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Development of Halogen Free Sustainable Polybenzoxazine Matrices and Composites for Flame Retardant Applications

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Abstract

In recent years, with the growing concern on energy crises, the development of new products from sustainable resources have been received much greater consideration owing to the environmental concerns caused by the rapid reduction of non-renewable fossil resources. The widespread utilization of polymeric materials led to a considerable increase in fire risk in our daily life due to their flammable behavior. Hence, the flame-retardant properties of polymeric materials are considered as one of the most significant criteria to use them in wide range of industrial applications. It is well known that mostly halogenated flame retardant materials are widely used for flame retardant applications. However, they release toxic gases and corrosive smoke during combustion, and consequently they contribute to serious environmental pollution. In this connection, in the present chapter we discussed the different types of non-halogen based environmentally friendly bio-based polybenzoxazine matrices developed from renewable and sustainable bio-phenolic materials viz., cardanol, eugenol, guaiacol and etc., and the composites obtained by reinforcing with varying weight percentages of flame resistant reinforcements/additives and their flame retardant properties obtained from different analytical techniques.

Keywords: Bio-phenols, sustainable polybenzoxazine, bio-based composites, flame retardancy, halogen free benzoxazine composites

1. Introduction

Most of the polymeric materials including synthetic and natural based, are extremely flammable in nature. The extensive usage of polymer based materials led to a substantial increase in fire risk in our day to day-life. For example, about 2 million fire accidents are reported in Europe every year, which cause more than about 4000 casualties and ~ 70000 injuries along with economic loss of about ~120 billion € [1, 2]. Thus, there are unwanted and excessive societal and economic burdens on the entire civilization, hence it is most essential to produce polymeric products with efficient flame retardant properties to avoid fire related losses.

In addition, the flame-retardant behaviour of polymeric materials are considered as one of the most important criteria to utilize them in the form of sealants, encapsulants, coatings, and matrices for different industrial applications [3–8].

In the recent years, due to the environmental, sustainable and economic aspect, growing attempts have been progressed for the synthesis of polymeric resin from natural renewable/sustainable feedstock instead of using fossil fuel/petroleum based raw materials [9–12]. The production of polymeric materials at present are mostly based on the petroleum feedstock and are used for wide range of industrial applications [13–16]. Bio-based matrices/composites already found numerous applications in the diverse fields of our everyday lives, such as in the automotive industry or in building and construction, aerospace, and so forth [17–23]. In this context, in order to improve their safe utility and also widen their area of application, it is essential to increase their fire/flame resistant behavior to make them suitable for indented applications. Hence, the development of polymeric materials with enhanced flame retardant behavior is warranted from sustainable bio-resources.

Usually, halogen based flame resistant additive materials has been extensively used into polymer matrix to enhance its flame resistant properties. The release the corrosive smoke and toxic gases by these additives during pyrolysis, consequently, give rise to serious ecological problems. Consequently, the development of polymeric materials free from halogens are considered to be a versatile approach. The method of enhancing the flame resistant properties of polymers without use of halogen based flame additives can be deliberated by the following three methodologies to obtain the flame retardant of polymers: (i) using intrinsically flame retardant polymeric materials, (ii) to suitable structural modification of existing industrial polymers, (iii) to introduce intrinsic flame resistant nano-reinforcements/fillers into polymers.

As a result, new research fields have been emerged in the material science in particular in the field of polymers and directed toward a completely or partial replacement of the petroleum-based materials. In this regard, polybenzoxazines possess very useful perspective due to their extraordinary molecular design flexibility [24–32], which easily facilitates and allows bio-based precursors for the production of varied molecular structured benzoxazines [33–57], consequently reducing/replacing the considerable utilization of the petroleum-based raw materials. The nitrogen atom in the skeleton of benzoxazines significantly enhances their flame retardancy, making them suitable for the fabrication of flame retardant components. Fire, Smoke, and Toxicity (FST) reduction behaviour of benzoxazine based materials have attracted industrial and academic attention as federal regulations become strict and new technologies emerge. It was reported that the many efforts have been made to syntheses of benzoxazines exploiting natural renewable resources using cardanol, urushiol, coumarine, eugenol, guaiacol, furfuryl amine and stearyl amine. In addition, silica/phosphorous/carbon reinforced benzoxazine hybrid materials expected to possess radiation resistant behaviour coupled with inherent flame retardant properties. Probable flame resistant mechanism of the polybenzoxazine resin is owing to the release of gaseous species on the surface. The gases including CO_2 , NO_2 , and H_2O might able to diminish the O_2 concentration around the burning area and diminish the heat of the surface. Another probable mechanism of PBz polymer, with flame resistant layer through the formation of char on the surface. The inert flame resistant layer might protect the benzoxazine from the external heat from the flame, thus performing as the O_2 protection layer. The high strength, excellent flame retardancy, radiation resistance, high thermal stability, low moisture absorption, low temperature cure, low shrinkage and low-k dielectric behaviour have made benzoxazine resins become an attractive for electronics and aerospace applications. Hence, in the present chapter,

the preparation, properties of some of the important and valuable halogen free bio-based flame retardant polybenzoxazines matrices and composites are reviewed and summarized.

2. Cardanol based polybenzoxazines for flame resistant applications

Cardanol is a naturally occurring combination of bio-phenolic materials isolated from cashew nut-shell agro- waste with exported worth of 1.39 USD million in the year 2020–2021 (Apr–Nov) by India [58]. The cardanol chemical structure is very exciting due to its reactive functional phenolic-OH group and an alkyl spacer with unsaturation in m-position will be applicable for several chemical reaction and functional group modifications [59–62]. Cardanol bargains one of the better probable material for green synthesis of benzoxazines due to their massive availability and very low cost of production. Also, cardanol competently alternative to petro-phenol (for example bisphenol-A (BPA) which is an endocrine disruptor) to prepare BPA-free polybenzoxazines. There are numerous auspicious ingenuities for replacing the petro-based phenolic resources with cardanol to form cardanol based polybenzoxazines.

The flame retardant properties of cardanol based polybenzoxazines are usually lower than those of petroleum based thermosets. However, solutions can be provided by either physical blending with flame retardants or by chemical modification. Several research groups attempted to solve these issues by designing multi amine precursors [63, 64] or by introducing, silica/silicon, phosphorus, boron, and furan [52, 65–70].

To improve the flame resistant properties, Bimlesh Lochab research group introduced the [71] halogen free eco-friendly hexa-functional cardanol (bio-based phenolic) benzoxazine with a phosphazene core (cyclophosphazene ring based benzoxazine monomer designated as CPN) as reactive flame retardant precursor. The CPN monomer showed good compatibility with cardanol and tris-p-aminophenylmethane based benzoxazine monomer (CPN₀). Higher loading of CPN in the monomer improved both the smoke density rating, vertical burning rating and also led to higher limiting oxygen index (LOI). Finally, the introduction of CPN network shows good compatibility with the polybenzoxazine phenolic thermosets with enhancement in flame resistant properties.

CPN monomer was synthesized as per the reported procedure (**Figure 1**). The phosphazene core with hexa-amine (2) was synthesised using phosphonitrilic chloride trimer (N₃P₃Cl₆), by base facilitated reaction with excess of 4-acetamidophenol to yield compound (1) and, which upon hydrolysis, gave the corresponding hexa-amine compound (2). Later, the synthesized hexa-amine (2) was reacted with 4-pentadecylsalicylaldehyde (3) to form the corresponding Schiff base which is then reduced to compound (4). Compound (4) undergoes intra-molecular cyclization reaction to form CPN (5). The renewable cardanol and phosphorous content in the CPN monomer are 65.7% and 3.4% respectively.

The cardanol (CPN₀) monomer was synthesised as per the procedure reported [71]. The monomer combinations are named as CPN_x, here x is percentage weight of CPN incorporated in the CPN₀ monomer and blends developed are named as CPN₁₀, and CPN₈₀. The polymerization of CPN, CPN₈₀, CPN₁₀, and CPN₀ was accomplished in a hot air oven at the temperature of 50°C, 100°C, 120°C, 150°C, 180°C, 200°C, 220°C, 240°C for each 1 h and followed by further heating at 240 °C for 0 h, 1 h, 1.5 h and 2 h. The prepared poly (CPN_x) (**Figure 2**) was utilized for further characterizations.

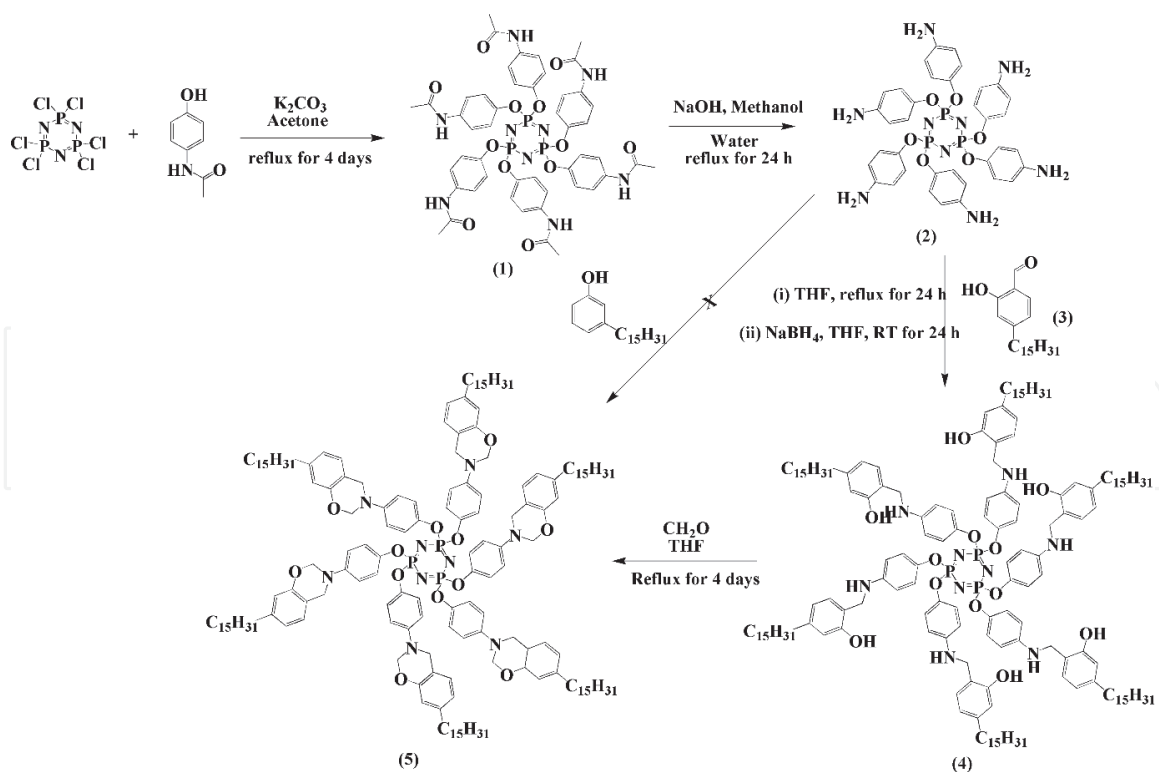


Figure 1.
Divergent approach for the synthesis of cardanol phosphazene benzoxazine monomer (CPN).

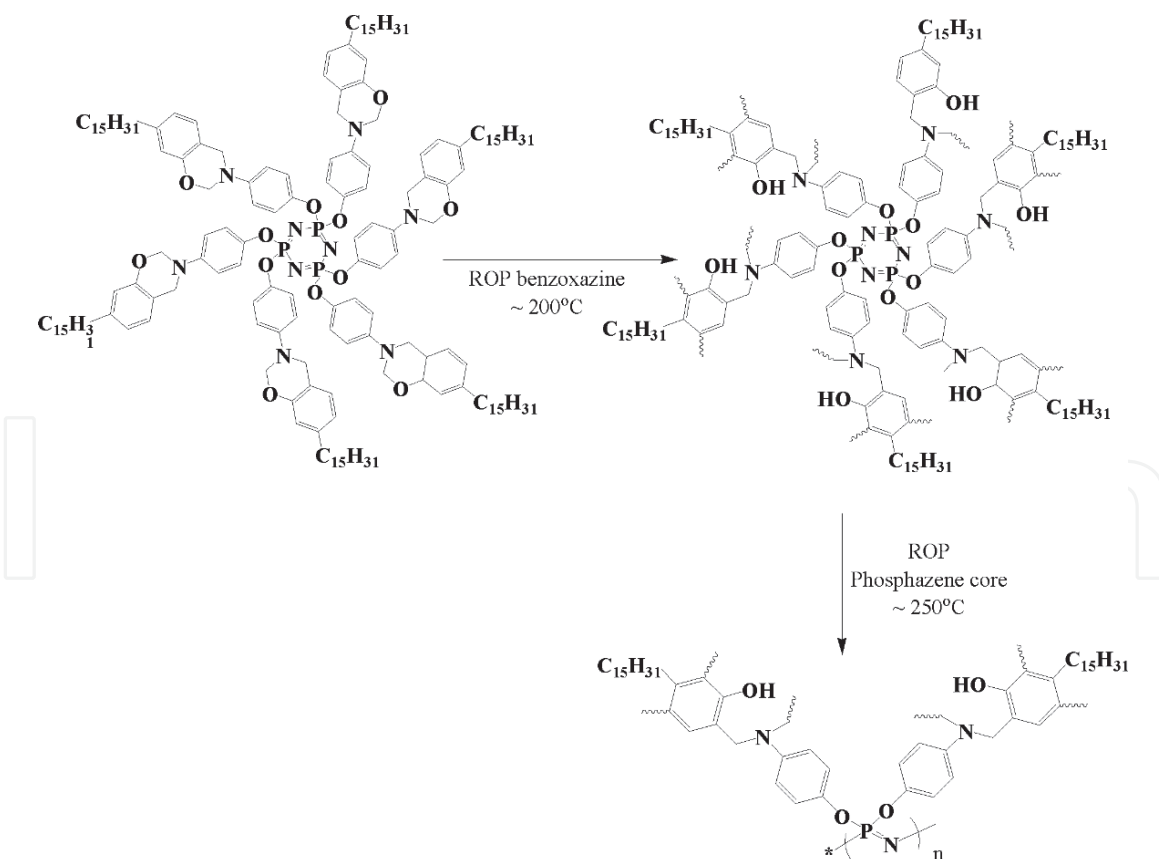


Figure 2.
Ring opening polymerisation of CPN monomer to form polyphosphazene polybenzoxazine.

The limiting oxygen index (LOI) of the polymers was calculated from TGA using van Krevelen's equation and the values obtained are presented in **Table 1**. If a polymer possesses the value of LOI is less than 20.9%, it burn simply in air; 21–28%

Samples	Phosphorus (%)	Cardanol (%)	Char(%) residue	LOI	UL-94	Smoke density	Reference
CPN ₀	0	70.40	14.0 (0 ^a)	23 (18 ^a)	V-2	77.70	[71]
CPN ₁₀	0.30	70.00	24 .0(7 ^a)	27 (20 ^a)	V-1	70.70	[71]
CPN ₈₀	2.70	66.80	32.0(26 ^a)	30 (28 ^a)	V-0	34.30	[71]
CPN	3.40	65.70	39.0(28 ^a)	33 (29 ^a)	V-0	33.90	[71]
C-trisapm (T)	0	70.40 ^b	8.30	20.82		54.60	[72]
CP ₁ T ₃	1.19	23.28 ^b	28.50	28.90		51.60	[72]
CP ₃ T ₁	3.56	69.83 ^b	42.70	34.58		47.50	[72]
CP	4.79	93.10 ^b	29.30	29.22		34.01	[72]
EP ₁ T ₃	2.09	21.97 ^b	28.70	28.98		35.39	[72]
EP ₃ T ₁	6.26	65.92 ^b	28.50	28.9		39.83	[72]
EP	8.34	87.89 ^b	32.40	30.46		18.80	[72]

^aAir atmosphere.

^bRenewable phenol (%).

Table 1.
Thermal and flame resistant (LOI, UL-94 and smoke density) properties of bio-based polybenzoxazine matrices and composites.

slowburning; 28 to 100% self-extinguishing; and > 100 is considered as inherently non-flammable [71]. From the **Table 1**, an increment in the value of LOI is reliant on the weight percentage content of phosphorous signifying the role played by CPN core in flammability. The vertical burning test (UL-94) was adopted to check the flammability features of poly(CPN_x) and the values obtained are presented in **Table 1**. The poly(CPN₀) was burnt immediately with a lower combustion time along with fire drippings. The flame resistance properties was increased with an increase in weight content of phosphorus which substantiates with LOI results.

A smoke density test was carried out to ascertain the relative quantities of smoke produced during burning of poly(CPN_x). The neat poly(CPN₀) indicated nearly very low residue char which crumbled in the mesh, whereas phosphazene containing poly(CPN₁₀), poly(CPN₈₀), and poly(CPN) exhibited high char residue and perceived smoke density rating of 77.7, 70.8, 34.3 and 33.9 respectively. The comparative variance in smoke density was observed as 6.9 and 43.4 with 10 wt% and 80 wt.% respectively with introduction of CPN proposing a substantial role frolicked by CPN core in the decrease of smoke density in case of poly(CPN₀).

Further to confirm the flame retardant mechanism, SEM was performed to check the morphology of the residual char samples after smoke density analysis and are depicted in **Figure 3**. From SEM images, it was noticed that the several undulations and ripples in the cases of poly(CPN₀), and poly(CPN₁₀) due to the presence of a higher amount of flammable matrix (**Figure 3a** and **b**). The formation of bigger cracks (20–30 μm) on exterior surface was observed in the residue of poly(CPN₀). The cracks were significantly decreased with the introduction of CPN, as observed from the exterior surfaces of poly(CPN₁₀), poly(CPN₈₀), and poly(CPN). Both poly (CPN₈₀), and poly(CPN) formed a extremely compact and thick charred layers with combined enlarged residual char. Analysis of interior surface morphology exhibited the development of bigger porous structures with smoother surface while a several honeycombed micro-structures with fizzes detached by precise tinny layers was perceived with higher in weight content of phosphorous in the residue. The larger surface area exhibited by such inter-connected system of voids alleviate

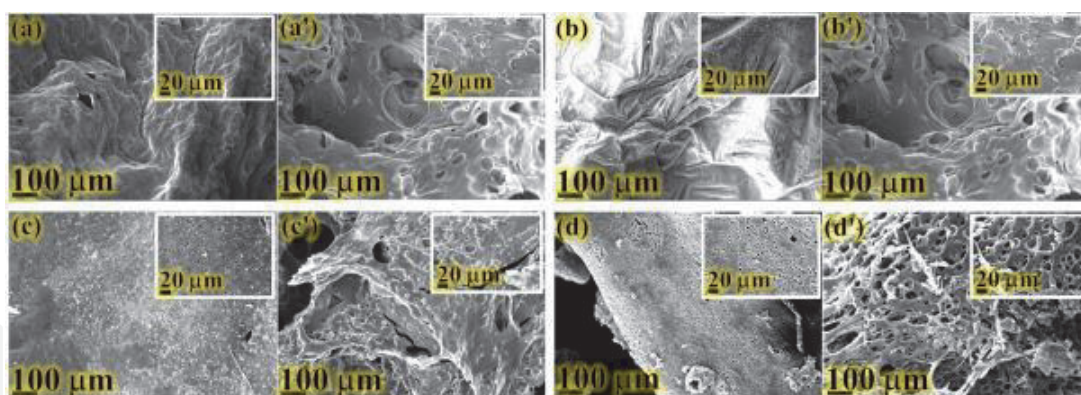


Figure 3. SEM images of exterior (a, b, c, d) and interior (a', b', c', d') surfaces of residual char (a, a') poly(CPN₀), (b, b') poly(CPN₁₀), (c, c') poly(CPN₈₀), and (d, d') poly(CPN) samples [71]. (Copyright 2018. Reproduced with permission from American Chemical Society).

altercation of heat and oxygen (air), which in turn contributes to an enhanced resistance against flame.

Further, to improve the flame resistant behaviour of polymers, the same research group have reported [72] the introduction of hexacardanolphosphazene (CP) /hexaeugenolphosphazene (EP) as a flame retardant additives in to cardanol based tris-benzoxazine monomer (C-trisapm). The flame retardant properties of resulting matrices were studied using LOI, UL-94, and smoke density analysis.

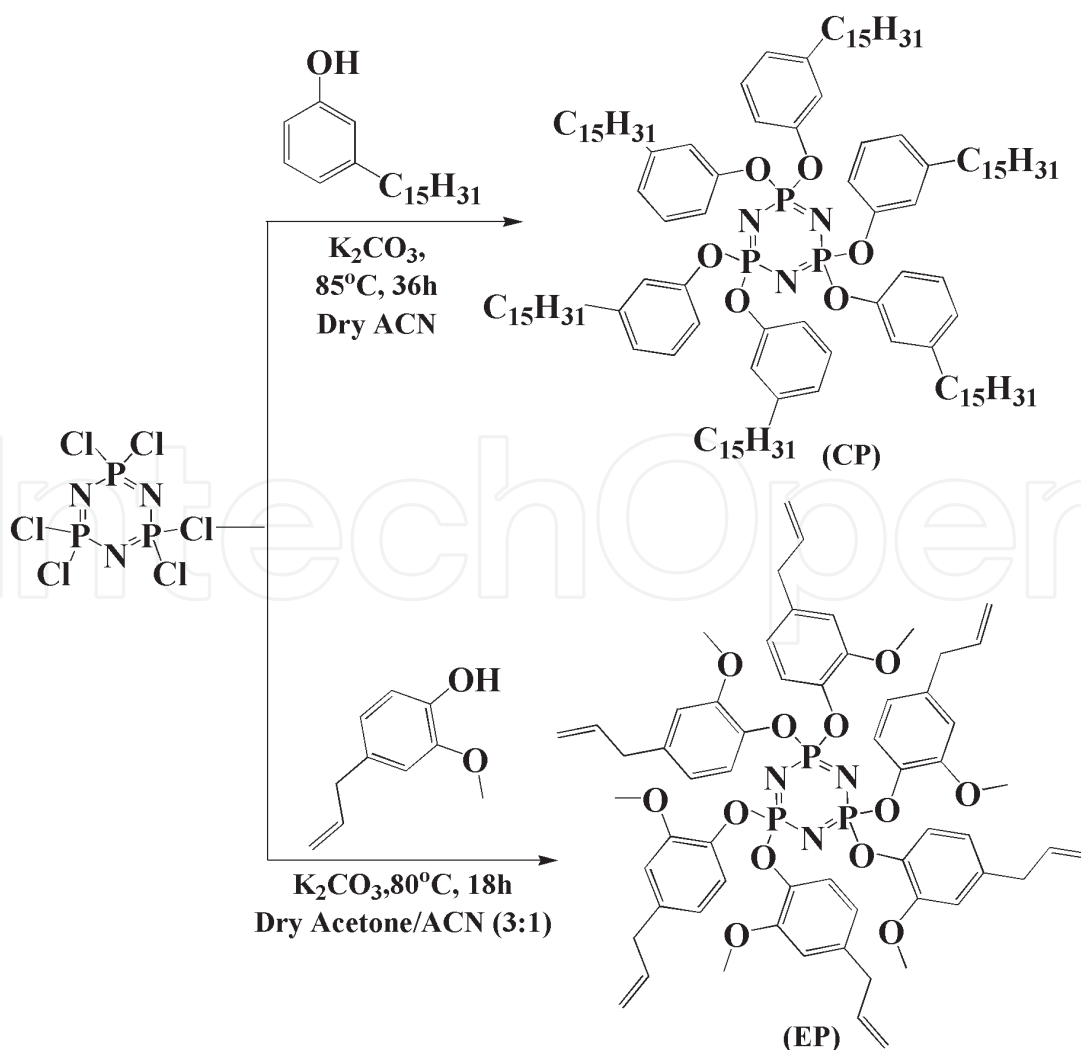


Figure 4. Synthesis of EP and CP.

Hexaegenolcyclotriphosphazene (EP) was synthesized (**Figure 4**) as per the reported procedure [72] as follows; in a 250 mL RB flask comprising a mixture of acetonitrile and acetone (1:3 ratio) under N₂ atmosphere, K₂CO₃ (143 mmol) was added. Eugenol (1.15 mmol) was dissolved in acetone and added to the above mixture, followed by the addition of N₃P₃Cl₆ (14.3 mmol). The reaction mixture was heated to 80°C and stirred for 18 h, and then allowed to cool to room temperature and evaporate the solvent. The residue was dissolved in ethyl acetate and the organic phase was washed with DM water, followed by addition of 5% NaOH and water until to obtain neutral pH. The organic layer was dried over sodium sulfate and the solvent was evaporated. Finally, the compound was purified by column chromatography using 10% ethyl acetate in hexane yield a white solid of EP.

Hexacardanolcyclotriphosphazene (CP) was synthesized (**Figure 4**) as per the reported procedure [72] using cardanol (115 mmol) was added with acetonitrile, followed by K₂CO₃ (143 mmol). A solution of N₃P₃Cl₆ (14 mmol) dissolved in acetonitrile was added to the reaction solution. The mixture was heated to 85°C and stirred for 36 h followed by work up as per the above procedure (EP). Finally, the crude compound was purified by column to get CP as a brown transparent liquid.

Polymer blend were prepared with three varying weight percentage of EP/CP, C-trisapm of 1:3, 1:1, and 3:1, by simple mixing of CP/EP and C-trisapm using tetrahydrofuran (THF) (**Figure 5**). After vaporizing the THF under the vacuum, the attained resultant mixture was thermally treated at 50, 100, 120, 160, 180, 200, 230, and 250°C for each 1 h. The blends are abbreviated as CPxTy or EPxTy where x and y are the weight percentage ratios in the blends, and T is represented for C-trisapm.

The LOI value of poly(C-trisapm) was changed from 20 to higher values (34.58 for CP₃T₁) in the case of blends. An introduction of 1.1 wt% of phosphorous (P) in C-trisapm indicated slow burning features and all other blends exhibited self-extinguishing features. The smoke density results, C-trisapm, which burns with a smoke emission of 37.80%, while those of CP and EP with P weight percentage contents of 4.75 and 8.34 wt% exhibit the value of smoke density of 34.01 and

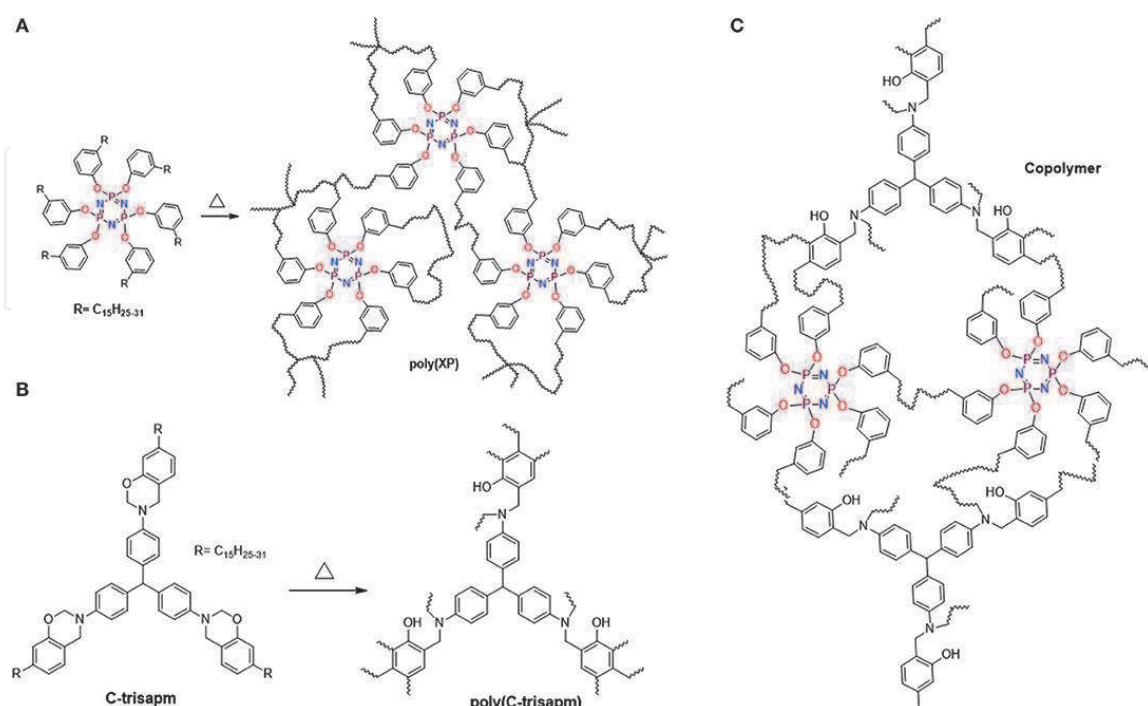


Figure 5. Plausible polymerization reactions: (A) self-crosslinking via double bonds, (B) oxazine ring-opening polymerization, (C) Co-polymerization: Co-reaction of double bonds and oxazine ring [72]. (Copyright 2020. Reproduced with permission from *Frontiers in Chemistry*).

18.80 wt% respectively. Reduction in values of smoke density are due to the higher amount of phosphazene moiety present in the polymers. The UL-94 test is a vertical burning test that decides the vertical burning properties of a polymers (**Table 1**). Neat polyhexacardanolcyclotriphosphazene (poly(CP)) and its reactive blends did not catch fire instantly, dissimilar to poly(C-trisapm). The flame resistant characteristics of cross-linked CP/C-trisapm blends was found to increase with increase in P weight percent content, which supports the results of values of LOI.

Morphology of both the interior and exterior surface of the char residue attained after smoke density test was determined using SEM analysis and the images are presented in **Figure 6**. With an increasing the weight percentage of CP, the surface exterior morphology reformed to smoother surface from rippled, whereas surface interior indicated a porous honey-combed structures detached by tinny layers of border. The founding of cracks and bubbles are agreed to the stiff outer layer in case of EP comprising co-polymers, which might have rupture to discharge the interchange of heat and oxygen, thus hindering the propagation of fire as a measure of structural safety.

To improve the flame and thermal properties, M. Alagar and his research team have reported [34, 36] hybrid approach using silica (nano-silica through in-situ sol-gel/or bio silica derived from rice-husk ash) as reinforcement in to cardanol based benzoxazine (**Figure 7**). Introduction of inorganic constituent 3-mercaptopropyl-trimethoxysilane (MPTMS) in to cardanol/furfurylamine based benzoxazine (BZ-C-F) via thiol-ene reaction followed by in-situ sol-gel techniques using tetraethoxysilane (TEOS). From thermal studies the percentage char yield indicates an increase of about 4.2 times (11.11 to 48.63%) and the values of LOI 21.94 to 36.95 for PBZ-C-F hybrids (**Table 2**) respectively. Functionalized bio-silica (FRHA) (0, 1, 5, 10, 15, and 20%) reinforced tri-substituted cardanol benzoxazine (CBz) (**Figure 8**), the value of LOI was increased with increase in weight percentage content of FRHA. Among the composites developed, 20 wt% FRHA reinforced CBz composites possesses the highest value of LOI of 36%, which is higher than that of values obtained for other composite samples. Also, the UL-94 vertical burning

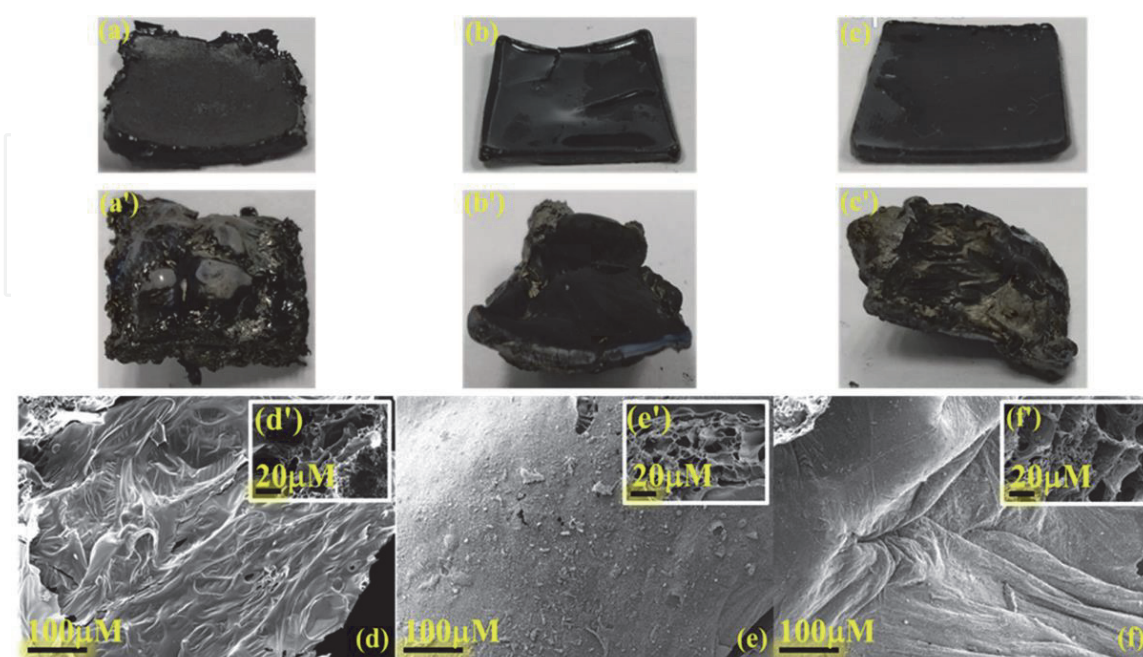


Figure 6.

Digital images of cured samples of (a) poly(CP), (b) poly(CP₃T₁), (c) poly(CP₁T₃) before (a, b, c) and after burning (a', b', c'); SEM images of poly(CP), poly(CP₃T₁), poly(CP₁T₃) surfaces of residual char: exterior (d, e, f) and interior (as inset) (d', e', f'), respectively [72]. (Copyright 2020. Reproduced with permission from *Frontiers in Chemistry*).

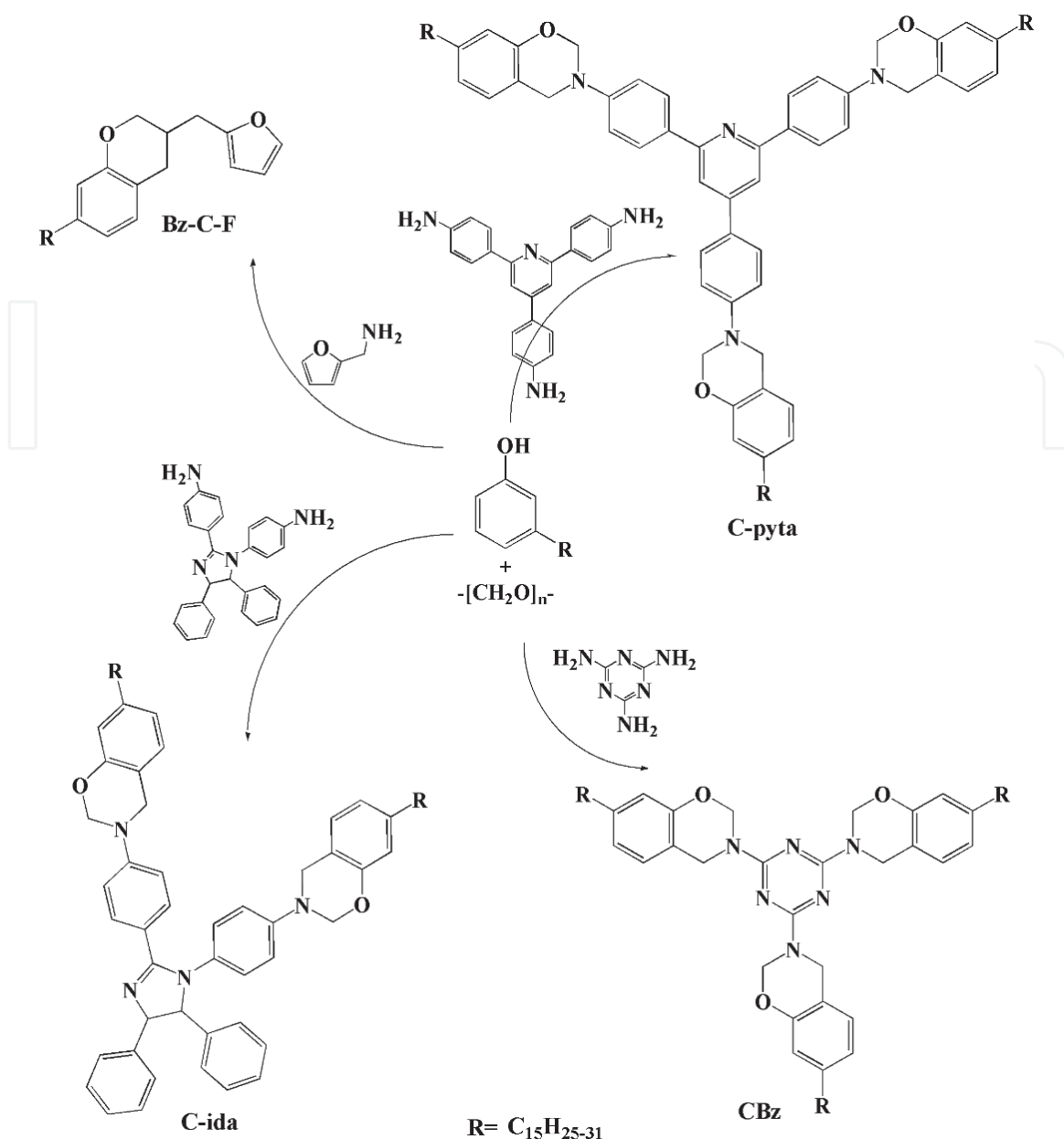


Figure 7.
Schematic synthesis of cardanol based benzoxazine monomers.

result (**Table 3**) indicates the neat CBz and CBz/FRHA (1 wt%) exhibit no rating, while 5 and 10 wt% FRHA reinforced CBz composites possess the V-2 rating. 15 and 20 wt% FRHA reinforced CBz composites showed the V-1 rating. The thermal stability and flame resistant behaviour of PBZ-silica hybrid materials are higher than those of neat PBZ as well as traditional PBA-a, due to the hybridization of silica component through chemical interaction. Further, the incorporation of higher amount of silica into the PBZ matrix reduced the volatile decomposition. In addition, the silica components offer the additional heat capacity which restricts the materials against thermal degradation.

In addition, the same research group have also reported [73] the eco-friendly cardanol-based benzoxazines (C-ida and C-pyta) synthesized from hetero-cyclic core amines (**Figure 7**), such as pyridine core triamine (pyta) and tetraarylimidazole core diamines (ida). Further, bio-composites were also prepared using 3-glycidoxypropyl-trimethoxysilane (GPTMS)-functionalized bio-silica (1, 3, 5, 7, and 10 wt%) obtained from rice husk. The thermal stability of developed PBz and its composites (**Figure 9**) is analyzed using TGA and the values obtained are presented in **Table 2**. As the bio-silica weight percentage content increases, the degradation temperature and the value

Samples	Char(%) residue	LOI	Reference
PBZ-C-F	11.11	21.94	[36]
PBZ-C-F-S-1	35.32	31.63	[36]
PBZ-C-F-S-2	41.51	34.10	[36]
PBZ-C-F-S-3	42.96	34.68	[36]
PBZ-C-F-S-4	43.77	35.01	[36]
PBZ-C-F-S-5	48.63	36.95	[36]
Poly(C-ida)	24.00	27.10	[73]
Poly(C-ida) + 1 wt% SiO ₂	27.00	28.20	[73]
Poly(C-ida) + 3 wt% SiO ₂	28.00	28.70	[73]
Poly(C-ida) + 5 wt% SiO ₂	30.00	29.50	[73]
Poly(C-ida) + 7 wt% SiO ₂	32.00	30.30	[73]
Poly(C-ida) + 10 wt% SiO ₂	35.00	31.50	[73]
Poly(C-pyta)	29.00	29.10	[73]
Poly(C-pyta) + 1 wt% SiO ₂	30.00	29.50	[73]
Poly(C-pyta) + 3 wt% SiO ₂	32.00	30.30	[73]
Poly(C-pyta) + 5 wt% SiO ₂	33.00	30.70	[73]
Poly(C-pyta) + 7 wt% SiO ₂	35.00	31.50	[73]
Poly(C-pyta) + 10 wt% SiO ₂	38.00	32.70	[73]
POSS-EPBz	24.00	24.00	[74]
POSS-GPBz	38.00	38.00	[74]
POSS-VPBz	36.00	36.00	[74]
SBz	20.00	25.00	[37]
SBz/FBS(1%)	21.00	26.0	[37]
SBz/FBS(3%)	23.00	27.00	[37]
SBz/FBS(5%)	25.00	28.00	[37]
SBz/FBS(10%)	27.00	29.00	[37]
FBz	46.00	36.00	[37]
FBz/FBS(1%)	47.00	36.00	[37]
FBz/FBS(3%)	48.00	37.00	[37]
FBz/FBS(5%)	50.00	38.00	[37]
FBz/FBS(10%)	53.00	39.00	[37]
PBZ-E-F	41.32	34.03	[75]
PBZ-E-F-S-1	53.64	38.96	[75]
PBZ-E-F-S-2	55.43	39.67	[75]
PBZ-E-F-S-3	62.78	42.61	[75]
PBZ-E-F-S-4	65.16	43.56	[75]
PBZ-E-F-S-5	67.54	44.52	[75]
PE-fa	52.00	38.30	[76]
PIE-fa	60.00	41.50	[76]

Samples	Char(%) residue	LOI	Reference
BGF-FPbz	52.4	38.50	[51]
BGF-SPbz	38.2	32.80	[51]

Table 2.
Thermal and flame resistant (LOI) properties of bio-based polybenzoxazine matrices and composites.

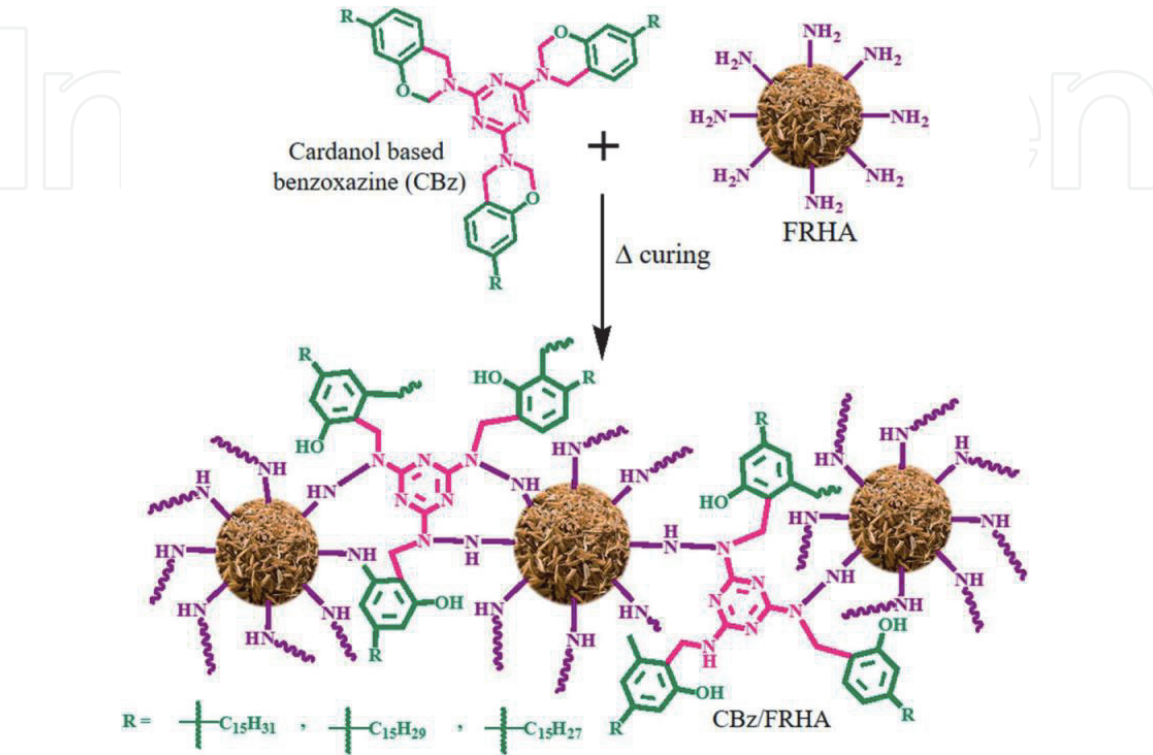


Figure 8.
The proposed schematic representation for the formation of CBz/FRHA composites [34]. (Copyright 2020. Reproduced with permission from Springer).

Samples	Char(%) residue	LOI	UL-94	Reference
CBz	12.00	22.00	—	[34]
CBz/FRHA (1 wt%)	18.00	25.00	—	[34]
CBz/FRHA (5 wt%)	32.00	30.00	V-2	[34]
CBz/FRHA (10 wt%)	36.00	32.00	V-2	[34]
CBz/FRHA (15 wt%)	40.00	34.00	V-1	[34]
CBz/FRHA (20 wt%)	47.00	36.00	V-1	[34]

Table 3.
Thermal and flame resistant (LOI and UL-94) properties of bio-based polybenzoxazine matrices and composites.

of char yield are increased. The presence of hetero-cyclic pyridine core and silica (Si-O-Si) inherently provides to the higher thermal stability. The LOI value of pyridine core cardanol-based polybenzoxazine possesses a higher residual char (29.1%) than that of other cardanol based PBz's. The values of LOI were increased with increase in weight percentage content of bio-silica. Among the composites studied, 10 wt% bio-silica reinforced composites indicated the LOI value of 32.7.

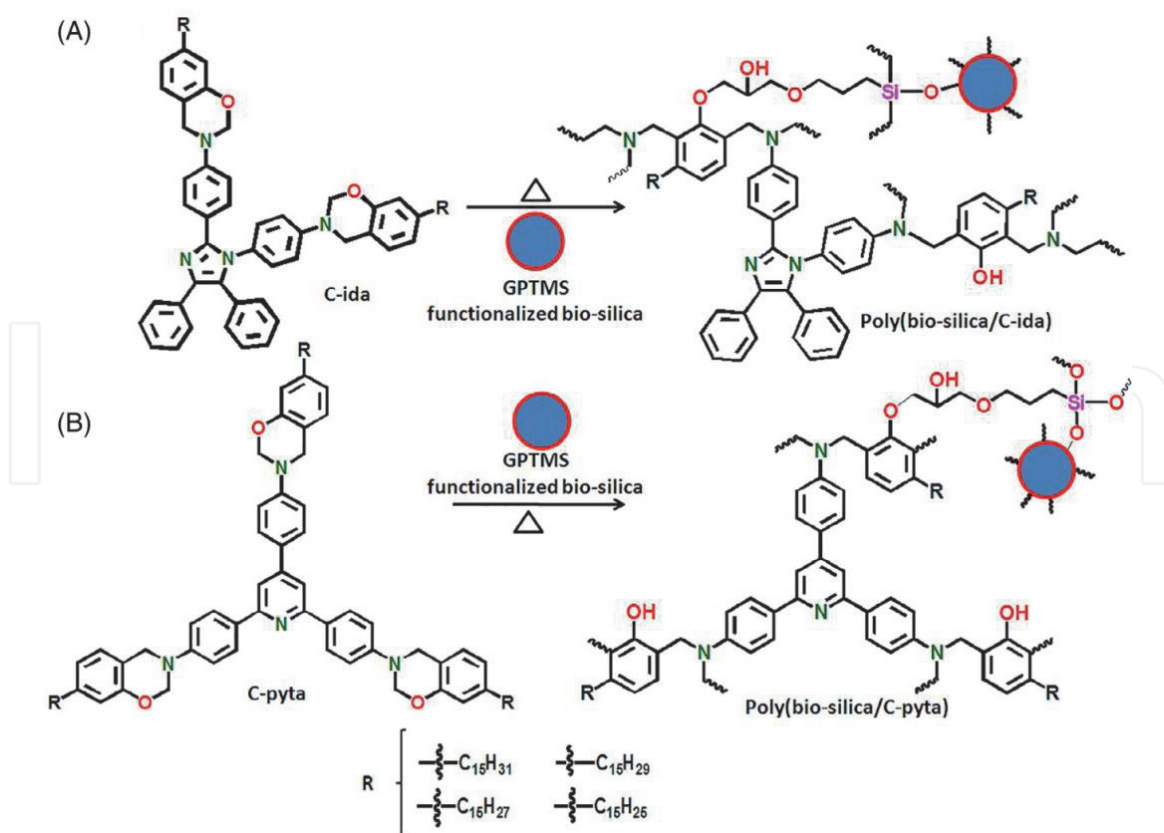


Figure 9. Preparation of bio-silica reinforced, (A) C-ida polybenzoxazine and (B) C-pyta polybenzoxazine composites [73]. (Copyright 2020, Reproduced permission from Society of Plastics Engineers).

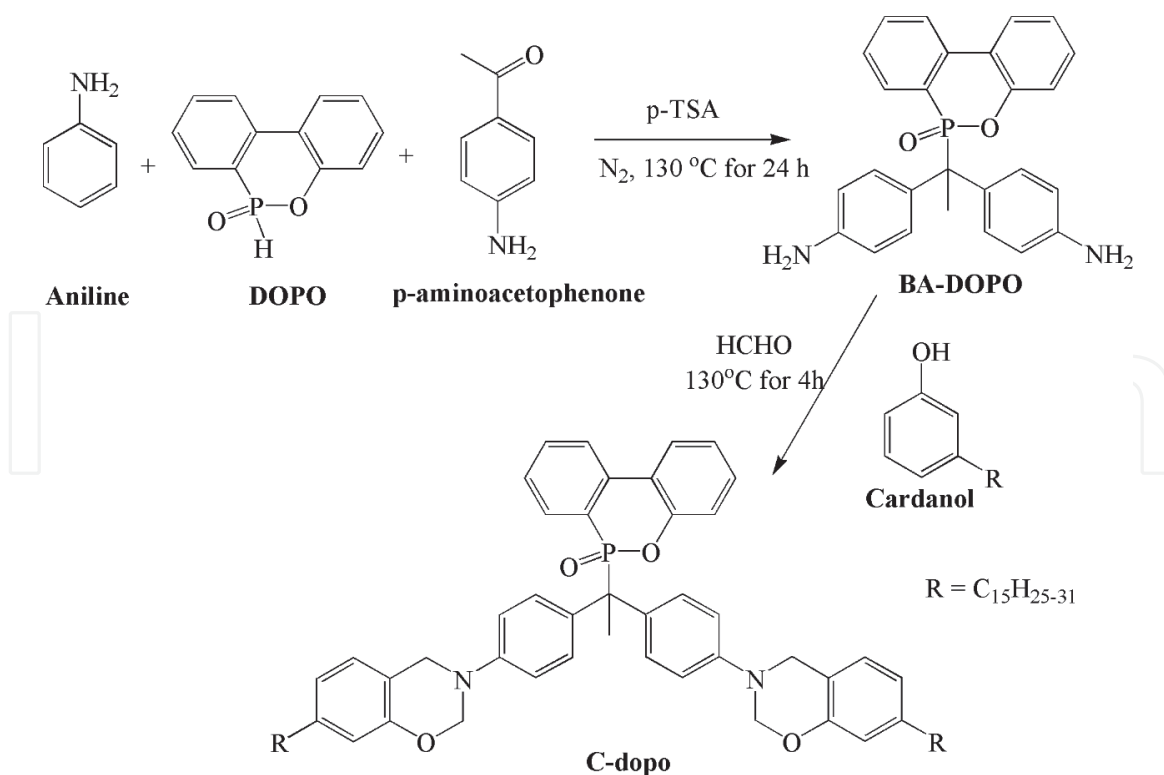


Figure 10. Synthetic routes of BA-DOPO and cardanol based benzoxazine monomer (C-dopo).

Xin Wang and Yuan Hu research group have reported [77] the phosphorus-containing cardanol based benzoxazine (C-dopo) monomer (**Figure 10**) and was synthesized using cardanol, DOPO-based diamine (BA-DOPO) and formaldehyde.

Later, epoxy (EP)-C-dopo composites was developed by thermally activated polymerization. To addition, to improve the flame resistant efficacy, BG nano-sheets was introduced in to EP-C-dopo systems. The influence of cardanol based benzoxazine and BG nano-sheet on thermal, and flame retardant properties of EP resin was studied. The flame retardant properties of cured EP and EP/C-dopo composites were studied using LOI and UL-94 vertical burning performance, as presented in **Table 4**. Neat epoxy has a LOI value of 25%, and burns aggressively with no UL-94 classification. The introduction of flame retardant C-dopo prompts a remarkable increment in the LOI values and UL-94 rating. 10 wt% C-dopo introduced EP/C-dopo-1 system shows the LOI value of 31% and V-1 rating in UL-94 test. Further, increasing the C-dopo amount marginally increase the LOI values and achieved as V-0 rating from UL-94. In contrast, in combination of 8 wt% C-dopo and 2 wt% boron-doped graphene (BG), the EP/C-dopo/BG-1 system passed V-0 rating from UL-94 test, signifying the presence of BG effectively depresses the ignition ability of the EP composites. Further, the EP/C-dopo/BG-2 and EP/C-dopo/BG-3 systems exhibit higher LOI values and UL-94 V-0 rating performance.

The flammability behavior of cured EP and EP/C-dopo composites was further analyzed with cone calorimeter. **Table 4** shows the total heat release (THR) and heat release rate (HRR) values of EP and EP/C-dopo composites. Numerous significant flame related parameters including time to PHRR (TPHRR), time to ignition (TTI), peak heat release rate (PHRR), THR, smoke produce rate (SPR) and fire growth rate index (FIGRA) are presented in **Table 4**. From the MCC data, neat EP shows a high PHRR value of 1262 kW/m². While, the PHRR of the 10 wt% EP/C-dopo composites decreases to 1119 kW/m². Subsequent increasing of C-dopo content leads to further reduction in PHRR values to 920 and 962 kW/m², respectively. Further introduction of BG nano-sheet in to EP/C-dopo composites leading to the further reduction in PHRR to 870 kW/m², 650 kW/m², and 716 kW/m² for EP/C-dopo/BG-1, EP/C-dopo/BG-2 and EP/C-dopo/BG-3, respectively. The most substantial PHRR reduction is perceived in case of EP/C-dopo/BG-2. THR of neat EP indicates the speedy heat release and reached the value of 84.7 MJ/m² at the end of combustion. In contrary, both of EP/C-dopo and EP/C-dopo/BG composites observed as lower heat release to certain amount, suggesting that the introduction of C-dopo and BG into EP possibly will trigger to reduce the combustible volatile product. The incorporation of C-dopo leads to a marginal reduction in TTI. Further, the introduction of BG into EP/C-dopo increases the TTI, owing to the “tortuous path” influence of BG that retards the volatilization of combustible degradation products. Neat EP, EP/C-dopo systems reveal no changes in the value of SPR, while

Sample	Formulations			LOI %	UL- 94	TTI (s)	T _{PHRR} (s)	PHRR (kW/m ²)	THR (MJ/m ²)	SPR m ² /s	FIGRA kW/ m ² s
	EP	CBz	BG								
EP	100	0	0	25	NR	53	110	1262	84.7	0.40	11.5
EP/C-dopo-1	90	10	0	31	V-1	49	92	1119	80.5	0.39	12.2
EP/C-dopo-2	85	15	0	32	V-0	50	95	920	79.4	0.40	9.7
EP/C-dopo-3	80	20	0	33	V-0	50	100	962	77.2	0.38	9.6
EP/C-dopo/BG-1	90	8	2	30	V-0	49	89	870	75.9	0.29	9.8
EP/C-dopo/BG-2	85	13	2	33	V-0	52	120	650	74.4	0.29	5.4
EP/C-dopo/BG-3	80	18	2	33	V-0	56	120	716	78.7	0.31	6.0

Table 4.
Formulations and flame retardant properties of neat EP, EP/CBz and EP/CBz/BG composites.

the EP/C-dopo/BG system indicate the lower value of SPR, designating that BG nano-sheet with proficient barricade effect can help as suppressant of smoke in the burning method. The FIGRA of the neat EP is $11.5 \text{ kW}/(\text{m}^2 \cdot \text{s})$. In comparison, excluding that the EP/C-dopo-1 system displays a marginally improved value of FIGRA, all other systems display lower value of FIGRA. The most noticeable result is perceived in case of EP/C-dopo/BG-2 ($5.4 \text{ kW}/(\text{m}^2 \cdot \text{s})$), suggesting the considerably inhibited fire hazards.

3. Eugenol based polybenzoxazines for flame resistant applications

Among renewable phenolic alternatives to substitute the conventional phenolic, eugenol appears as most imminent raw-materials for the sustainable PBz's production owing to their abundance availability and low cost production. Eugenol is obtained from several bio-sources including, clove, tulsi, cinnamon, pepper, turmeric, and thyme. The eugenol structure is very exciting as allyl functional group permits additional cross-linking with numerous functional groups. In addition, the phenolic group offers numerous chemical reactions and formation of products including esterification, cyanogenation, alkylation, and novalac, epoxy and BZs, etc.

Sarojadevi Muthusamy research group reported [74] the successful synthesis of the polyhedral oligomeric silsesquioxane (POSS) tethered PBz nano-composites using renewable bio-phenols (eugenol, guaiacol, vanillin), POSS-octaamine with paraformaldehyde through Mannich reaction. The developed POSS-PBz nano-composites (**Figure 11**) from sustainable bio-sources have a great potential application as high-performance materials owing to its excellent thermal and flame resistant properties. Thermal and flame resistant properties of POSS-PBz nano-composites were determined using TGA under nitrogen atmosphere. The char yield percent and LOI values (**Table 2**) are found to be 24, 38, 36 and 27.1, 32.7, 31.9 respectively for POSS-EPBz, POSS-GPBz, and POSS-VPBz. Among the nano-composites developed POSS-GPBz nanocomposites shows better thermal and flame resistant properties over other two POSS-PBz systems.

Alagar group have also reported [37] the new type of bio-based PBz's synthesized using eugenol and furfurylamine/stearylamine through greener synthetic

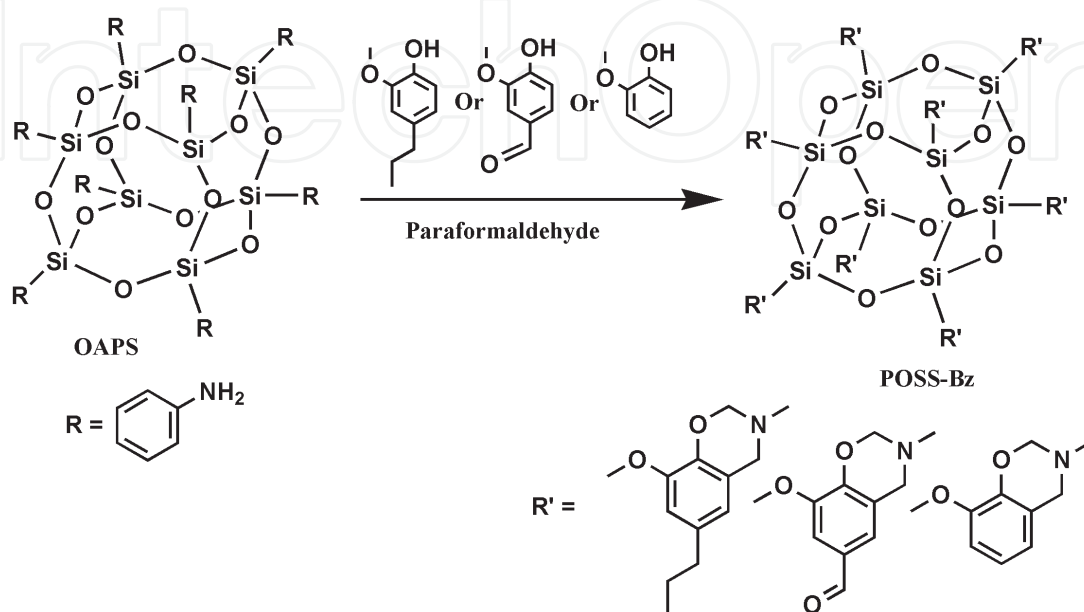


Figure 11.
Synthesis POSS based renewable benzoxazine monomers.

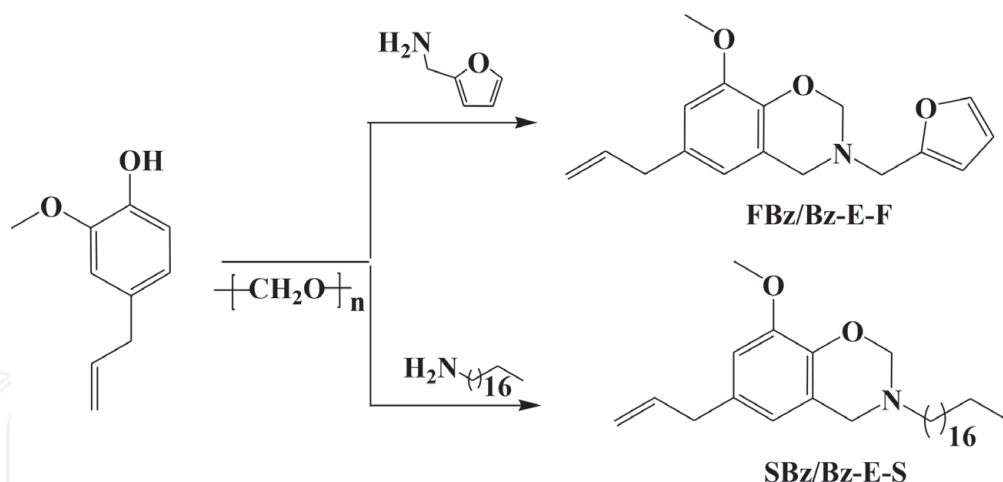


Figure 12.
Synthesis of eugenol based benzoxazine monomers using different amines.

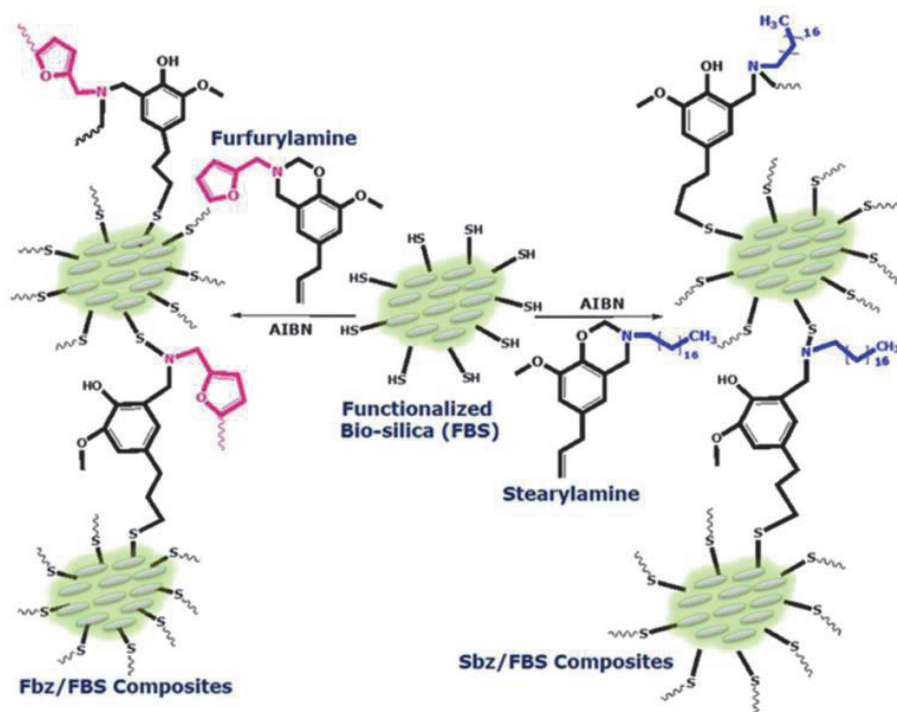


Figure 13.
The schematic representation for the formation of FBS/FBz and FBS/SBz [37] composites.

approach (**Figure 12**). The synthesized benzoxazine monomers were further reinforced with varying weight percentage content (0, 1, 3, 5, and 10 wt%) of bio-silica obtained from rice-husk to fabricate PBz hybrid composites (**Figure 13**). The TGA results obtained inferred that the developed bio-silica reinforced PBz composites possess the higher thermal and improved flame resistant properties. The furfuryl amine based PBz (FBz), the char yield value was increased to 53% from 46%. In case of stearyl amine based PBz (SBz), the char yield value was increased to 27% from 20%. The value of char yield of SBz is lower than that of FBz because of the presence of long aliphatic chain. In common, the polymeric materials with LOI values more than 26 are considered as flame-retardant materials, it was found that the bio-silica reinforced bio-based PBz's composites possess the LOI values of 25 to 39 (**Table 2**), signifying an enhanced flame resistant nature of the developed bio-based PBz composites.

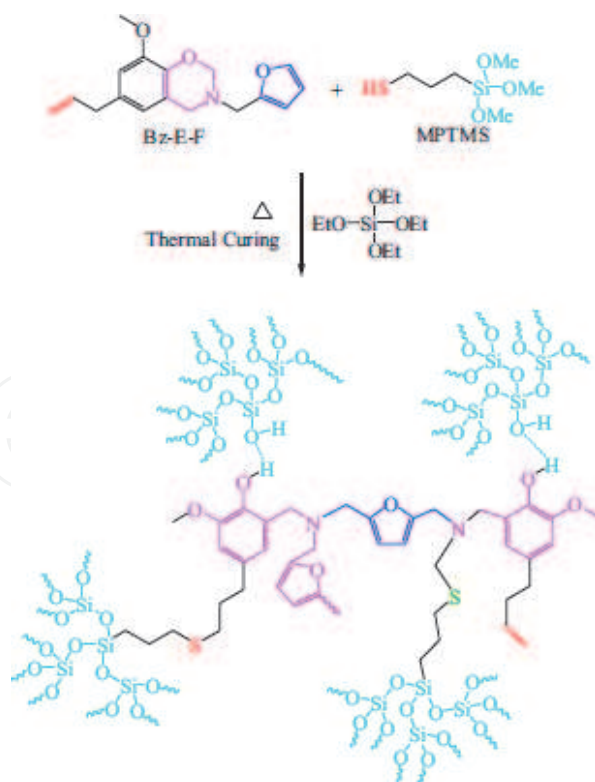


Figure 14.
Schematic representation for the preparation of renewable PBz-E-F-silica hybrids [75].

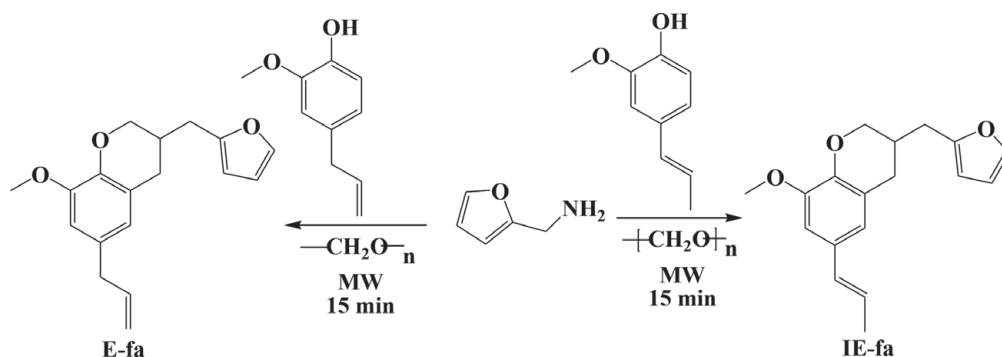


Figure 15.
Synthesis of renewable bio-based isomeric benzoxazine E-fa and IE-fa.

In addition, the same group have further reported [75] the high thermal and flame resistant PBz-silica hybrid materials were synthesized using eugenol and furfurylamine via sol-gel-techniques (**Figure 14**). An inorganic component of TEOS was introduced into eugenol- benzoxazine (BZ-E-F) with the help of MPTMS as a coupling agent viz. thiol-ene click approach. The thermal studies indicate that the char yield increases to 67.54 from 41.32 (neat PBz) and LOI increased to 44.52 for PBZ-E-F silica hybrid from 34.03 for neat PBz (**Table 2**).

Bimlesh Lochab research group have reported [76] the synthesis of sustainable bio-based benzoxazine monomers (**Figure 15**) using isomeric phenols, eugenol (E) and iso-eugenol (IE), and furfurylamine (fa) to form E-fa and IE-fa monomer, respectively. The monomers differ in the position of the double bond in the p-substituted propylene unit forming non-conjugated Vs. conjugated alkylene chain with the benzene ring containing benzoxazine in E-fa and IE-fa respectively. In comparison to other bio-based PBz's, both PE-fa and PIE-fa exhibited the higher thermal stability and high flame resistant properties. The char residue values of PE-fa and PIE-fa are 52 and 60 respectively and the LOI values observed are 38.3 and 41.5 respectively (**Table 2**).

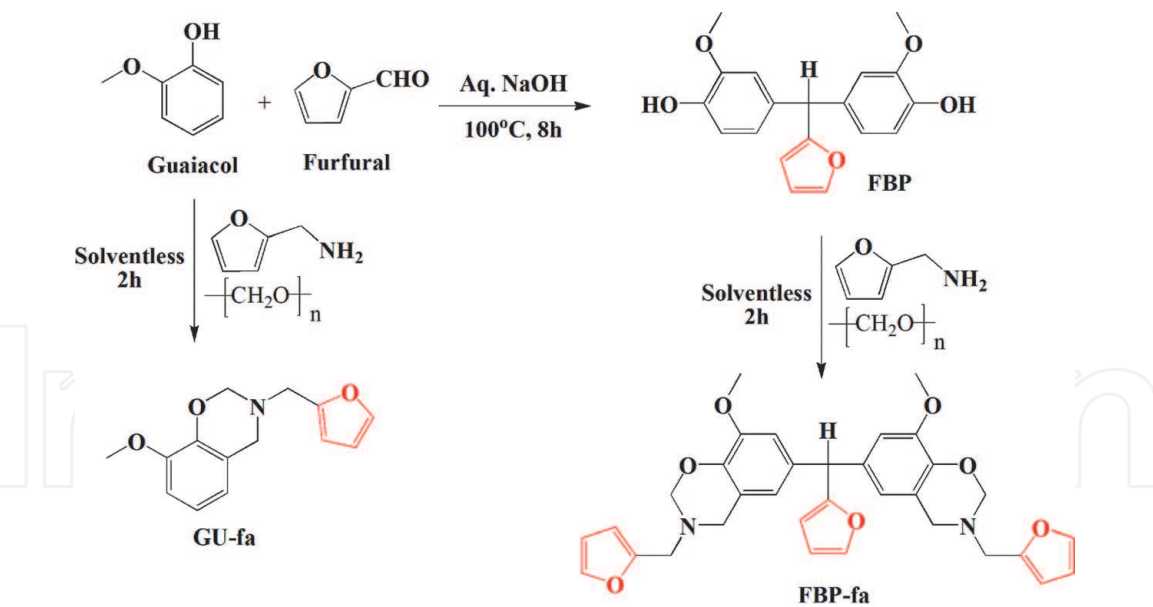


Figure 16.
Synthesis of fully bio-based mono and tri-furan functional mono and bis-benzoxazine resin.

4. Guaiacol based polybenzoxazine for flame resistant applications

Kan Zhang research group have developed [78] the fully bio-based tri-furan functional bis-benzoxazine resin (**Figure 16**) and was synthesized using furfural, guaiacol, furfurylamine and paraformaldehyde via a two-step reaction approach. In the first step, bio-based bis-phenol containing furan ring was synthesized using furfural and guaiacol via base mediated condensation reaction. Then the bio-based sustainable tri-furan functional bis-benzoxazine (FBP-fa) was synthesized using bio-based bis-phenol, furfurylamine and paraformaldehyde through greener approach. The flammability behaviour of poly(GU-fa) and poly(FBP-fa) was assessed using LOI. As a result, poly(GU-fa) and poly(FBP-fa) show LOI values of 39.9 and 42.3 respectively. Both PBz's possess better LOI values in the self-extinguishing region (LOI > 28). Also MCC analysis was utilized further to assess the flammability performance of poly(GU-fa) and poly(FBP-fa). From the MCC characterization of poly(GU-fa) and poly (FBP-fa) display HRC values of 79.6 and 30.4 J/gK, respectively (**Table 5**).

Sample	Char residue (%)	LOI %	HRC (J/gK)	THR (KJ/g)	Reference
Poly(GU-fa)	56	39.9	70.6	6.5	[78]
Poly(FBP-fa)	62	42.3	30.4	5.8	[78]
Poly(RES-a)	55		79.7	15.9	[45]
Poly(RES-ac)	74		30.7	6.0	[45]
Poly(RES-ch)	59		73.4	14.2	[45]
Poly(RES-fa)	64		54.0	9.3	[48]
Poly(API-fa)-1	63	42.7	22.5	11.2	[79]
Poly(API-fa)-1	66	43.9	20.2	9.4	[79]
Poly(NAR-fa)	64		31.9	6.6	[80]

Table 5.
Formulations and flame retardant properties of bio-based polybenzoxazines.

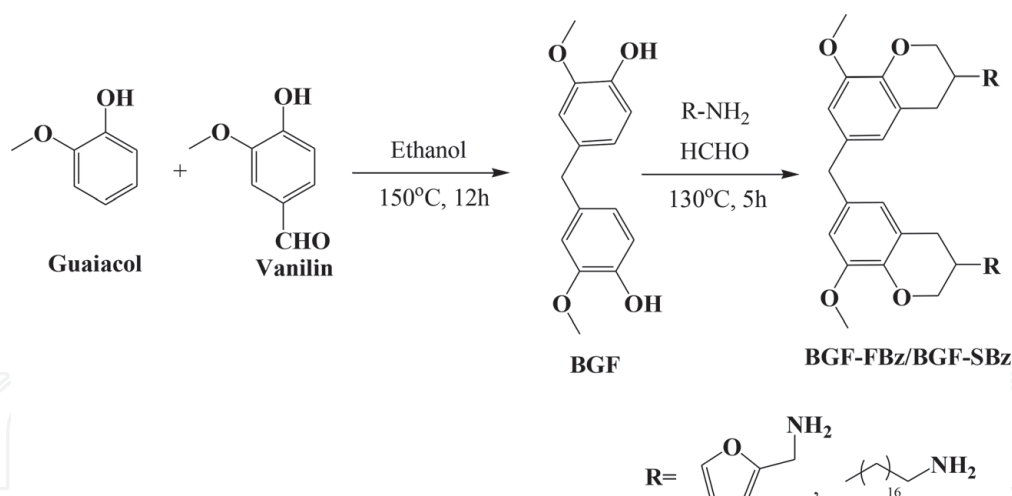


Figure 17.
Synthesis of bisguaiacol-F (BGF) and BGF based benzoxazine monomers.

Further, poly(GU-fa) infers the THR value of 6.5 KJ/g, whereas poly(FBP-fa) displays a fairly lower THR value of 5.8 KJ/g. The data of flame related properties of both PBz's are presented in **Table 5**. Unexpectedly, the HRC value of developed poly(FBP-fa) gives significantly lower value than that of earlier reported polymers. Furthermore, poly(FBP-fa) displays very lower flammability characteristics than that of many other reported PBz's. It is well-known that the HRC value less than 300 J/gK can be observed as self-extinguishing while, whereas the HRC values less than 100 J/gK are designated as non-ignitable materials.

M. Sarojadevi research group have also synthesized [51] the BGF and BGF-based benzoxazines (**Figure 17**) viz., bis[(3-(furan-2-yl) methyl)-3,4-dihydro-2H benzoxazin-6-yl] methane and bis[(3-octadecyl)-3,4-dihydro-2H benzoxazin-6-yl] methane as an substitute to BPA. The LOI values (**Table 2**) of the BGF-FPBz and BGF-SPBz was found to be 38.5 and 32.8 respectively indicating the high flame retardancy. As expected, the developed PBz's with these LOI values are greater than 26 endorsing outstanding flame resistant property.

5. Resveratrol based polybenzoxazine for flame resistant applications

Hatsuo Ishida and Kan Zhang group reported [45, 48] the series of thermally stable and flame resistant resveratrol-based tri-functional benzoxazine monomers

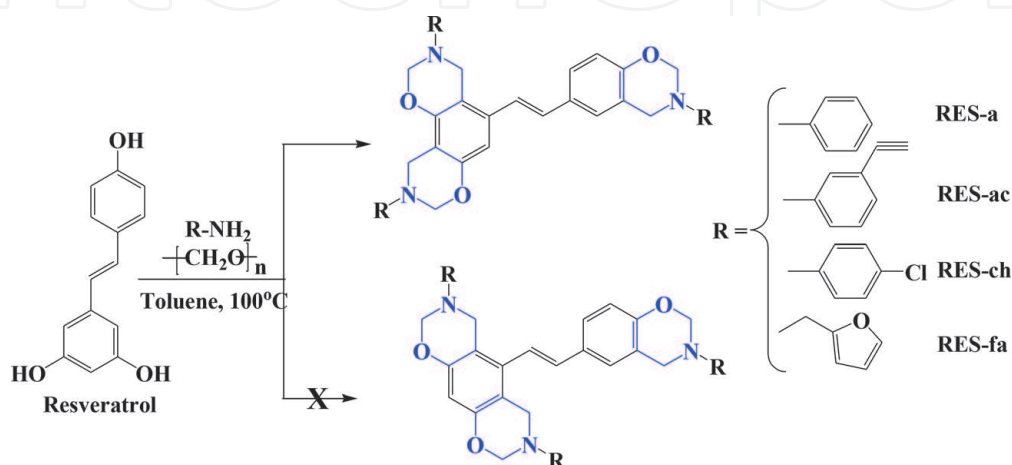


Figure 18.
Synthesis of resveratrol-based tri-functional benzoxazine monomers.

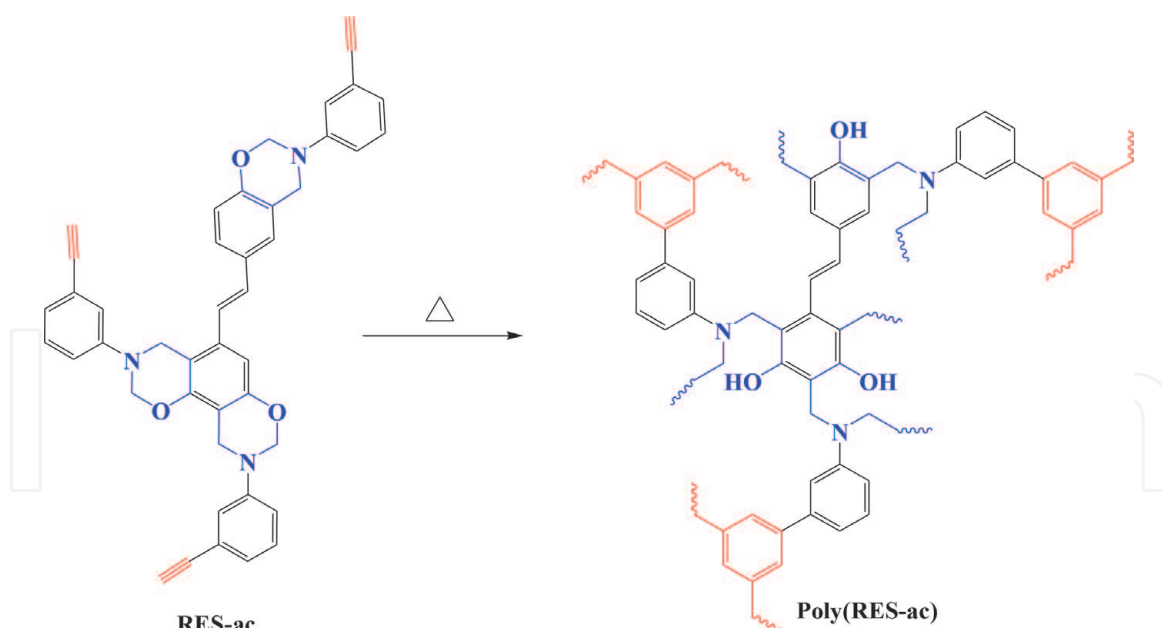


Figure 19.
Schematic representation of proposed thermal behaviors of RES-ac.

(**Figure 18**) have been produced using resveratrol, different amines (aniline, 4-chloroaniline, 3-aminophenylacetylene, and furfurylamine) and paraformaldehyde. The thermal and flammability performances of the developed PBz's are studied using TGA and MCC respectively. Among the benzoxazine studied, resveratrol-based, tri-functional benzoxazines containing acetylene possesses the highest thermal stability with a value of T_g over the 350°C , 10% weight loss at 465°C , and char yield of 74%. Further, the developed polybenzoxazine infers the extremely low heat release capacity of 30.7 J/gK and total heat release value of 6.0 kJ/g .

MCC analysis was performed to analyse the quantitative features of flame resistance of PBz's. Usually, the extreme value of specific HRR can be used to assess the HRC, which is considered as unique best single interpreters for the flame resistance of materials. Here, poly(RES-a), poly(RES-ch), poly(RES-ac) (**Figure 19**), and poly(RES-fa) were analysed at the heating rate of 1°C/s over the temperature range $100 \sim 750^\circ\text{C}$. As illustrated in MCC results (**Table 5**) of poly(RES-a), poly(RES-ch), poly(RES-ac) and poly(RES-fa) indicate HRC values of 79.7, 73.4, 30.7, and 54 J/gK , respectively. Moreover poly(RES-a), poly(RES-ch), and poly(RES-fa) exhibit THR values of 15.9, 14.2, and 9.3 KJ/g , while poly(RES-ac) shows a lower THR value of 6.0 KJ/g . The data obtained from thermal and flame resistant properties for PBz's are presented in **Table 5**. The value of HRC for poly(RES-ac) is significantly lesser than those of other polymers. Moreover, the HRC value of poly(RES-ac) is even lower than that of the thermosets from ortho-amide and ortho-imide benzoxazines, which exhibited one of the lowest HRC values of all polymers. Obviously, the PBz formed from the ring opening polymerization along with the cyclo trimerization of acetylene results in a considerable HRC reduction. Thus, the newly developed resveratrol-based tri-benzoxazine monomer containing acetylene group has greatest prospective applications as anti-flammable and fire resistant matrix for advanced composites.

6. Apigenin based polybenzoxazine for flame retardant applications

Kan Zhang research group reported [79] the synthesis of a new fully bio-based bis-benzoxazine (API-fa) (**Figure 20**) using apigenin as phenolic precursor and

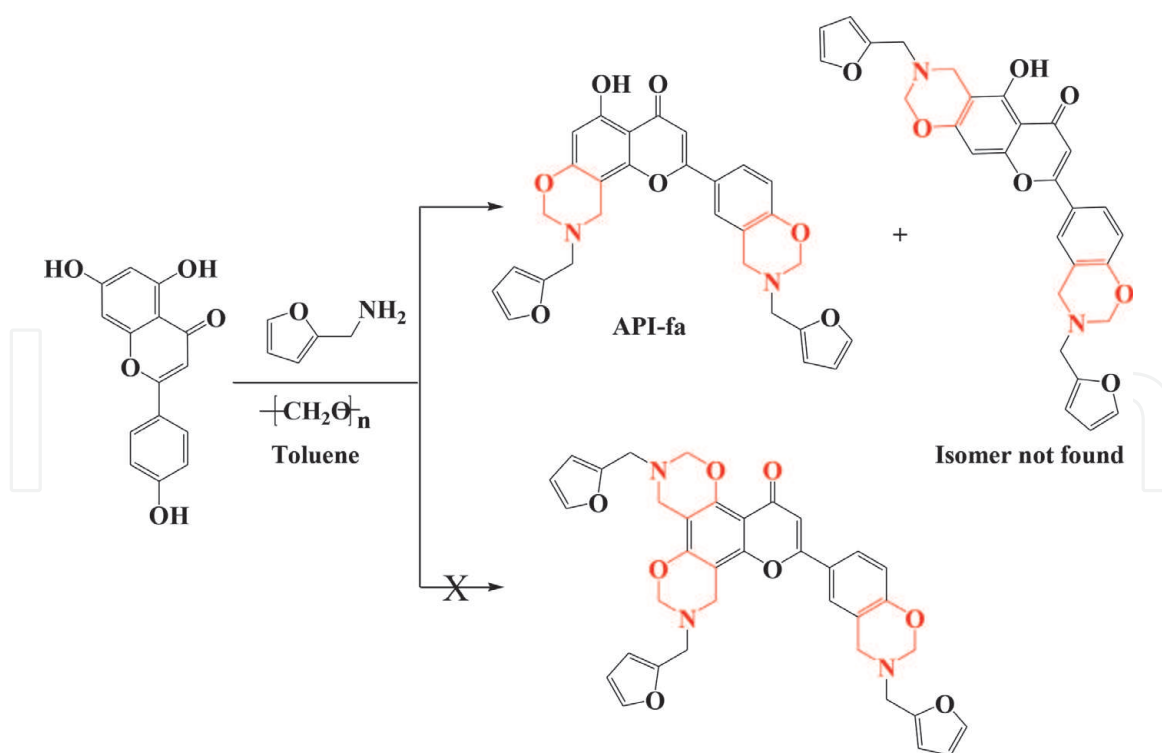


Figure 20.
Synthesis of apigenin-based bis-benzoxazine (API-fa).

furfurylamine as amine precursor both derived from bio-sources. The well-structured intra-molecular hydrogen bond in API-fa is probable to be a stable latent heat formulation, which prolongs the shelf life of the Bz resin. Besides, the benzopyrone and furan rings with carbon–carbon double bonds in the API-fa are proficient of making further cross-linking networks, which are anticipated to considerably increase the mechanical, thermal and flame resistant properties of the resulting PBz thermosets. Remarkably, the thermal possessions of the API-fa based PBz achieved in this work are considerably higher than those of recently reported PBz's. The resulting polymerized PBz thermoset developed from API-fa indicates the high glass transition temperature of 376°C, a higher char residue of 66%, with an extremely lower heat release capacity of 20.2 J/gK (**Table 5**).

Thus, the LOI values obtained for poly(API-fa)-1 and poly(API-fa)-2 are as high as 42.7 and 43.9, respectively (**Table 5**). From the MCC analysis of poly(API-fa)-1

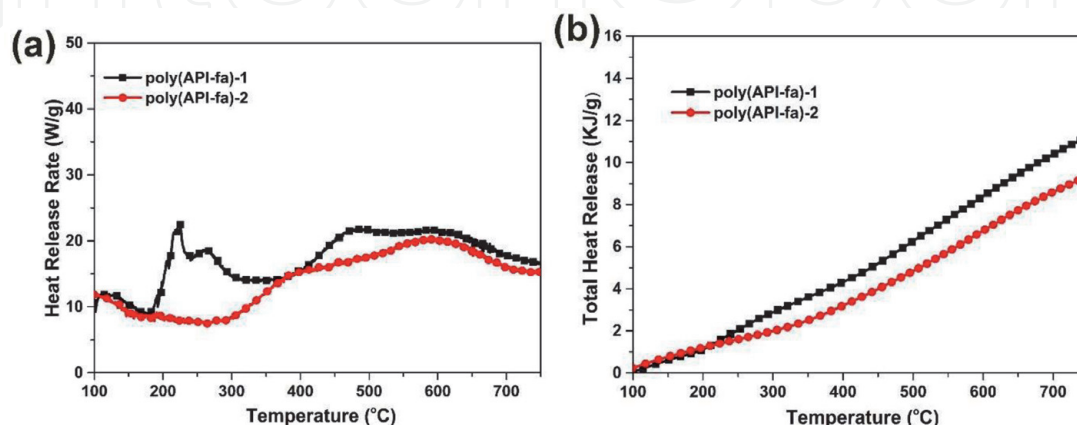


Figure 21.
Microscale combustion calorimetric (MCC) analysis of poly(API-fa)-1 and poly(API-fa)-2. (a) heat release rate, and (b) total heat release as a function of the temperature [79]. (Copyright 2020, reproduced permission from Royal Society of Chemistry).

and poly(API-fa)-2 was presented in **Figure 21**. **Figure 21a**, HRR maximums are perceived at 225°C and 591°C for poly(API-fa)-1 and poly(API-fa)-2, respectively. Also, the values of HRC are observed as 22.5 and 20.2 J/gK respectively. Furthermore, poly(API-fa)-1 indicates the THR value of 11.2 KJ/g, whereas poly(API-fa)-2 shows a moderately lower value of THR (9.4 KJ/g) (**Figure 21b**). These results support the very exceptional flame retardant behaviour of apigenin based polybenzoxazines.

7. Naringenin based benzoxazine for flame retardant applications

Kan Zhang et al., synthesized [80] a fully bio-based benzoxazine monomer (NAR-fa) using Naringenin, furfurylamine and paraformaldehyde (**Figure 22**). Thermal properties of the resulting co-polymeric thermosets were maintained or slightly enhanced, while those related to flame retardancy improved to about 38 and 51% for THR and HRC, respectively (**Table 5**).

Figure 23 displays the graphic representation of the HRR as a function of temperature, where the maximum HRR is detected at 455°C. From **Figure 23**, it was calculated a HRC and THR of 31.9 J/gK and 6.6 KJ/g, respectively. The HRC value for poly(NAR-fa) is significantly lower than those reported for PBz's with high

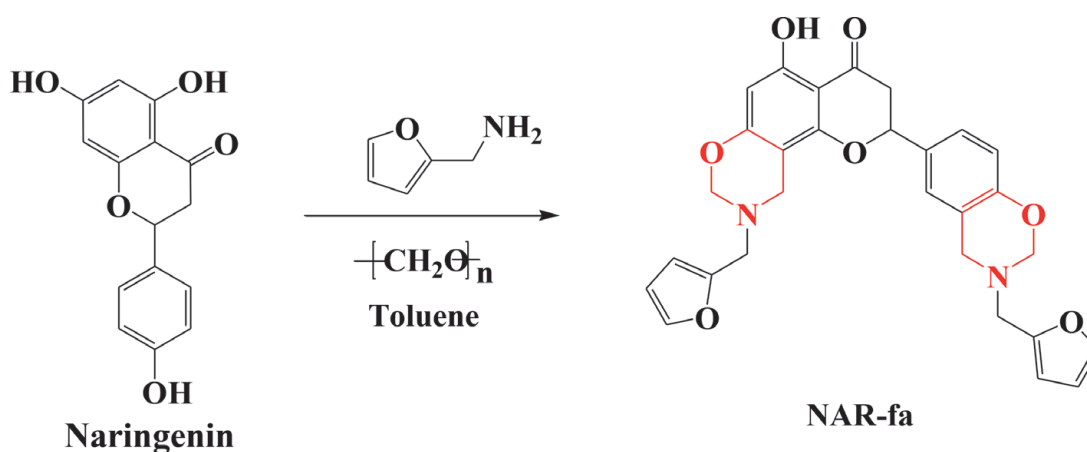


Figure 22.
Synthesis of fully bio-based naringenin-benzoxazine monomer (NAR-fa).

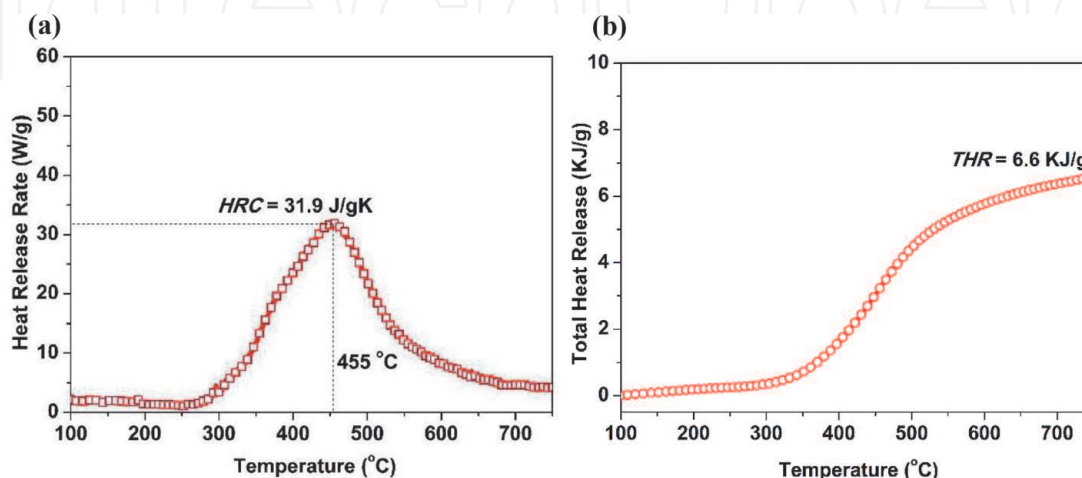


Figure 23.
Microscale combustion calorimetric (MCC) analysis of poly(NAR-fa). (a) heat release rate, and (b) total heat release as a function of the temperature [80]. (Copyright 2020, reproduced permission from Royal Society of Chemistry).

flame resistance properties attained upon polymerization of ortho-imide and ortho-amide functionalized benzoxazine monomers. These results show that poly (NAR-fa) can indeed be classified as non-ignitable given that its HRC is lower than 100 J/gK.

8. Phloroglucinol based polybenzoxazine for flame retardant applications

Phloroglucinol (P) is also a kind of bio-based renewable phenolic material widely occurred in greenery plants, and it contains three phenolic hydroxyl groups can form a three-arm benzoxazine monomer, which possibly increase the cross-linking density of cured PBz resin result in higher thermal stability, mechanical behaviour and other properties. Zuomin Zhan et al. reported [81] the development of fully bio-based low temperature cured polybenzoxazines. In order to achieve high thermal stability, bio-mass-derived phloroglucinol (P) as phenol source, furfurylamine (FA) or P-amino benzoic acid (PABA) as amine source and paraformaldehyde were used to synthesize two novel fully bio-based benzoxazines (**Figure 24**). The obtained fully bio-based polybenzoxazines possesses a high char yield of 53.0%, low HRC of 37 J/gK and a low THR of 8.3 kJ/g.

The key combustion parameters, including HRC, THR, PHRR and TPHRR, were obtained and summarized in **Table 6**. MCC curves of all system exhibited dissimilar two heat release peaks. HRC, THR and PHRRs of P(P-paba) were 86 J/gK, 12.3 kJ/g, 79.6 W/g and 39.6 W/g respectively and only about half of P(BA-a) (169.0 J/g-K, 23.6 kJ/g, 166.6 W/g and 94.0 W/g). Its TPHRR2 (528°C) was 9°C higher than that of P(BA-a) (519°C). These consequences were ascertained that the formation of H-bonding in the molecular structure of P(P-paba) might effectively diminish the

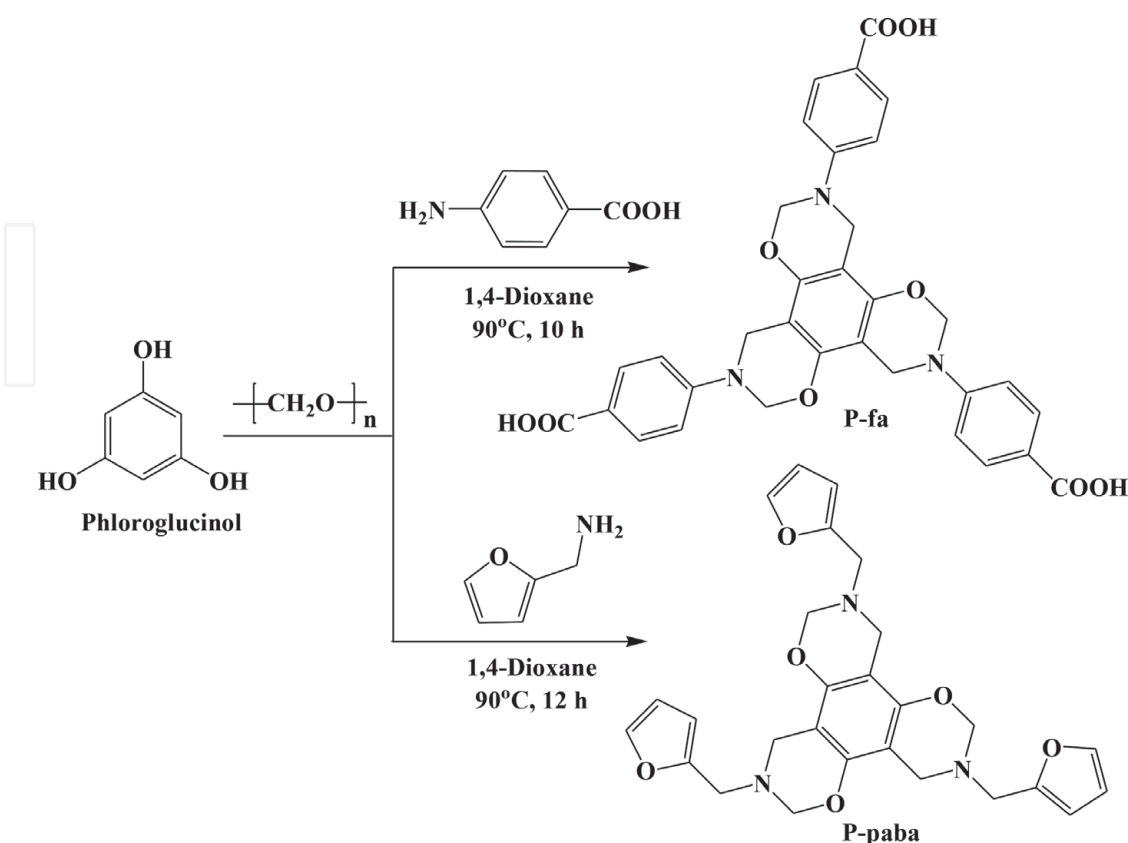


Figure 24. Synthesis phloroglucinol based benzoxazine monomers (P-fa and P-paba).

Sample	Char residue (%)	HRC (J/gK)	THR (KJ/g)	PHRR ₁ (W/g)	T _{PHRR1} (°C)	PHRR ₂ (W/g)	T _{PHRR2} (°C)	Reference
P(P-fa)	53	37	8.3	37.8	348	21.8	441	[81]
P(P-fa (9.5) + P-paba (0.5))	52	39	9.4	34.5	323	22.9	441	[81]
P(P-fa (9) + P-paba (1))	53.3	38	9.2	34.0	312	22.3	454	[81]
P(P-fa (8) + P-paba (2))	50.3	45	9.8	39.7	305	23	465	[81]
P(P-paba)	34.7	86	12.3	79.6	300	39.6	528	[81]
P(BA-a)	30.6	169	23.6	166.6	448	94.0	519	[81]

Table 6.
Thermal and flame retardant properties of bio-based phloroglucinolbased tri-functional polybenzoxazines.

heat release values. Though, TPHRR1 of P(Ppaba) was about 300°C, signifying again that the degradation of benzoxazine diminished without Mannich structure formation. In comparison with P(P-paba), HRC value of 37 J/gK, THR value of 8.3 kJ/g and PHRRs value of 37.75 W/g and 21.84 W/g of P(P-fa) diminished considerably, and merely 20–35% of those of P(BA-a), specifying that the presence of furan group could enhance the additional cross-linking density and greatly decrease the heat release of fully bio-based sustainable benzoxazine resins. Thus, it may possibly be expected that P(P-paba) and P(P-fa) had possesses best flame resistant behaviour than that of P(BA-a).

9. Summary and conclusion

In the present chapter, we have reviewed the synthesis of bio-based benzoxazine monomers with varying molecular design including mono, di, tri, tetra, hexa, and octa functional oxazine using renewable bio based raw materials such as cardanol, eugenol, guaiacol, vanillin, phloroglucinol, naringenin, apigenin, resveratrol, furfurylamine, stearylamine and etc. The present chapter also discusses the preparation of polybenzoxazine bio-composites using bio-silica, silica particle through sol-gel approach and boron complexes and their thermal and flame resistant properties using various characterization techniques including LOI, UL-94 vertical flame test, smoke density, SEM analysis, and MCC. Data obtained from the thermal and flame resistant analysis, the newly developed resveratrol, phloroglucinol, naringenin, apigenin based multi-functional benzoxazine has greatest prospective applications as anti-flammable and fire resistant matrix for advanced composites for several applications. Especially, the HRC and TRC value of poly(RES-ac) is ominously lower than that of the thermosets from ortho-amide and ortho-imide benzoxazines, which exhibited one of the lowest HRC values of all polymers. Thus, this newly developed resveratrol-based tri-benzoxazine monomer containing acetylene group has greatest prospective applications as anti-flammable and fire resistant matrix for advanced composites. Consequently, these developments might be very useful in fabricating new products for the next generation’s high-performance and flame retardant uses by exploiting eco-friendly, sustainable and cost competitive bio-based polybenzoxazine matrices and composites for varying range of industrial and engineering applications.

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