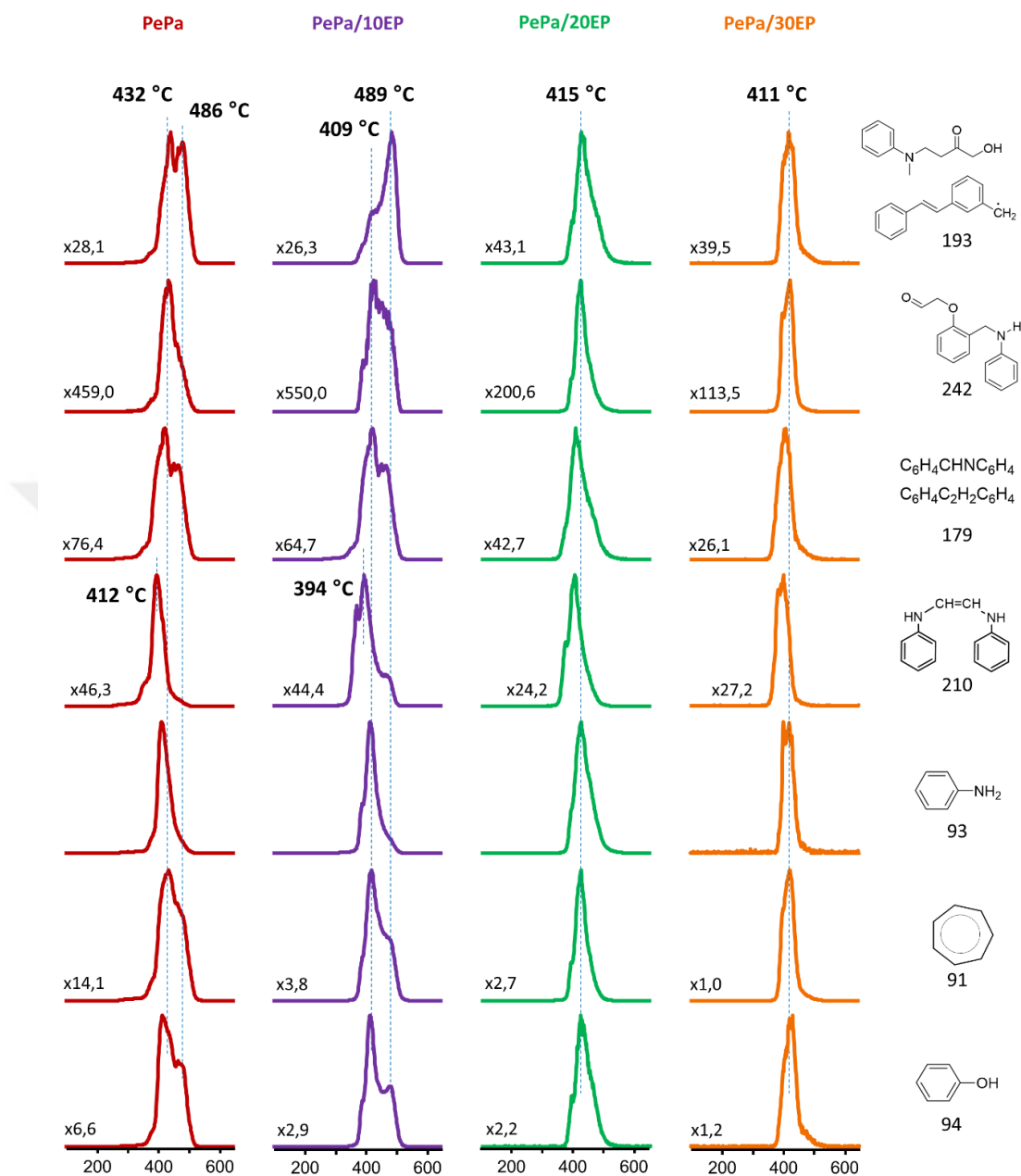


Figure 3.35. Single Ion Curves of PePa polymer and PePa/EP composites

In conclusion, addition of epoxy resin to polybenzoxazine was resulted to higher glass transition temperature. Although the interaction of epoxide ring of epoxy and hydroxyl group of polybenzoxazine resulted to higher crosslinking density, the char yield of composites almost same due to the lower benzene content of epoxy resin compared to polybenzoxazine.

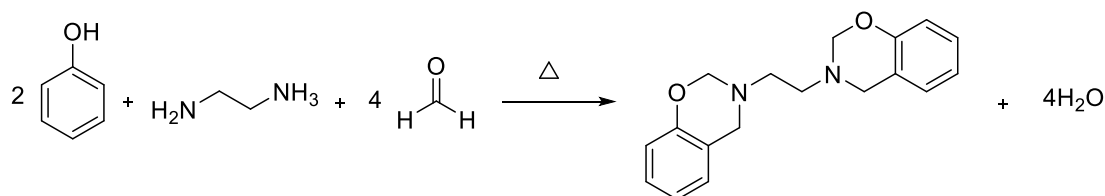
3.6. Polybenzoxazine (Peda)/BDBA Composites

The benzoxazine monomer, Peda, based on phenol and ethylene diamine was synthesized. The monomer was cured to obtain polybenzoxazine with high crosslinking density due to the contribution of difunctional amine moiety. Furthermore, aromatic boronic acid was mixed with the monomer and cured to achieve polybenzoxazine composites with improved crosslinking. Benzene-1,4-diboronic acid (BDBA) was used as the aromatic boronic acid derivative to obtain polybenzoxazine composite with enhanced thermal stability and char yield.

It has been determined that the thermal properties were improved as the amount of BDBA in the composite was increased. This behavior may be associated with the condensation reactions of B-OH groups of boronic acid and hydroxyl group of benzoxazine group. Structural and thermal characterizations were investigated by NMR, FTIR, TGA, DSC and DP-MS techniques.

3.6.1. Synthesis of Benzoxazine Monomer (Peda)

The benzoxazine monomer based on phenol and ethylene diamine was prepared by the reaction shown in Scheme 3.11 [17, 62].



Scheme 3.11. Synthesis of benzoxazine based on phenol and ethylene diamine

Proton NMR spectra of synthesized benzoxazine monomer, Peda, is shown in Fig 3.36. The spectrum of Peda showed intense resonance peaks at 2.98 ppm due to methylene protons of (C1) ethylenediamine. The oxazine ring protons at 4.04 ppm and 4.90 ppm corresponding to the methylene protons (C2 and C3) of Ar-CH₂-N and O-CH₂-N, respectively are observed. The resonance signals of phenyl ring protons are detected in the range of 6.76-7.14 ppm.

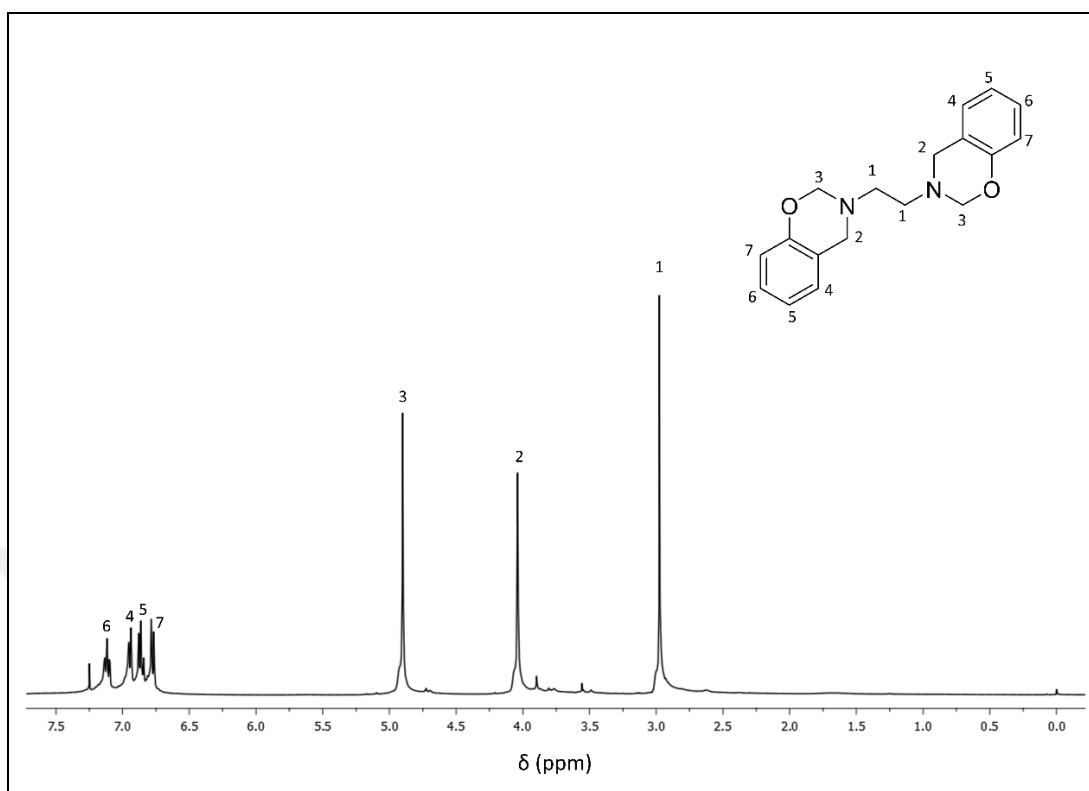


Figure 3.36. ^1H NMR spectrum of Peda monomer

The signal at 49.2 ppm in ^{13}C NMR spectrum (Fig. 3.37) was assigned to the ethylene diamine carbons (C1). The resonance signals at 50.4 and 82.7 ppm were associated with the C2 and C3 carbons of the oxazine ring, respectively. Signals at 116.4 ppm (C8), 120.0 ppm (C4), 120.6 ppm (C6), 127.6 ppm (C5), 127.8 (C7) and 153.96 ppm (C9) were assigned to the resonances of the carbons indicated.

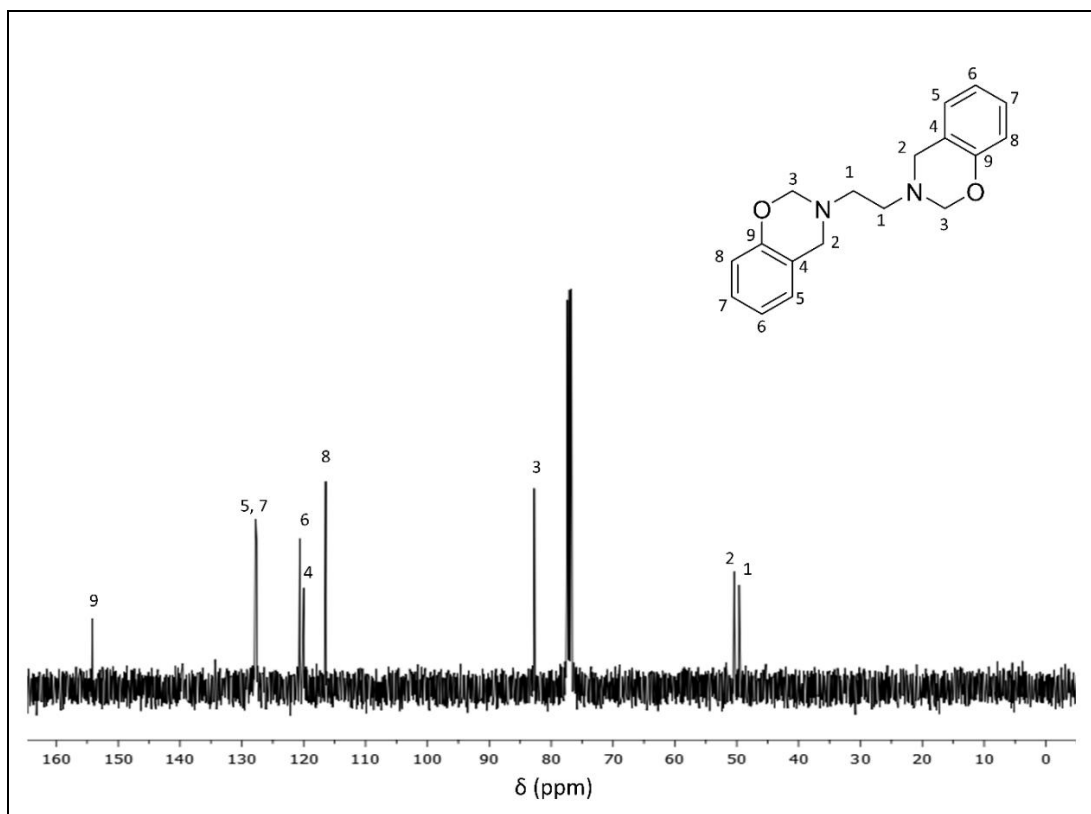


Figure 3.37. ^{13}C NMR spectrum of Peda monomer

Benzoxazine monomer, Peda, was also characterized by the DP-MS method and the mass spectrum is shown in Fig 3.38. The peak at 296 Da is due to the molecular ion of benzoxazine monomer (Peda). In addition, presence of strong peaks due to fragments $\text{HOC}_6\text{H}_4\text{CH}_2\text{NCH}_2$ (148 Da), $\text{HOC}_6\text{H}_4\text{CH}_2$ (107 Da) and C_6H_6 (78 Da) supported the proposed structure of the benzoxazine monomer based on phenol and ethylene diamine.

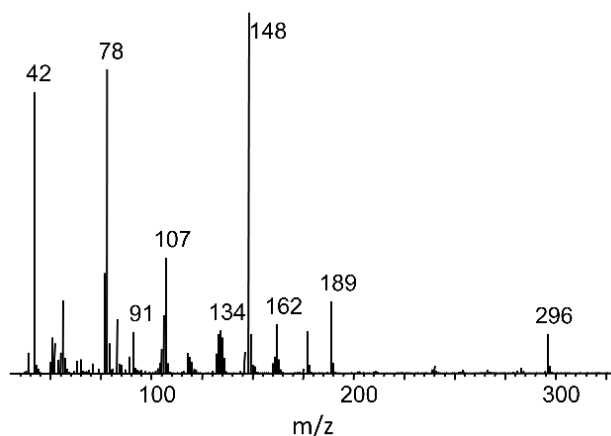
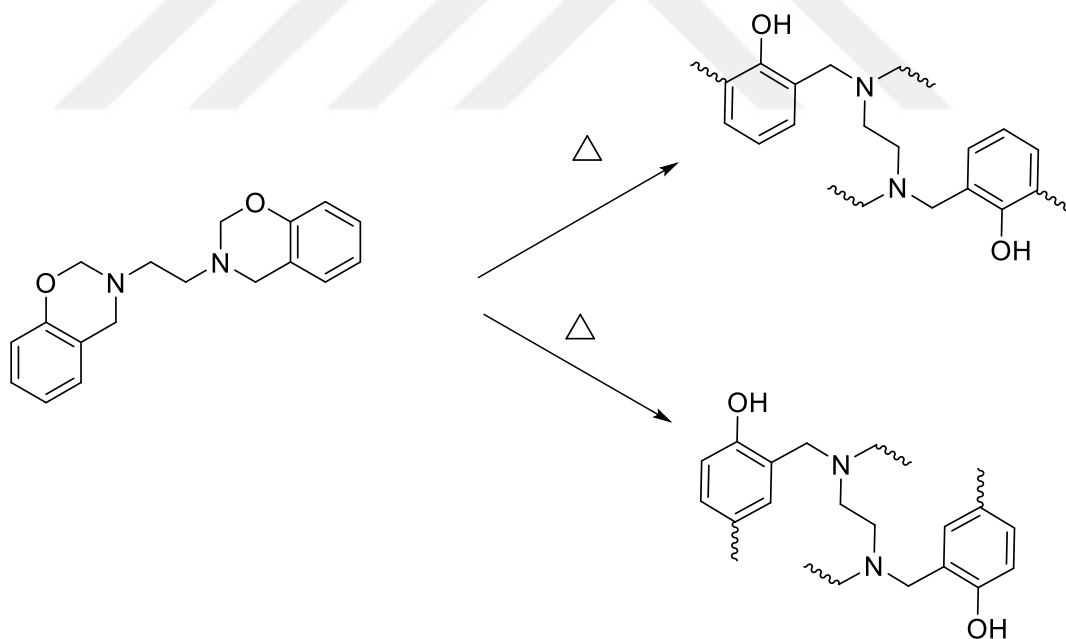
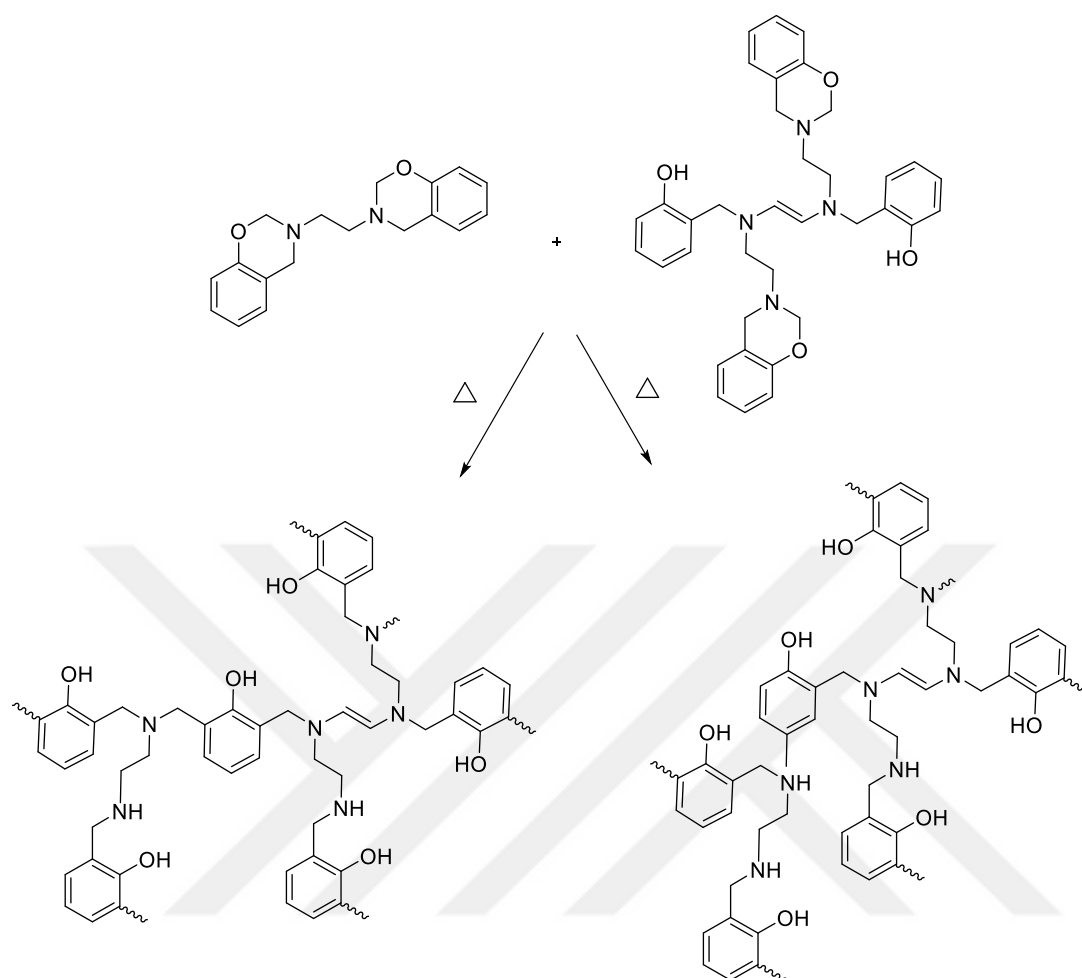


Figure 3.38. Mass spectrum of Peda monomer

Benzoxazine monomer based on phenol and ethylene diamine was heated step-wise curing temperature program in a vented oven. The monomer polymerized by ring opening polymerization reaction. The possible polymerization pathways was shown in Scheme 3.12.

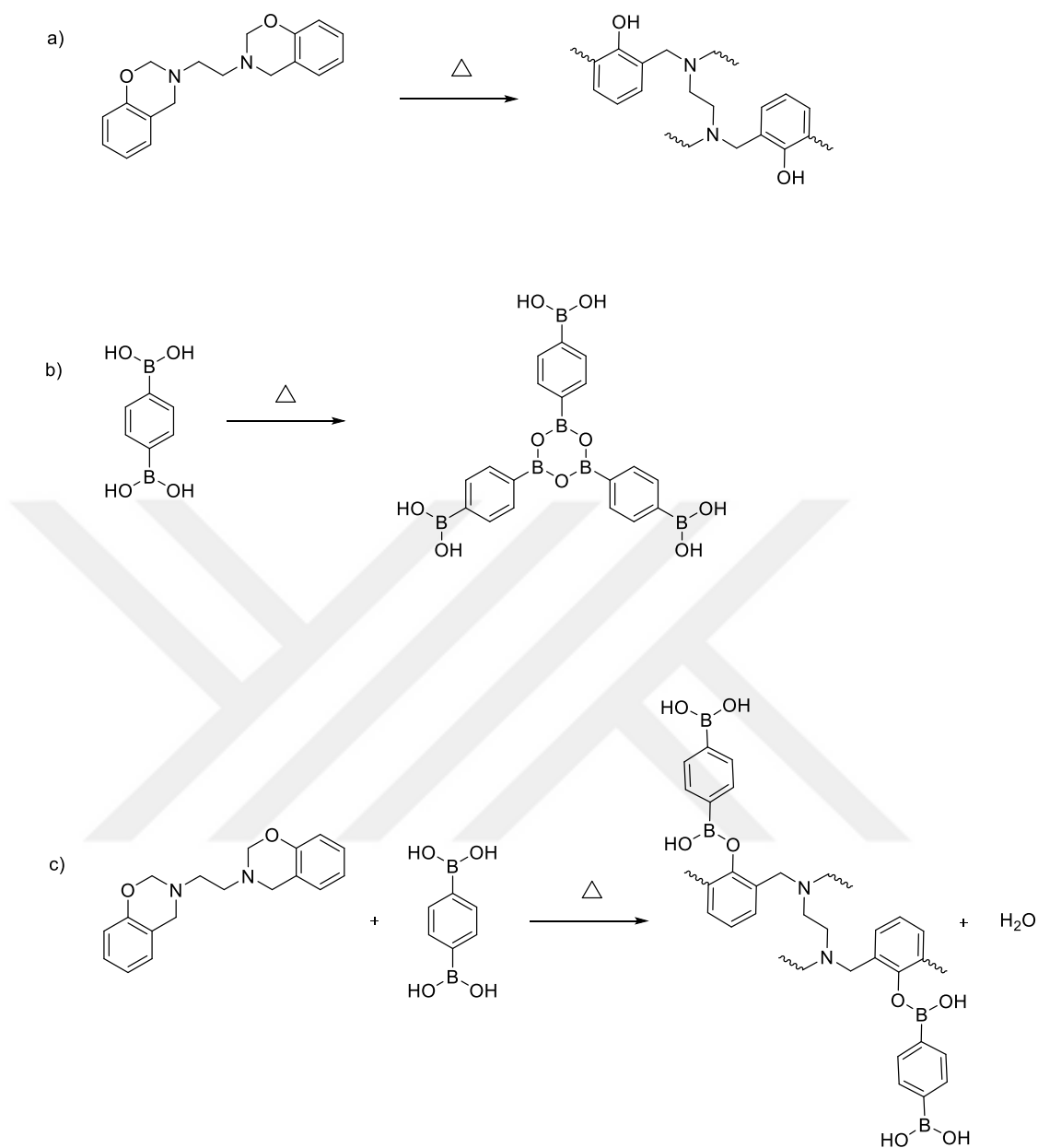




Scheme 3.12. Polymerization pathways of benzoxazine monomer based on phenol and ethylene diamine (Peda)

3.6.2. Preparation and Characterization of PPeda/BDBA Composites

Various amounts (5, 10, 15 and 20%) of benzene-1,4-diboronic acid (BDBA) was mixed with monomer and the mixtures were polymerized to obtain Peda/BDBA composites with enhanced thermal stability and char yield. The improved thermal properties were achieved by the condensation reaction between B-OH and hydroxyl groups of polybenzoxazine. The proposed polymerization pathway given in the literature and possible interactions of BDBA with itself and with Peda monomer are shown in Scheme 3.13.



Scheme 3.13. Possible reactions during polymerization of PPeda/BDBA

Mixtures involving 5, 10, 15 and 20 wt% BDBA were prepared and cured with a step-wise curing program. The composites involving different weight ratios of BDBA (PPeda/5BDBA, PPeda/10BDBA, PPeda/15BDBA, and PPeda/20BDBA) were analyzed with FTIR technique. The spectra of Peda monomer, PPeda polymer, and PPeda/20BDBA composite are shown in Fig 3.39. Characteristic peaks of

benzoxazine aromatic ether at 1024 and 1219 cm^{-1} , due to C-O-C stretching modes, were observed for the Peda monomer. The presence of absorbance peak at 915 cm^{-1} was confirmed the presence of benzene with an attached oxazine ring. The characteristic absorbance peaks of oxazine ring were disappeared in the spectra of PPeda polymer and PPeda/20BDBA composite supporting the completion of ring opening polymerization reaction. In the presence of BDBA, new absorbance peaks at 642 cm^{-1} due to out-of-plane deformation mode of BO_2 group was exhibited. The strong bands in the FTIR spectrum of the composite at around 1388 and 1034 cm^{-1} were attributed to B-O-C and B-C stretching vibrations, respectively. These linkages may be generated by the interactions of BDBA and benzoxazine monomer. Thus, the interaction and new bond formation of BDBA and monomer were identified.

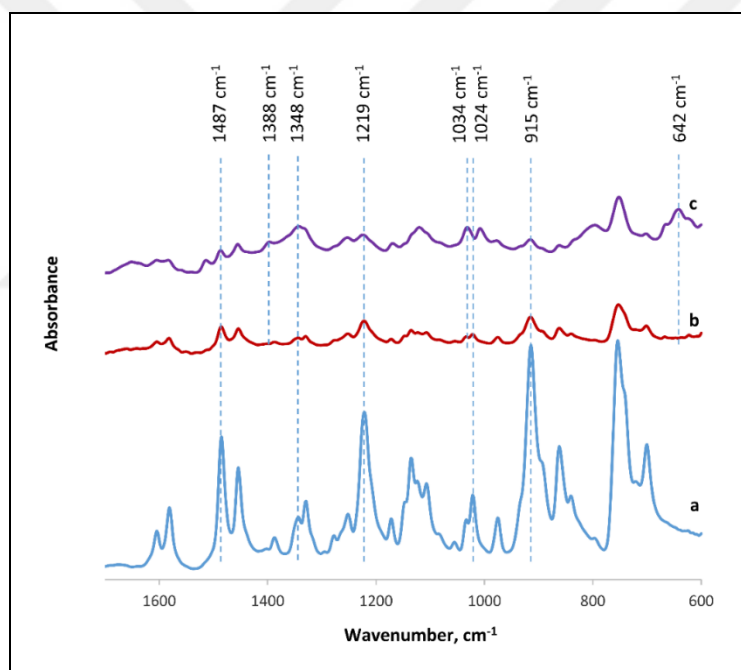


Figure 3.39. FTIR spectra of a) Peda monomer, b) PPeda polymer and c) PPeda/20BDBA composite

3.6.3. Thermal Analysis of PPeda/BDBA composites

DSC curves of Peda monomer, PPeda polymer and PPeda/BDBA composites are given in Fig 3.40. The endothermic peak at about 109 $^{\circ}\text{C}$ is the melting point of Peda monomer. The monomer has two exothermic peaks at 191 and 248 $^{\circ}\text{C}$ indicating two

separate processes. This behavior is generally observed in the presence of impurities. However, the monomer had high purity as can be seen in NMR spectra (Fig 3.36). Hence, it may be proposed that the polymerization of Peda monomer occurred by dual-mode processes. The disappearance of the exothermic peaks for the polymer and its composite supported the completion of polymerization by applied the curing program.

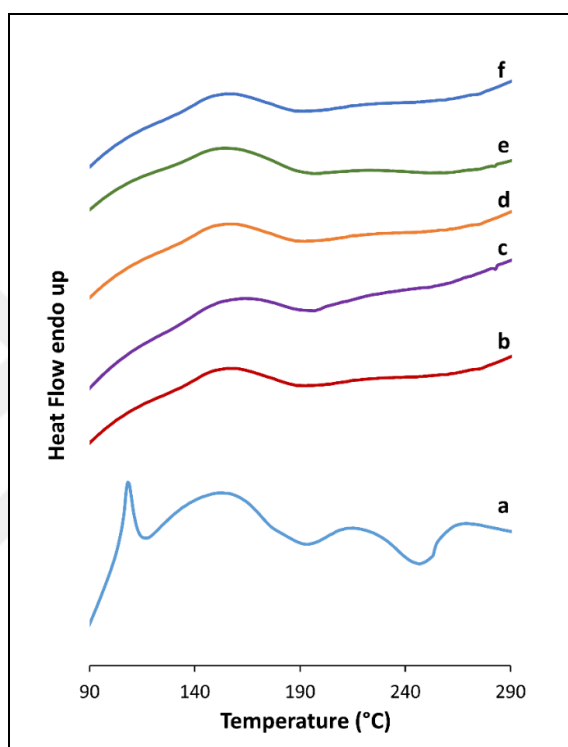


Figure 3.40. DSC curves of a) Peda monomer, b) PPeda polymer c) PPeda/5BDBA, d) PPeda/10BDBA, e) PPeda/15BDBA and f) PPeda/20BDBA

The thermal stability and char yield of the samples evaluated by TGA technique and the curves are shown in Fig 3.41 and the data tabulated in Table 3.7. The result of TGA analysis pointed out that the initial decomposition temperature ($T_{5\%}$) of the composites were decreased by the inclusion of BDBA. However, thermal decomposition was completed at higher temperature regions upon the addition of BDBA at high temperature regions (up to 400 °C). The char yields of the polymer composites were increased as the amount of aromatic boronic acid was increased.

The char yield of the neat polymer was 49%, whereas the composites involving 5, 10, 15, and 20% BDBA were 53, 55, 57 and 61%, respectively.

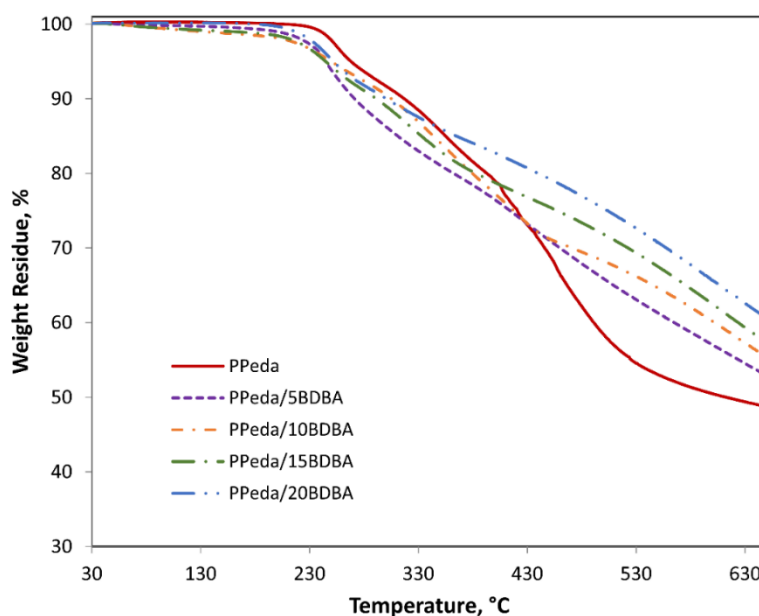


Figure 3.41. TGA curves of a) Peda monomer, b) PPeda polymer c) PPeda/5BDBA, d) PPeda/10BDBA, e) PPeda/15BDBA and f) PPeda/20BDBA

The PPeda/BDBA composites showed higher thermal stability and char yield compared to neat polybenzoxazine. The enhancement in thermal properties in the presence of BDBA may be regarded as an evidence for the interaction between additive and monomer resulting improved crosslinking.

Table 3.7. TGA data for PPeda polymer and PPeda/BDBA composites involving 5, 10, 15 and 20wt% BDBA

Sample	T _{5%} (°C)	Char yield % at 650 °C
PPeda	267	49
PPeda/5BDBA	245	53
PPeda/10BDBA	249	55
PPeda/15BDBA	244	57
PPeda/20BDBA	252	61

The total ion current curves (TIC) and pyrolysis mass spectra at the maximum of the peaks of TIC curves of pristine polymer and composites are shown in Fig 3.43. All samples show two separate peaks indicating multi-step degradation and/or presence of chains with different thermal stabilities.

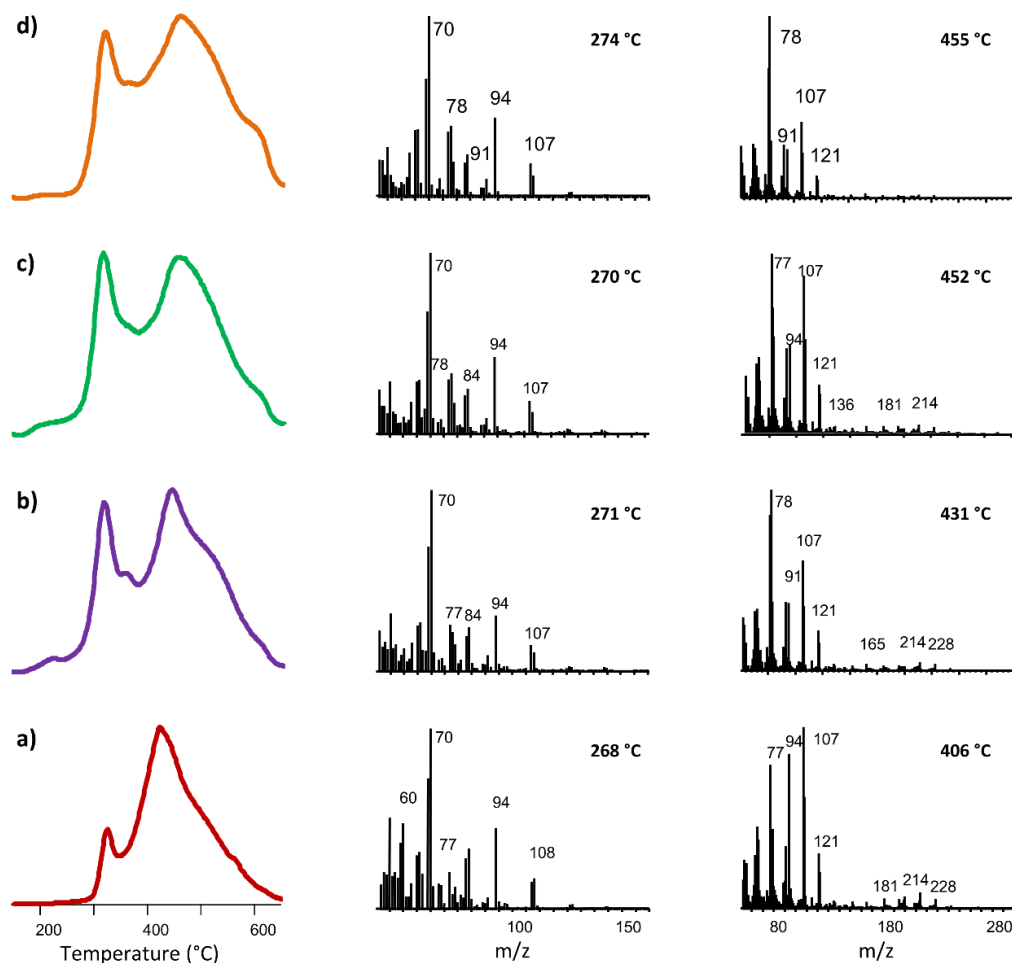


Figure 3.42. Total ion current curves of a) PPeda polymer, b) PPeda/10BDDBA, c) PPeda/15BDDBA and d) PPeda/20BDDBA composites

The TIC curves of polymer and composites showed an intense low-temperature peak with maximum at around 270 °C and high temperature peaks with maxima in the range of 400-460 °C. The maxima of high temperature peaks of the composites was increased by the increase in BDDBA content. The pyrolysis mass spectra were dominated with peaks at 70 ($\text{CH}_2\text{NCH}_2\text{CHNH}$), 77 (C_6H_5), 91 (C_7H_7), 94 ($\text{C}_6\text{H}_5\text{OH}$), 107 ($\text{HOC}_6\text{H}_4\text{CH}_3$), 121 ($\text{HOC}_6\text{H}_4\text{CH}_2\text{N}$) due to typical fragments of polymer that may be generated during pyrolysis.

Single ion evolution profiles of monomer (296 Da), $\text{CH}_2\text{NCH}_2\text{CHNH}$ (70 Da), HOC_6H_5 (94 Da), $\text{C}_6\text{H}_5\text{CH}_2$ (91 Da), $\text{HOC}_6\text{H}_4\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NCH}_2$ (178 Da) detected during the pyrolysis due to polymer fragments. The relative yields of 91 Da and 178 Da evolved at elevated temperatures were increased by inclusion of BDBA. The decomposition of these fragments at high temperature related with the phenolic chains upon loss of amine structure. Moreover, the relative intensities of the fragments $\text{C}_6\text{H}_5(\text{HO})\text{BOC}_6\text{H}_4\text{CH}_2\text{NHCH}_2\text{CHNH}$ (268 Da) and $\text{C}_6\text{H}_4\text{OB}(\text{C}_6\text{H}_5)\text{N}(\text{CH}_3)\text{CH}_2$ (223 Da) were detected with increasing in their abundances upon addition of BDBA. These fragments were obtained by the reactions between phenolic hydroxyl groups of polybenzoxazine and BDBA during ring opening polymerization (Scheme 3.13). The formation of covalent bond between additive and monomer enhances the crosslinking density and so thermal stability. The peaks maxima of decomposition temperature of these fragments shifted to higher temperatures by the inclusion of BDBA. In addition, 300 Da and 312 Da fragments were associated with $\text{CH}_2\text{C}_6\text{H}_4\text{OB}(\text{C}_6\text{H}_5)\text{OC}_4\text{H}_4\text{CH}_2$ and $(\text{C}_6\text{H}_5\text{BO})_3$, respectively. Significant raises in their relative intensity with loading of BDBA supported these assignments.

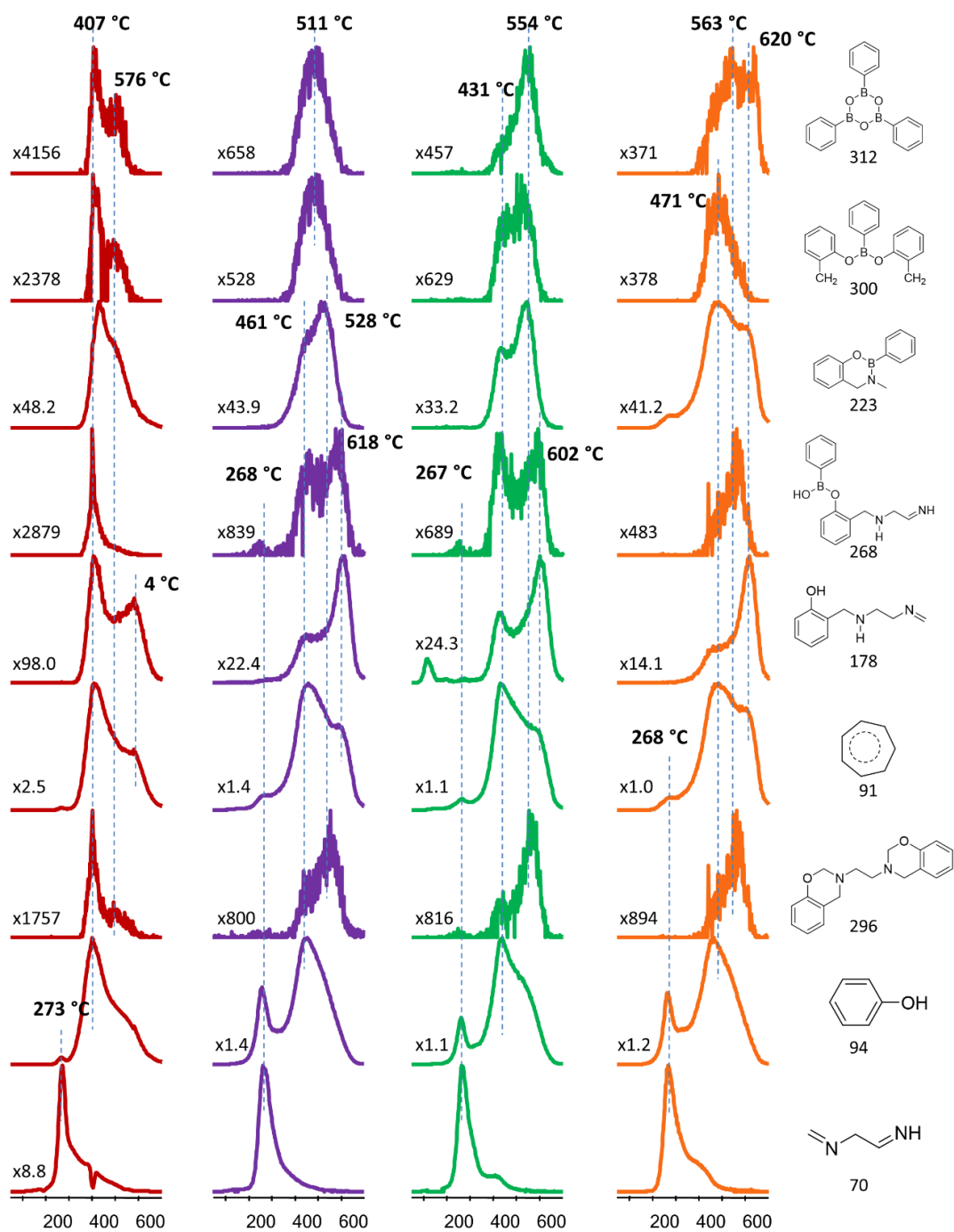


Figure 3.43. Single ion evolution profiles of PPeda polymer and PPeda/BDBA composites

CHAPTER 4

CONCLUSION

In this work, polybenzoxazines and polybenzoxazine composites involving various additives namely aromatic diboronic acid, boric acid, Cloisite 10A clay, ZrB_2 , and epoxy resin were prepared. The effects of additives on thermal characteristics benzoxazine polymers and composites were investigated. In the first part, benzoxazine monomer based on phenol and aniline and its composites with various additives were prepared. In the second part, di-functional benzoxazine monomer based on phenol and ethylene diamine and its composites by inclusion of aromatic diboronic acid were prepared. The structural and thermal characteristics of the benzoxazine monomers, polymers and composites were analyzed by NMR, FTIR, XRD, DSC, TGA, DMA and DP-MS techniques.

Polymerization of benzoxazine based on phenol and aniline is generally obtained by the ring opening of oxazine ring to form Mannich base that reacts mainly ortho and para positions of phenol and aniline ring. In addition, generation of dimers and low molecular mass oligomers that may be produced contribute to the complex polymerization mechanism.

The changes in thermal characteristics of as-synthesized and pure benzoxazine monomers by the addition of BDBA were analyzed. It was observed that the neat resin of pure benzoxazine monomer has higher thermal stability. However, by inclusion of BDBA to the as-synthesized benzoxazine monomer higher thermal improvement was obtained. Actually, the as-synthesized monomer includes dimer and/or low mass oligomeric structures. These compounds may readily interact with the additives by condensation reactions of B-OH groups with hydroxyl groups of benzoxazine, and so showed higher improvement in thermal properties.

Moreover, the effect of boric acid on thermal characteristics of polybenzoxazine based on phenol and aniline was investigated. In general, improvement in thermal stability was detected upon addition of boric acid. Condensation reactions between B-OH groups and OH groups of phenol or/and monomer took place during the ring-opening polymerization. Generation of boraxine by self-condensation reactions was also detected. As a consequence of these interactions, thermal stability and char yield of the product were increased.

The organically modified clay (Cloisite 10A) was preferred as an additive due to the fact that C10A has benzyl group similar to the monomer. The composites were obtained as exfoliated and/or intercalated distribution modes. These composites showed better thermal properties compared to the neat resin may be due to the barrier effect of silicate layers of C10A.

The increase in thermal stability and char yield of polybenzoxazines by addition of ZrB_2 particles was explained by the linking effect and extremely high melting temperature of ZrB_2 particles. The interaction of monomer/polymer and ZrB_2 particles were supported by the presence of the peaks due to B-O stretching vibrations in the FTIR spectra.

The composites with epoxy resin showed higher glass transition temperature compared to pristine polybenzoxazine. This behavior was related to the increase in crosslinking density because of the ring opening reactions of the epoxide ring by the phenolic hydroxyl functionalities present in the polybenzoxazine precursor.

The difunctional monomer based on phenol and ethylene diamine was also prepared. The composites with BDBA showed higher thermal stability and char yield. The improvements in thermal properties were related to new fragments formed by the interaction of monomer and additive and higher decomposition temperature of phenolic fragments.

The composites of monomer based on phenol and aniline with low weight% loading additives were compared (Table 4.1). Boric acid provided higher improvement in

crosslinking density due to the condensation reactions of B-OH groups with hydroxyl groups of benzoxazines shifting decomposition of phenolic backbone to higher temperatures. Cloisite 10 A showed higher char yield due to barrier effect. However, the $T_{5\%}$ of composite involving BA was lower compared additives C10A and ZrB_2 . Therefore, C10A may be the best filler for improvement of both thermal stability and char yield in the case of low loading composites preparation.

Table 4.1. $T_{5\%}$ and char yields of PPa, PPa/5BA, PPa/5C10A and PPa/5ZrB₂

Sample	$T_{5\%}$ (°C)	Char yield% at 650 °C
PPa	354	43
PPa/5BA	318	55
PPa/5C10A	340	55
PPa/5ZrB ₂	344	46

The composites of phenol and aniline based benzoxazine monomer with boron involving compounds namely BDBA, BA and ZrB_2 showed significant increase in char yield by loading of %20 additive (given in Table 4.2). However, thermal decomposition of composite involving ZrB_2 started at higher temperature.

Table 4.2. $T_{5\%}$ and char yields of neat polymers and composites involving BDBA, BA and ZrB_2

Sample	$T_{5\%}$ (°C)	Char yield% at 650 °C
PaBz	306	40
PPa	318	43
PaBz/20BDBA	250	58
PPa/20BA	302	63
PPa/20ZrB ₂	366	61

The PPeda neat polymer of the di-functional benzoxazine monomer based on phenol and ethylene diamine showed enhanced char yield because of higher cross-linking density. In general, it was expected that di-functional polybenzoxazines have higher char yield compared to mono-functional polybenzoxazines. However, PaBz provided higher improvement by inclusion of BDBA due to higher possibility of condensation reaction. In other words, PPeda di-functional polybenzoxazine gave lower extent reaction due to steric hindrance.

Table 4.3 . T_{5%} and char yields of PaBz, PPeda, PaBz/20BDBA and PPeda/20BDBA

Sample	T_{5%} (°C)	Char yield% at 650 °C
PaBz	306	40
PPeda	267	49
PaBz/20BDBA	250	58
PPeda/20BDBA	252	61

In general, polybenzoxazine composites were prepared with various additives. Improvement in thermal stabilities and increase in char yields were recorded upon incorporation of these additives by the chemical and physical interactions between the monomer, polymer and additives.

APPENDIX A

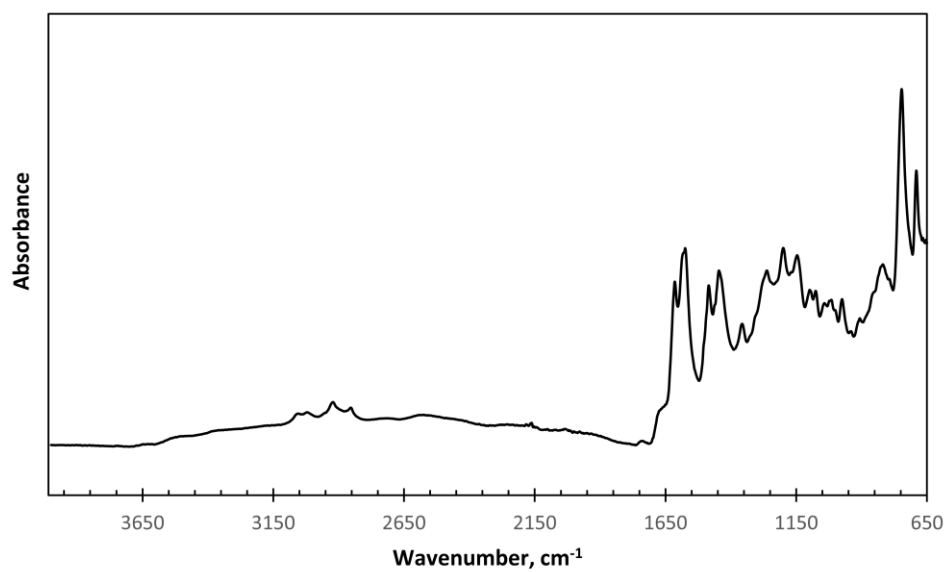


Figure A.1. FTIR Spectrum of PPa/1C10A

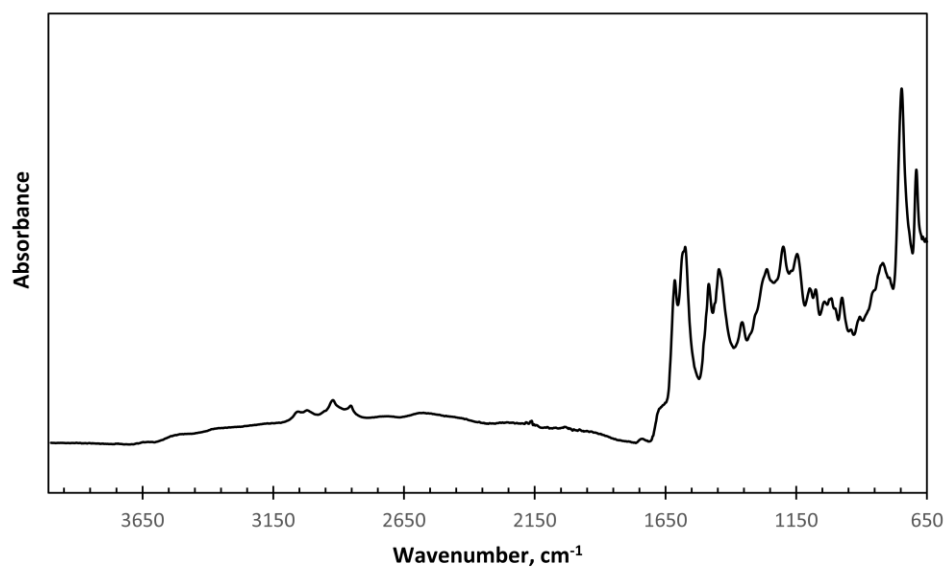


Figure A.2. FTIR Spectrum of PPa/3C10A

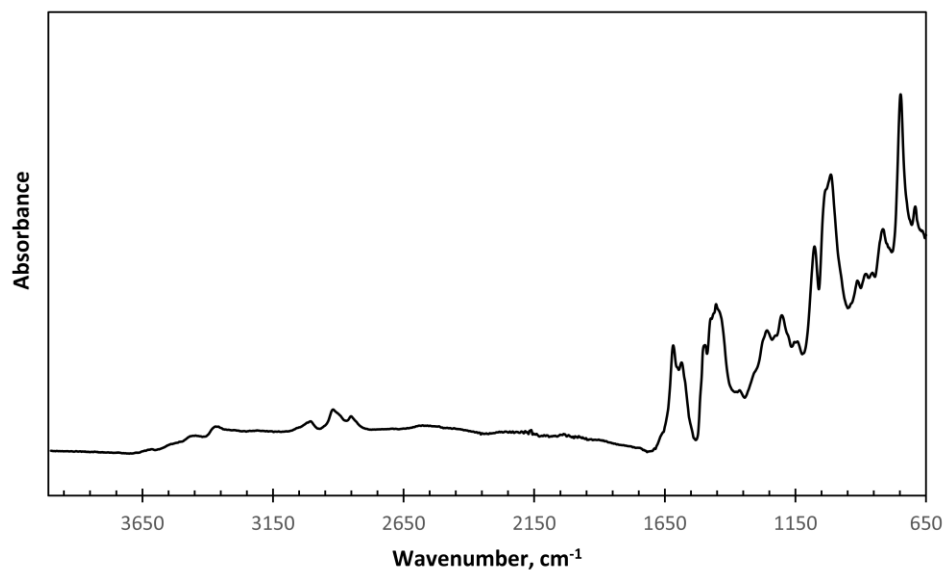


Figure A.3. FTIR Spectrum of PPa/5C10A

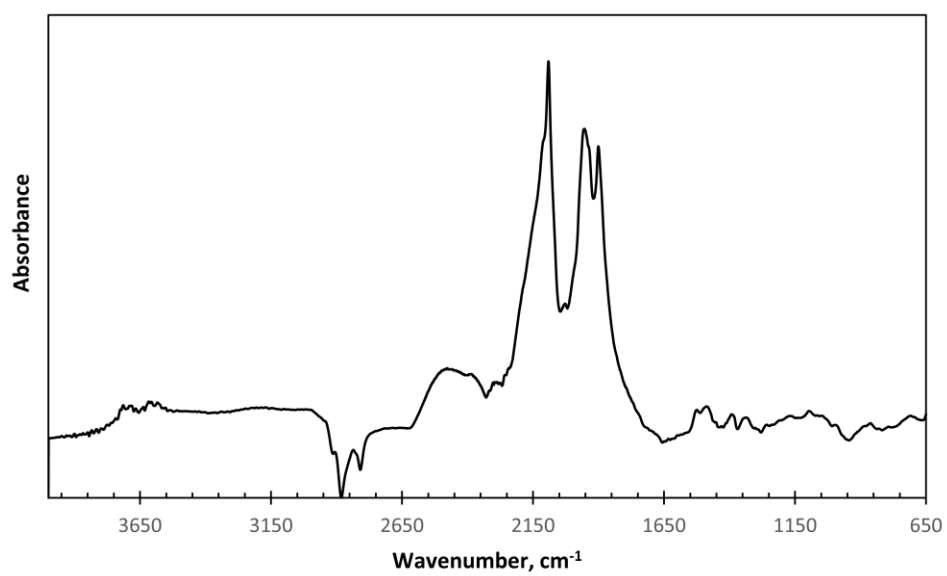


Figure A.4. FTIR Spectrum of PPa/5ZrB₂

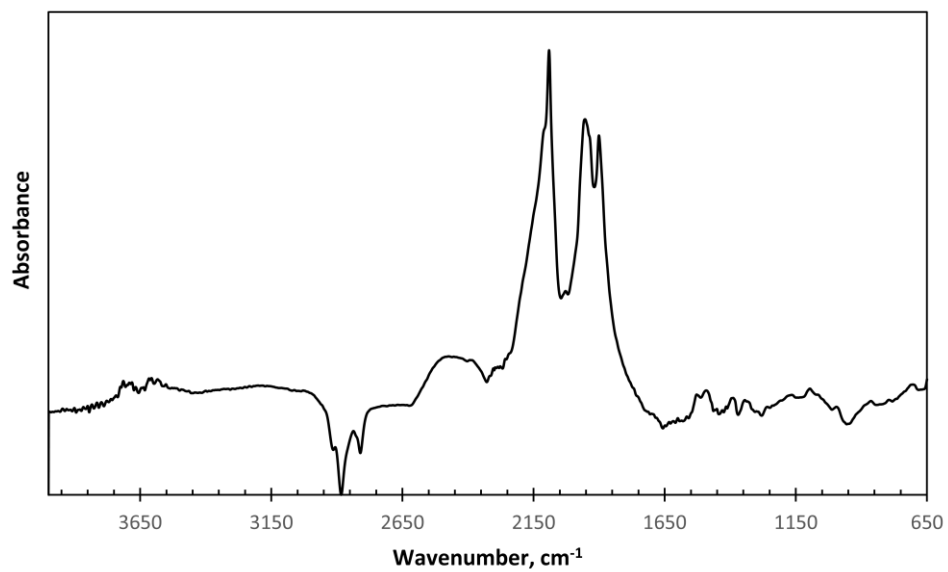


Figure A.5. FTIR Spectrum of PPa/10ZrB₂

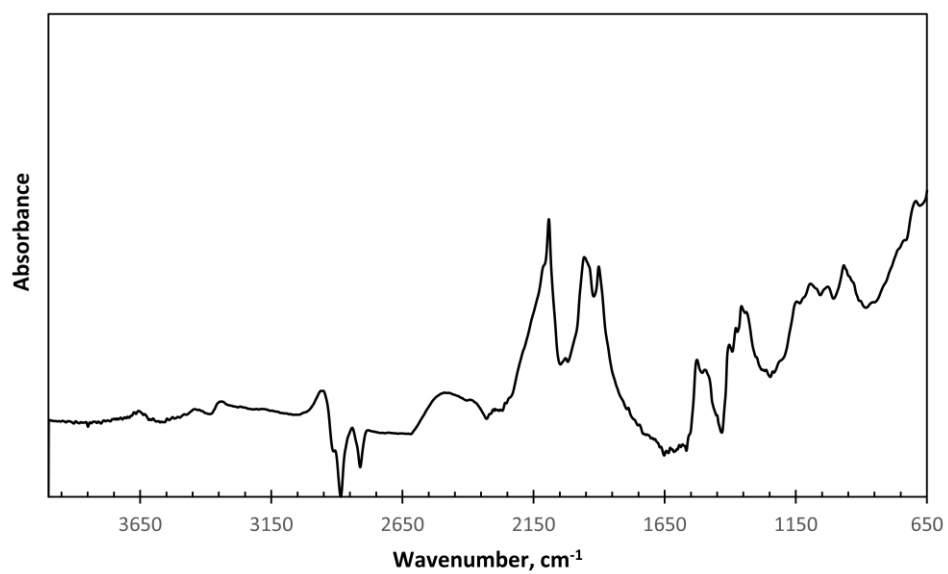


Figure A.6. FTIR Spectrum of PPa/15ZrB₂

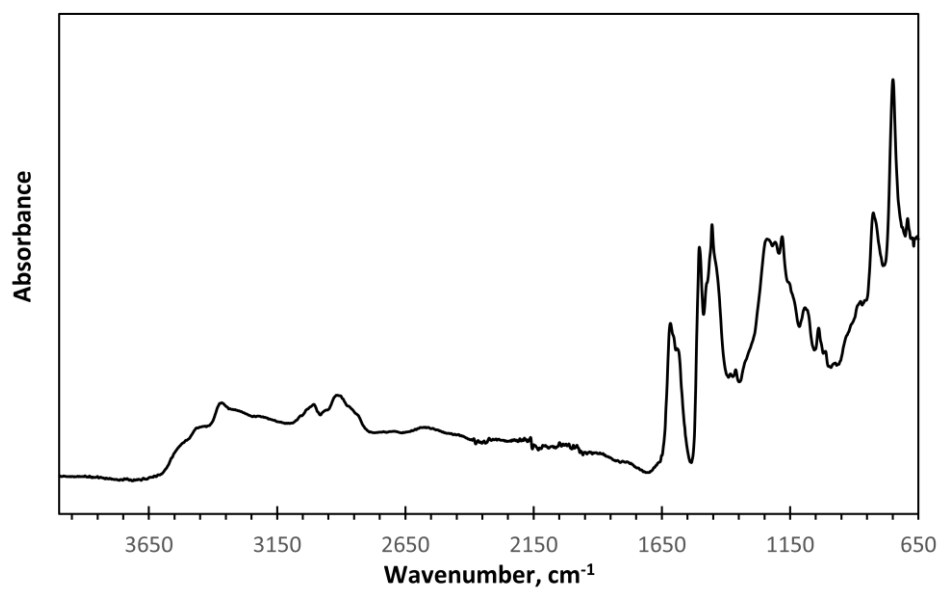


Figure A.7. FTIR Spectrum of PPa/10EP

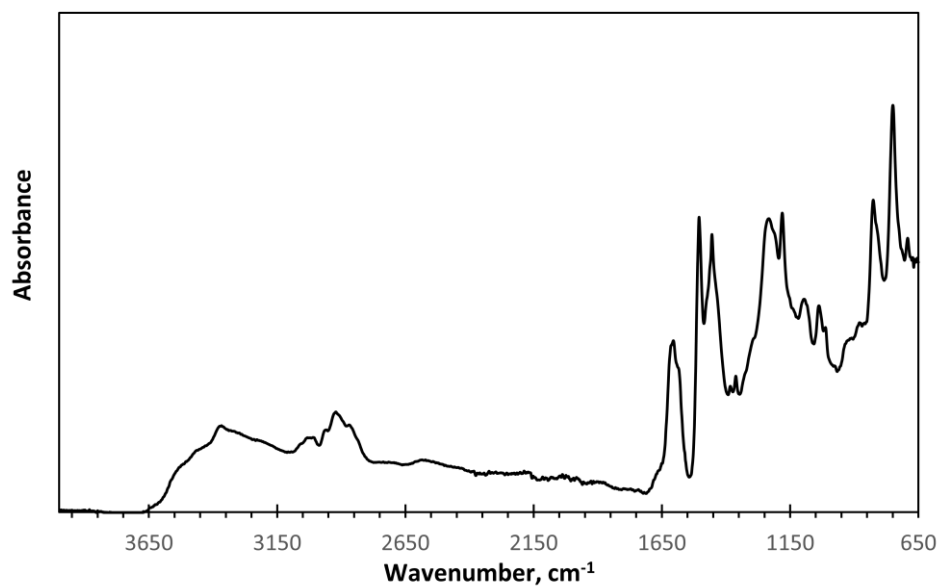


Figure A.8. FTIR Spectrum of PPa/20EP

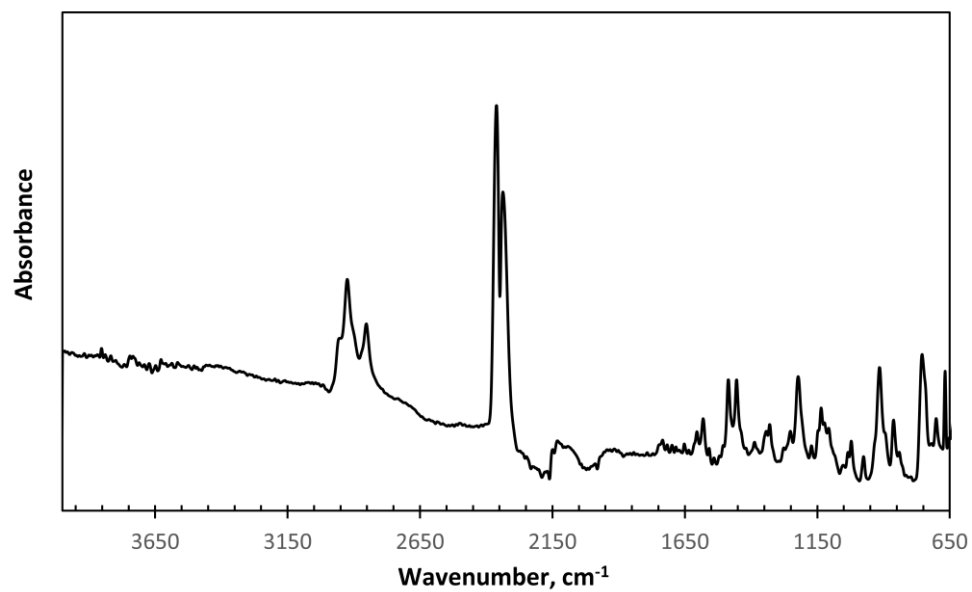


Figure A.9. FTIR Spectrum of PPeda/5BDBA

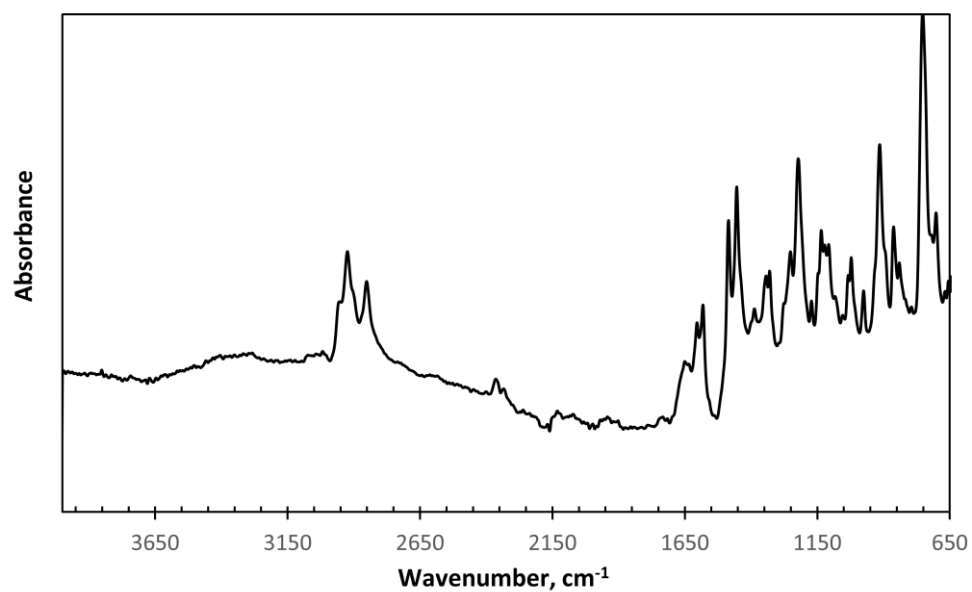


Figure A.10. FTIR Spectrum of PPeda/10BDBA

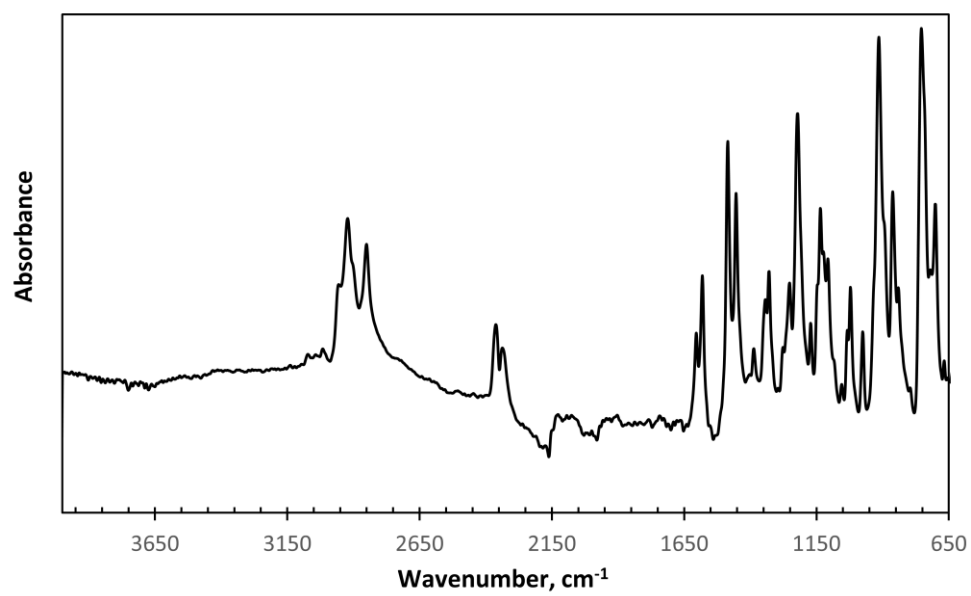


Figure A.11. FTIR Spectrum of PPeda/15BDBA

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