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Tuning the architecture and performance of multifarious benzoxazine resin based on guaiacol and polyethylenimine

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Abstract

Molecular designing flexibility offered by benzoxazine chemistry, has been utilized to synthesize side-chain benzoxazine functionalized resins, in one-step approach via reaction of polyethylenimine (PEI) and guaiacol. The functionalization of polyethylenimine bearing amine functionalities, with benzoxazine groups as side-chains, is expected to confer a densely cross-linked network in the resulting thermoset. In the present work, guaiacol has been chosen as bio-based phenol, and polyethylenimine enriched with primary, secondary, tertiary amine groups, has been employed as an amine co-reactant. The reactants stoichiometry (phenol: amine: paraformaldehyde) has been varied from **2:1:4** to **20:1:40** molar ratio, resulting in a series of side-chain type guaiacol based benzoxazine-functionalized polyethylenimine resins (**G-pei**), which differ in percentage of oxazine functionalization. All the resins prepared have been characterized using FTIR, ^{1}H, ^{13}C NMR spectroscopies, and the evolution of oxazine functionalization in the resins has been monitored via ^{1}H NMR spectroscopy. The polymerization behaviour in resins has been evidenced using non-isothermal DSC studies, which reveals that **G-pei** resins exhibit peak polymerization temperature (T_{peak}) below 200°C. Temperature sweep rheological experiments

have been performed to obtain flow behaviour and processing window of the developed resins, where an evident reduction in the viscosity of resins has been observed around 100°C, thereby making it an appropriate temperature for processing. The influence of polar groups on the surface property of thermosets has been investigated by performing contact angle measurements, which reveals the hydrophilic nature of prepared thermosets. Thermal degradation behaviour of the multifarious bio-based thermosets, has been studied using thermogravimetric analysis, where maximum degradation temperature (T_{max}) for the cured specimens has been found to be above 300°C, with a high char yield (30 to 50%). The influence of dense network on the glass transition temperature of thermosets, has been additionally studied by DSC experiments. The adhesive performance of side-chain type benzoxazine-functionalized polyethylenimine resins, enriched with oxazine functionalities as well as polar groups, has been evaluated by lap shear strength values, which have been observed in the range of 22 to 49 Kg/cm^2.

Keywords: Benzoxazine; guaiacol; polyethylenimine; side-chain; functionalized
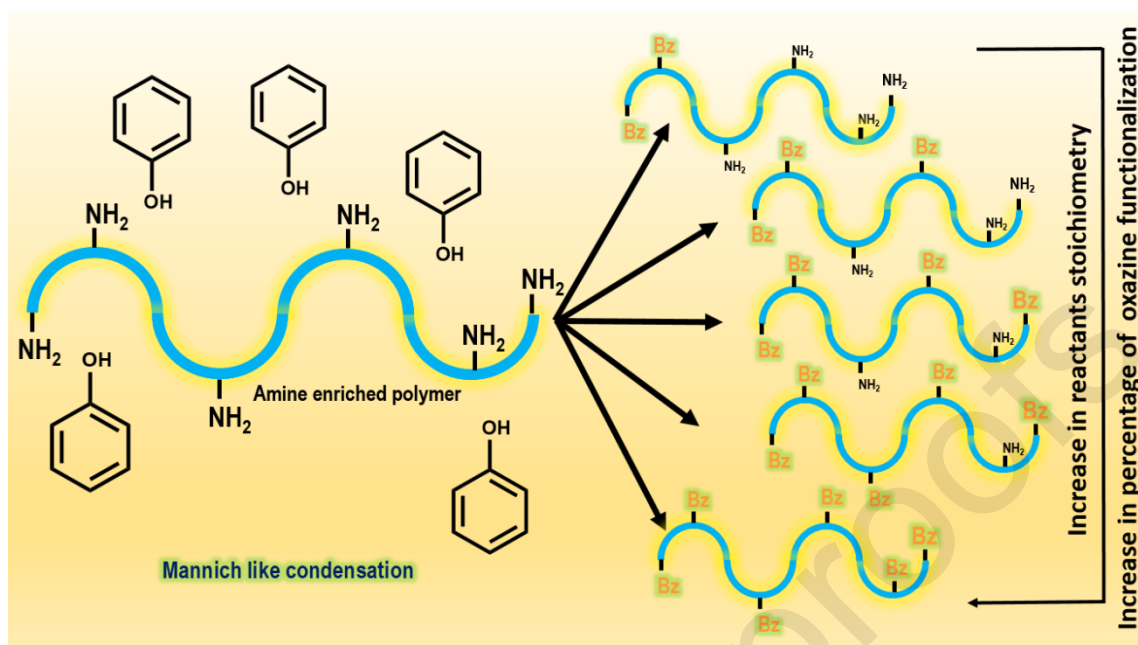
1. Introduction

Molecular designing flexibility offered by benzoxazine resins, has surely been the research interest for academia, which has led them to make plethora of attempts [1-10] to synthesize polybenzoxazine thermosets, a strong contender of mechanically robust epoxy and thermally stable bismaleimides. Polybenzoxazines, a class of phenolic thermosetting resins, have emerged as advanced performance materials[11], and are associated with properties including, high glass transition temperature[12], low water absorption[13], high dimensional stability[14-16], high char yield[17], appreciable mechanical performance, and excellent FST (Fire, smoke and toxicity) properties[18, 19]. In addition, polybenzoxazine thermosets are obtained by heating one component formulations, which involves oxazine functionalities undergoing ring opening polymerization to form cross–linked phenolic structure[17]. Unquestionably, the utilization of polybenzoxazine is expected to grow significantly in near future, and will certainly become an important asset for the polymer industry [20].

To explore the panorama of applications, variety of benzoxazine resins have been developed over the past decade using different synthetic approaches. Moreover, with the advent of sustainable development, researchers have now focused their interest to develop inexpensive sustainable polybenzoxazines, using plausible combinations of bio-based raw materials.[21-24] Bio-based benzoxazine resins are conventionally synthesized using either phenols of natural origin such as cardanol[25], eugenol[26], guaiacol[21], vanillin[27], or naturally occurring amines including stearylamine, and furfurylamine [28]. Comparing the thermal and mechanical performance of bio-based benzoxazine resins with their petro-based analogues, the former shows inferior performance. Several attempts have been made to improve the performance of bio-based polybenzoxazines, by making structural modifications, such as inclusion of aromatic precursors[29], or functionalities which are able to provide additional cross-linking sites[30-35]. It is to be noted that, increasing the degree of oxazine functionality in a polymerizable entity, has been considered as a basic approach to increase the cross-link density in the material, thereby enhancing thermal as well as the mechanical performance.

Research on benzoxazine resins has been mostly limited to three or four oxazine rings, by utilizing multifunctional phenol or amine as raw materials. Reports utilizing petro-based raw materials, to establish the role of multiple oxazine moieties on the performance of polybenzoxazine thermosets are available. Endo *et al.* reported di, tri-, and tetrafunctional benzoxazine monomers based on phenylaminomethyl phenol (PAMP), with oxazine moieties arranged one after the other. It was observed that increase in number of oxazine rings, resulted in a decrease in curing temperature from 264°C (mono) to 237°C (tetra). In addition, weight loss during the polymerization of monomers was also investigated, where a decrease in weight loss was reported

4

with increase in number of oxazine rings in the monomers.[36] Tetrafunctional fluorene-based benzoxazines comprising of both flexible aliphatic chain as well as rigid aromatic structure in their backbones, have also been reported and demonstrates good processability, excellent thermal stability, as well as high glass transition temperature (T_g) values ranging from 291 to 307°C.[37] Attempts towards establishing the structure-property relationship, on increasing the oxazine functionality in bio-based benzoxazine resins are also available. Lochab *et al.* reported a homologous series of cardanol based benzoxazine monomers, where the degree of functionality was varied from mono- to tetra-functional. It has been reported that, on increasing the number of oxazine rings in the monomer resulted in lowering of polymerization temperature and thus obviate the requirement of curing accelerators. In addition, it was suggested that degree and vicinity of oxazine functionality, significantly influence the cross-link density, and consequently the performance of end material.[38] It is to be noted that functionality in benzoxazine resins has also been extended to octa-functional monomers, however the synthetic approach involves multiple steps. Wu *et al.* reported the synthesis of multifunctional benzoxazine groups hybridized with polyhedral oligomeric silsesquioxane (POSS), via click reaction of octa-azido functionalized POSS with 3,4-dihydro-3-(prop-2-ynyl)-2H-benzoxazine.[39] The curing temperature for the benzoxazine groups was found to be relatively low (~120°C), and noticeable improvement in thermal performance was observed. Furthermore, Thirukamaran *et al.* reported an alternative route to prepare POSS octa-functionalized with benzoxazine groups, via Mannich like condensation of octaminophenyl POSS with bio-based phenols. The polymerization behaviour of the POSS octa-functionalized with benzoxazine monomers was investigated, and benzoxazine

groups were observed to polymerize at temperatures in the range of 231 to 251°C with low enthalpy of polymerization (42 - 45 J/g). [40]

Interestingly, grafting of benzoxazine groups as side-chains into a polymer backbone has been considered as an important way of introducing dense network, and functionalities for specific applications. In view of the same, Yagci research group has reported the synthesis of benzoxazine-functionalized polystyrene macromonomers, which involves Mannich like condensation of phenol, formaldehyde and amine-functionalized polystyrene. The synthesized macromonomers undergoes thermal polymerization, and displayed a curing exotherm centered above 250°C in DSC traces. In addition, the glass transition temperature for the polystyrene segment was found to be 105°C. [41] Ishida *et al.* has reported the synthesis of side-chain type benzoxazine-functionalized cellulose, by performing click reaction between ethynyl-monofunctional benzoxazine monomer and azide-functionalized cellulose. DSC thermogram showed that the benzoxazine-functionalized cellulose exhibited a polymerization exotherm which initiates at 145°C, and reaches peak around 195°C. Furthermore, benzoxazine-modified cellulose demonstrate a broader decomposition temperature range from 270 to 500°C with high char yield (~44%).[42] Recently, Kiskan *et al.* has reported the step-wise synthesis of non-symmetric main-chain oligobenzoxazine with side-chain naphthoxazines, utilizing the difference in reactivity of phenols towards Mannich like condensation. DSC studies revealed that the oligomer undergoes polymerization which initiates at 162°C, and attains a maxima at 205°C. In addition, thermal degradation analysis of the oligomer revealed, two major degradations at 309°C, and 398°C along with 18% char yield.[43]

As can be seen, side-chain benzoxazine functionalized polymers has intrigued the research interest and to boost the same, a unique one step approach has been adopted. In the present work, polyethylenimine, an amine functionalized polymer, enriched with primary, secondary and tertiary amines has been employed as an amine co-reactant. Mannich condensation of amine functionalities in polyethylenimine with guaiacol and paraformaldehyde, has been performed which yields side-chain type guaiacol based benzoxazine-functionalized polyethylenimine resins (**G-pei**). In addition, the architecture of side-chain type **G-pei** resins, has been tuned by varying the reactant stoichiometry, which results in resins differing in percentage composition of oxazine functionalities. Oxazine moieties in **G-pei** resins undergoes ring opening polymerization leading to multifarious bio-based thermosets. Polymerization and rheological behaviour of the resins has been investigated to obtain the processing window of the resins. The dense network in the developed thermosets is expected to improve the thermal degradation behaviour, which has been studied by thermogravimetric analysis. The presence of polar groups has been reported to improve the wettability of the resins, thereby improving the adhesion performance and the same has been investigated by obtaining lap shear strength values.

2. Experimental

2.1 Materials

Guaiacol was purchased from TCI chemicals. Polyethylenimine (branched, M_n ~600 g/mol, M_w ~800 g/mol) was procured from Sigma Aldrich (^{1}H-NMR presented in supplementary section as **Figure S1**). Polyethylenimine (PEI) is enriched with primary, secondary and tertiary amines present in 25:50:25 ratio respectively.[44] Paraformaldehyde was obtained from Merck.

Chloroform, sodium sulfate (anhydrous) were purchased from Fisher scientific. Distilled water has been used throughout the course of this work.

2.2 Characterization

Fourier transform infrared (FT-IR) spectra were recorded using Thermofischer Scientific Nicolet IR 200 spectrometer within the spectral range of 500 – 4000 cm^{-1} and a resolution of 4 cm^{-1}. The instrument was purged using N_2 in order to remove the gaseous impurities present within the setup. Liquid samples were uniformly coated on the KBr pellet. Uniform size (~ 1 mm thick) pellets were prepared with solid polybenzoxazine and KBr powder (1/10) using hydraulic press. Bruker AC 400 MHz Fourier transform nuclear magnetic resonance (FT-NMR) spectrometer was utilized to obtain the ^{1}H and ^{13}C NMR spectra of the samples. The spectrum was recorded using deuterated chloroform ($CDCl_3$) with tetramethylsilane (TMS) as the internal standard. Curing behaviour of the samples was analyzed using differential scanning calorimeter (DSC) (TA Instruments Q 2000) which was first calibrated for temperature and enthalpy using standards indium and zinc. For DSC scans, samples (5 ± 1 mg) were sealed in aluminium pans and heated from 30 to 250°C at 10°C /min under nitrogen atmosphere. Thermal equilibrium was attained within 1 min of sample insertion, and the exothermic reaction was considered to be complete when the signal levelled off to the baseline. Anton Paar Rheometer MCR-102 was used to study the rheological behaviour of the resin. Temperature-sweep experiment was performed in oscillatory mode for temperature range 50-250°C at 5°C/min. A constant strain of 0.5% and constant angular frequency of 10 rad/s was maintained during each interval. Parallel plate accessory with diameter 25 mm was employed for the present study and 0.5 mm gap thickness was maintained to perform the experiments. Drop Shape Analyser (DSA100E) was used to

measure contact angle and surface free energy of the thermosets was calculated at room temperature. Specimens for surface measurements were prepared by coating a glass slide with resin followed by its polymerization. The thickness of the polybenzoxazine coating was kept sufficient to avoid the possible effect of the hydrophilic glass on the measurements. The flat surfaces of the thermosets were used for the measurement of contact angle with respect to deionized water and dimethylformamide as the probing liquid. Thermal behaviour of the thermosets was investigated using a Thermogravimetric analyzer (TA instrument Q500) under nitrogen atmosphere (flow rate = 50 mL/min) in the temperature range of 30 to 800°C, at a heating rate of 20°C /min. A sample mass of 10 ± 0.5 mg was used for each experiment. Glass transition temperature of cured specimen was obtained using TA instruments DSC Q2000 under nitrogen atmosphere. All the specimens (~5mg) were subjected to three heating/cooling cycle ranging from room temperature to 300°C at 20°C /min. Adhesive strength of the resins has been quantified in terms of lap shear strength (LSS) of bonded stainless steel plates and was measured in accordance with ASTM standard D1002 using the Universal Testing System (International equipment) at a crosshead speed of 1.3 mm/min. The strength obtained in tensile mode has been multiplied by reduction factor (Thickness/Length) and has been reported in Kg/cm^2.

2.3 Preparation of side-chain type guaiacol based benzoxazine-functionalized polyethylenimine resins, (G-pei)

Mixture of guaicol, polyethylenimine (PEI), and paraformaldehyde in stoichiometric ratio, was refluxed for 8 h in chloroform (30 ml) as reaction medium. On the completion of reaction, contents were cooled, and filtered in order to separate the unreacted paraformaldehyde. The organic layer was washed repeatedly with distilled water and dilute sodium hydroxide solution

(0.01 M), followed by drying with sodium sulphate. The solvent was evaporated under reduced pressure to obtain a yellow viscous liquid. It is to be noted that reaction conditions including solvent as well as reaction completion time, was optimized and the details has been discussed in subsequent section. The absolute amount of reactive primary amines in PEI is not defined, due to its polymeric nature and the associated polydispersity. In view of the same, the reactant stoichiometry has been varied, resulting in a series of side-chain type benzoxazine-functionalized polyethylenimine resins, which have been designated as **G-pei(P:A),** where P:A is the stoichiometric ratio of guaiacol: PEI, used during the synthesis of resin. The calculations for obtaining the amount of reactants for a particular stoichiometry, has been performed by considering the weight average molecular weight of PEI (M_w 800 g/mol). It is to be noted that, weight average molecular weight has been preferred over number average molecular weight, as the former highlights the presence of molecules with higher molecular weight, and is thus more relevant. Molar quantities used for a reactant stoichiometry, designation, and yield of side-chain type guaiacol based benzoxazine-functionalized polyethylenimine resins, are presented in supplementary section as **Table S1**.

2.4 Procedure for preparation of specimen for evaluation of adhesive performance of side-chain type guaiacol based benzoxazine-functionalized polyethylenimine resins, (G-pei)

Side-chain benzoxazine functionalized resins, prepared in the present work have been evaluated for their adhesive performance, by following the ASTM standard D1002. To quantify the adhesion strength, small amount of the liquid resin was coated on stainless steel plates (15 mm × 15 mm) maintaining thickness of the adhesive layer in the range of ∼ 0.1-0.2 mm, and plates were clamped onto each other using paper clips. The assembly was kept in air oven at 100°C for 24 h

to polymerize the resins. Testing of six replicates for a side-chain type benzoxazine functionalized resin was performed, and the average lap shear strength value along with the standard deviation has been reported.

3. Results and Discussion

3.1 Side-chain type guaiacol based benzoxazine-functionalized polyethylenimine resins, (G-pei)

Polyethylenimine (PEI), a polymer enriched with primary, secondary and tertiary amine functionalities, has been employed as an amine co-reactant, to synthesize side-chain type benzoxazine-functionalized polyethylenimine resins. Mannich like condensation of primary amine groups with phenol in the presence of paraformaldehyde is well reported, and consequently primary amine groups of PEI will be participating in the reaction to generate oxazine functionalities. It is to be noted that, secondary amine groups of PEI, are also capable of participating in the condensation with phenol in presence of paraformaldehyde,[45] and are expected to yield Mannich base structures as a side product. Further, the substituents on the phenol/amine reactant have been reported to play a significant role on the equilibrium involving synthesis of benzoxazine from Mannich base.[46] It is expected that the electron donating effect of methoxy groups by resonance in guaiacol, will increase the stability of C-O bond in oxazine ring, thereby shifting the equilibrium to benzoxazine. Subsequently, the possibility of Mannich bases originating from reaction of primary amine and guaiacol has been excluded. Further, polarity of the reaction medium can influence the nucleophilicity of primary as well as secondary amine groups, and is expected to affect the feasibility of above mentioned reactions. In order to investigate the same, the reaction was performed using ethanol, chloroform, and toluene as reaction medium. It was observed that, performing the reaction in ethanol resulted in

11

precipitation of white solids, which has been assumed as a result of uncontrolled triazine formation,[47] and therefore was not considered suitable for the synthesis. It is worth mentioning, that triazine formation can be prevented by utilizing higher amounts of phenol[41]. Accordingly, reaction in ethanol was performed with 10:1:20 reactant stoichiometry, which again resulted in the precipitation of the contents after a period of time. Further, toluene was opted as the reaction medium and surprisingly, no oxazine signals were observed in the ^{1}H-NMR spectra, even after continuing the reaction for 24 h. Chloroform turned out to be an appropriate reaction medium for the synthesis of **G-pei** resins. It is to be noted that, nucleophilicity of primary and secondary amine groups remains similar in polar aprotic solvents.[48] In view of the same, it was expected that primary as well as secondary amine groups of PEI, will undergo condensation with phenol and paraformaldehyde, resulting in resins comprising of oxazine functionalities, Mannich base structures, according to the reaction scheme presented as **Figure 1**. Moreover, synthesis of side-chain type benzoxazine functionalized resin under solvent-less conditions was also attempted, however the viscosity of the contents was evidently high, and was then considered inappropriate for the present work. It is essential to note that, conventionally, washing of organic fractions is usually performed using 0.1 to 3 M NaOH solutions to remove unreacted components. However, in the present work, multiple washing of organic fractions has been performed using diluted NaOH solution (0.01M), in view of the polarity associated with the prepared resins. It has been observed that, on increasing the concentration of basic solution for washing, the yield of **G-pei** resins reduces drastically.
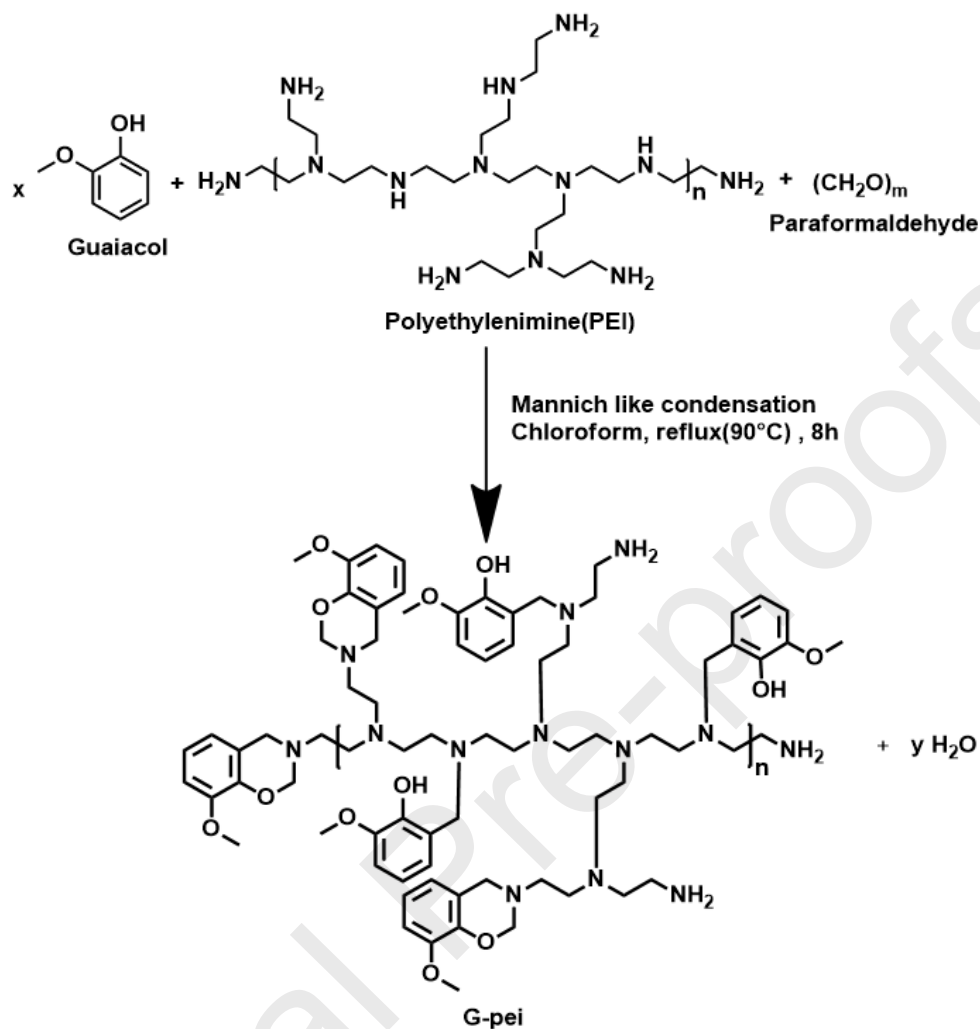
Figure 1. Reaction scheme showing the Mannich like condensation of guaiacol with polyethylenimine (PEI) in presence of paraformaldehyde, to yield side-chain type guaiacol based benzoxazine-functionalized polyethylenimine resins (**G-pei**), containing oxazine moieties, Mannich bases and polar groups. (where, **x** is the number of moles of guaiacol, **y** is the number of moles of water molecules produced as a result of condensation of primary as well as secondary amines with guaiacol, **n** can take values as ~1-2 repeating units in PEI)

As already mentioned, that one of the reactants involved in the present study is an oligomer, and the access of the reactive groups is crucial, thereby performing the optimization of reaction completion time is also crucial. In view of the same, Mannich like condensation of guaiacol, PEI and paraformaldehyde (10:1:20), was monitored by analyzing the evolution of characteristic oxazine signals in FTIR (**Figure 2**) and ^{1}H-NMR (**Figure 3**) spectra, recorded at 0.5h, 2h, 3.5h, 5h, 6.5h, 8h time intervals. The characteristic IR absorption bands for oxazine functionality appeared at 1240 and 1050 cm^{-1}, which are attributed to asymmetric and symmetric stretching of C-O-C (oxazine) bond.[49] In addition, the presence of oxazine ring was also characterized by the appearance of band at 929 cm^{-1}, which is associated with out-of-plane bending vibrations of the aromatic oxazine ring. FTIR spectra (**Figure 2**) of the reaction contents, recorded at different time intervals, reveals a visible increase in the intensity of the above mentioned oxazine characteristic bands after 8h. In addition, the reaction completion time was optimized by ^{1}H-NMR spectroscopy, where the characteristic oxazine resonances appearing at ~ 4.9 ppm (ArOCH_2N) and ~ 3.9 ppm (ArCH_2N) were monitored with respect to time.[49] ^{1}H-NMR spectra (**Figure 3**) of the reaction mixture recorded at different time intervals, displayed an evident increase in the intensity of oxazine resonances. In order to gain insight, percentage of oxazine functionalization was calculated at different time intervals, and was found to increase from 0 (0.5 h) to 20.05% (6h), which further remains practically unaltered even after continuing the reaction for 8 h (20.63%). Accordingly, it was concluded that, reaction time of 8 h, using chloroform as reaction medium, was sufficient to prepare side-chain type benzoxazine functionalized polyethylenimine resins (**G-pei**) in appreciable yields (~70%). The detailed procedure adopted to calculate the percentage of oxazine functionalization has been presented in supplementary section. The full

scale ^{1}H-NMR spectra of resins labelled with integration values are presented in supplementary section as **Figure S2-S7**. The percentage of oxazine functionalization calculated at different time intervals are tabulated in supplementary section as **Table S2**.
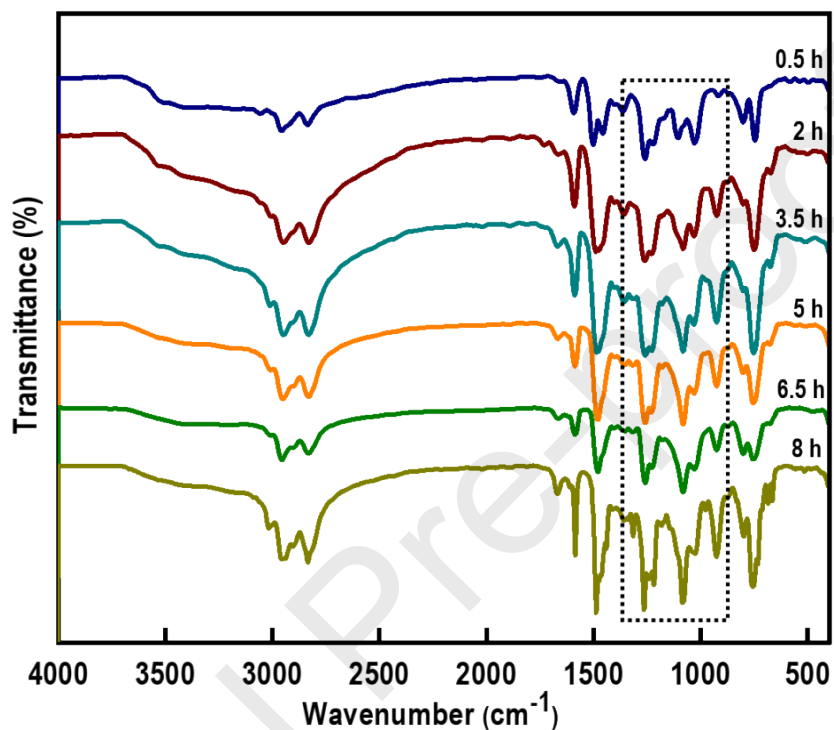
Figure 2. FTIR spectra of reaction contents (employing 10:1:20 reactant stoichiometry) recorded at different time intervals (0.5h, 2h, 3.5h, 5h, 6.5h, 8h), showing the evolution of the characteristic oxazine bands (1240 cm^{-1}, 1050 cm^{-1} and 929 cm^{-1}) with respect to reaction time.
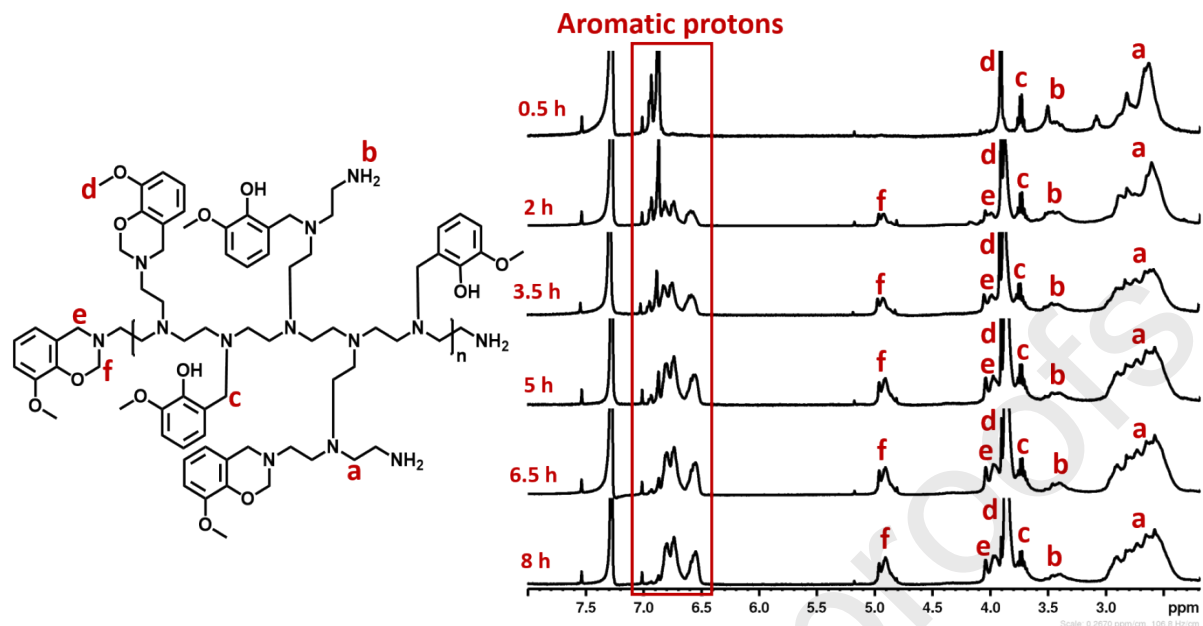
Figure 3. ^{1}H NMR spectra (recorded in CDCl$_3$) of reaction contents (employing 10:1:20 reactant stoichiometry), recorded at different time intervals (0.5h, 2h, 3.5h, 5h, 6.5h, 8h), showing the evolution of the characteristic oxazine resonances centered at 4.9 ppm with respect to reaction time

The absolute amount of reactive primary amines in PEI is not defined, due to its oligomeric nature and the associated polydispersity. In view of the same, the architecture of side-chain type benzoxazine-functionalized polyethylenimine (**G-pei**) resins, was tuned by varying the reactants (Phenol: Amine: Paraformaldehyde) stoichiometry from **2:1:4** to **20:1:40**. It is to be noted that oxazine formation was not evidenced in the reactions employing stoichiometry less than **6:1:12**. This could be due to preferable reaction of phenol with secondary amine groups of PEI, to generate Mannich base structures and was confirmed by the appearance of resonance peak at 3.7 ppm (Ph-C**H**$_2$-N-, Mannich base) in the ^{1}H-NMR spectra presented in supplementary section

as **Figure S8-S9**. The characteristic oxazine resonances were observed in the ^{1}H-NMR spectra of the reaction contents utilizing **6:1:12** stoichiometry (supplementary section, **Figure S10).** However, the extraction of the resin was difficult, in view of its similar solubility as that of the reactants and the product was obtained in negligible quantity. The presence of oxazine functionality in **G-pei** resins prepared using stoichiometry above **6:1:12,** was first indicated by FTIR spectroscopy. FTIR spectra (**Figure 4**) of the **G-pei** resins, shows the presence of characteristic oxazine signals at 1240 cm^{-1} and 1050 cm^{-1}, attributed to asymmetric and symmetric stretching of C-O-C (oxazine bonds), respectively. In addition, the appearance of band at 929 cm^{-1}, associated with out-of-plane bending vibrations for aromatic oxazine ring was also observed. Furthermore, absorption bands attributed to aliphatic C-H stretching bands appeared at 2840 cm^{-1} and aromatic C-H stretching was observed at 3018 cm^{-1}. Moreover, hydroxyl group of Mannich base structures was also identified by the appearance of broad band at 3420 cm^{-1}.[49]
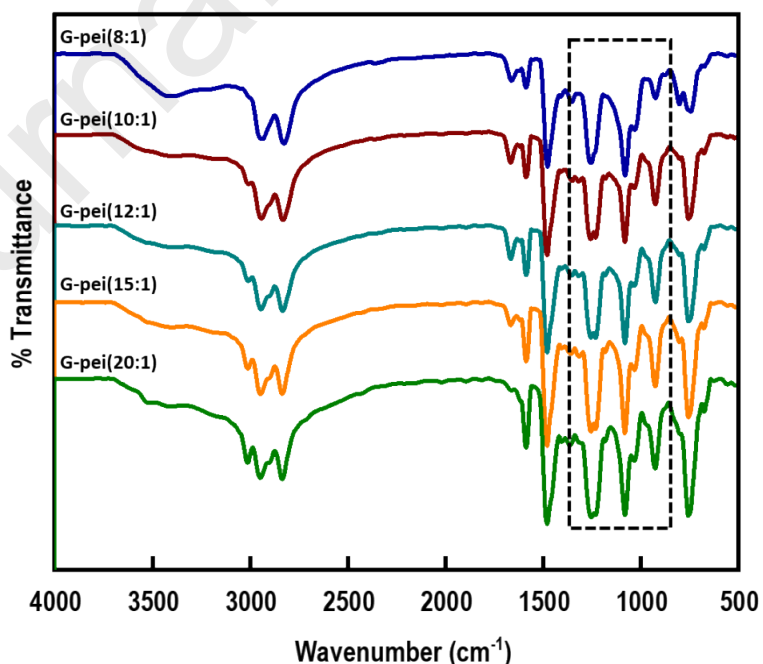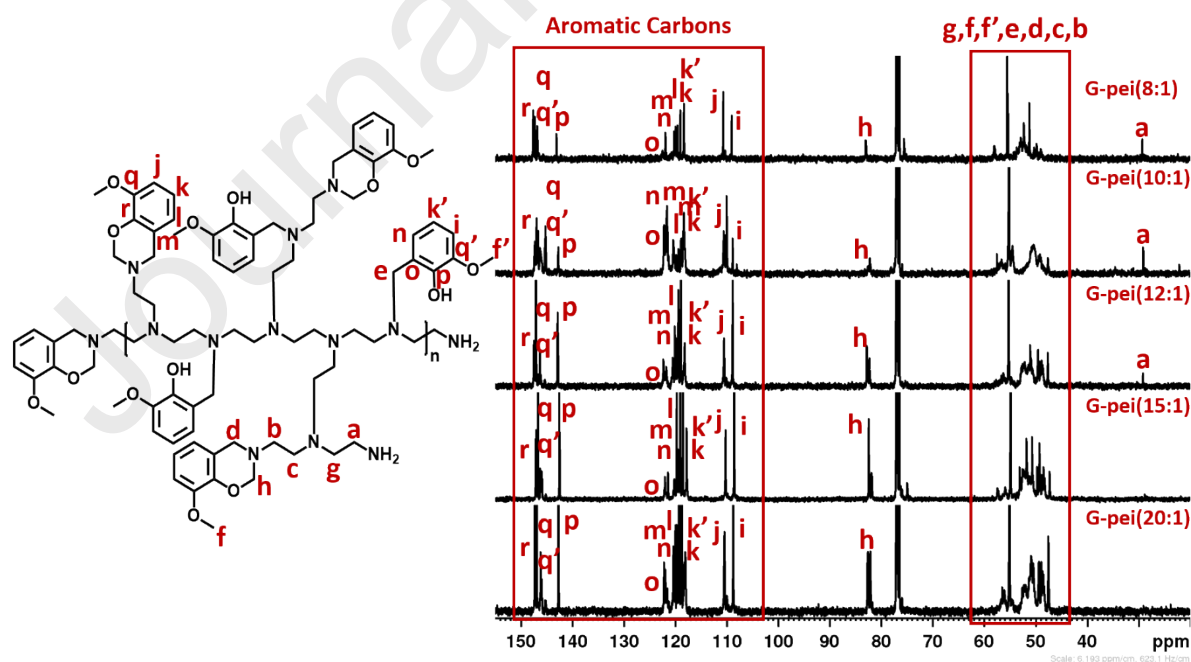
Figure 4. FTIR spectra of side-chain type guaiacol based benzoxazine functionalized polyethylenimine resins (**G-pei**), prepared by varying reactant stoichiometry from **8:1:16** to **20:1:40**, indicates the presence of oxazine functionality in the resins.

Side-chain type benzoxazine-functionalized polyethylenimine (**G-pei**) resins were additionally characterized using ^{1}H-NMR spectroscopy, and the spectra are presented as **Figure 5**. The characteristic oxazine resonances at ~ 4.9 ppm (ArOCH_2N) and ~ 3.9 ppm (ArCH_2N) appeared for all resins.[31, 33, 49] In addition to this, resonances centered at ~ 2.0-3.0 ppm (-NCH_2CH_2N-), ~ 3.4 ppm (-CH_2NH_2),[50] ~ 3.7 ppm (-NCH_2Ph), and ~ 3.8 ppm (-OCH_3) were observed. It is to be noted that, usually oxazine signals are observed as sharp singlets, however, the prepared resins comprises of multiple oxazine rings in slightly different chemical environment, resulting in broad and multiple oxazine signals.[36] Moreover, the broadness of the oxazine signals increases with increase in reactant stoichiometry utilized to prepare resins, and was assumed as a result of simultaneous increase in the percentage of oxazine functionalization. To validate the same, percentage of oxazine functionalization was calculated for resins, and was found to increase from 3.6 % (**G-pei(6:1)**) to 27.8 % (**G-pei(15:1)**), however a slight decrease to 26.1% was observed for **G-pei(20:1)**. The detailed procedure adopted to calculate the percentage of oxazine functionalization has been presented in supplementary section. Full scale ^{1}H-NMR spectra of **G-pei** resins labelled with integration values are presented in supplementary section as **Figure S8-S15**. The percentage of oxazine functionalization calculated for **G-pei** resins, prepared by varying reactant stoichiometry, are tabulated in supplementary section as **Table S3**. Moreover, it can be observed that, intensity of the resonances associated with the protons of primary amine groups

(~ 3.4 ppm), decreases with increase in reactant stoichiometry utilized to prepare resins, and becomes negligible in the spectra of **G-pei(15:1)** as well as **G-pei(20:1)** resins, suggesting significant conversion of primary amine groups into oxazine functionality. In addition, intensity of the resonances associated with the methylene proton of Mannich base (~ 3.7 ppm), intensify on increasing reactant stoichiometry utilized to prepare resins, which indicates a simultaneous consumption of secondary amine groups in PEI. The structure of side-chain type benzoxazine-functionalized polyethylenimine resins was further validated using $^{13}CNMR$ spectroscopy and the spectra of resins are presented as **Figure 6**. The presence of oxazine ring in the resins has been additionally confirmed by appearance of oxazine signals at ~51 (Ar$\underline{C}$H$_2$N, labelled as **d**) and ~82 ppm (ArO$\underline{C}$H$_2$N, labelled as **h**).[49] Furthermore, resonance at ~35 ppm ($\underline{C}$H$_2$NH$_2$, labelled as **a)** was found to be absent for resins **G-pei(15:1)** as well as **G-pei(20:1)**, and additionally supports the significant conversion of primary amine groups to oxazine moieties. Moreover, resonances at ~48 ppm ((Oxazine)-N$\underline{C}$H$_2$CH$_2$N-, labelled as **b**), ~49 ppm (-(Oxazine)-NCH$_2\underline{C}$H$_2$N-, labelled as **c**), ~52 ppm (Ph$\underline{C}$H$_2$N-, labelled as **e**), ~55 ppm (-O$\underline{C}$H$_3$, labelled as **f,f'**), ~56 ppm (-$\underline{C}$H$_2$CH$_2$NH$_2$, labelled as **g**) ~108 - 148 ppm (aromatic carbons) were also observed.
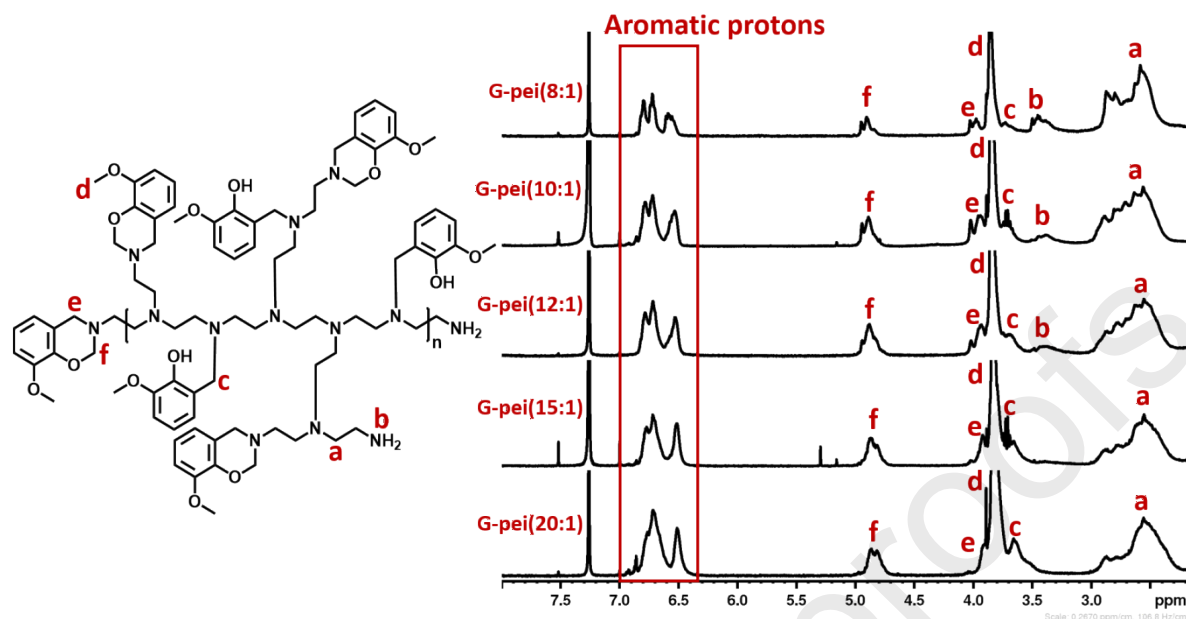
Figure 5. ¹H NMR spectra (recorded in CDCl₃) of series of side-chain type guaiacol based benzoxazine-functionalized polyethylenimine resins (**G-pei**), prepared by varying reactant stoichiometry, confirms the presence of oxazine functionalities, Mannich bases and polar groups in the structure.
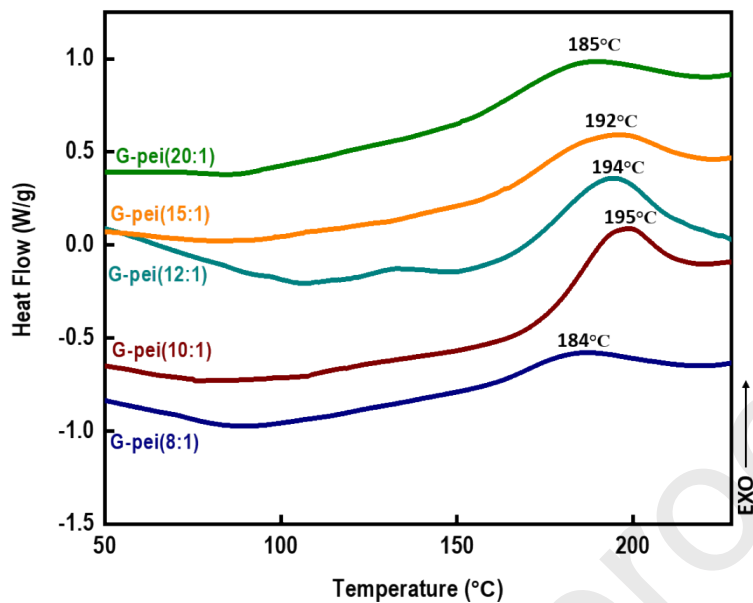
Figure 6. ^{13}C NMR (recorded in CDCl$_3$) spectra of series of side-chain type guaiacol based benzoxazine-functionalized polyethylenimine resins (**G-pei**), prepared by varying reactant stoichiometry, confirms the presence of oxazine functionalities, Mannich bases and polar groups in the monomers

3.2 Polymerization of side-chain type guaiacol based benzoxazine-functionalized polyethylenimine resins (G-pei)

Side-chain type benzoxazine functionalized polyethylenimine resins (**G-pei**) have been synthesized, which comprises of oxazine functionalities, Mannich bases and amine groups. To investigate the polymerization behaviour of prepared resins, non-isothermal DSC experiments were performed. The curing parameters, including the onset temperature (T_{onset}), peak temperature (T_{peak}), enthalpy of polymerization, were obtained for **G-pei** resins and are tabulated in **Table 1.** DSC traces of **G-pei** resins revealed, the presence of curing exotherm associated with ring opening polymerization of oxazine functionality, below 200°C (**Figure 7).** This has been credited to the acceleration caused by the available primary amine groups and phenolic structure of Mannich bases. [51, 52]

Figure 7. DSC traces of the side-chain type guaiacol based benzoxazine-functionalized polyethylenimine resins (**G-pei**), prepared by varying reactant stoichiometry.

Table 1. Curing parameters of the side-chain type guaiacol based benzoxazine-functionalized polyethylenimine resins (**G-pei**).

Designation	Molar stoichiometry		T_{onset} (°C)	T_{peak} (°C)	Enthalpy of polymerization (J/g)
	Guaiacol	Amine			
G-pei (8:1)	8	1	155	184	36
G-pei(10:1)	10	1	175	195	52
G-pei(12:1)	12	1	165	194	74
G-pei(15:1)	15	1	160	192	53
G-pei(20:1)	20	1	156	185	53

22

On comparing the results, resin designated as **G-pei(8:1),** showed relatively low peak polymerization temperature (184°C), which is credited to the acceleration predominantly caused by primary amine groups. Further, resin designated as **G-pei(20:1),** displayed a curing exotherm centered at low temperature (185°C), and is mainly ascribed to the catalytic effect of phenolic structure of Mannich bases. Furthermore, resin designated as **G-pei(10:1),** demonstrates curing behaviour, with an exotherm centered at relatively higher temperature (~195°C), which is assumed as a result of relatively lesser number of primary amine groups available for acceleration. The curing parameters of resins labelled as **G-pei(12:1)** and **G-pei(15:1)**, revealed slight lowering of polymerization temperatures, which can be primarily attributed to the autocatalytic effect of the nearby oxazine rings, as their vicinity increases with increased percentage of oxazine functionalization. It is worth mentioning that, the fabrication of cured specimens from **G-pei** resins was performed at 100°C for 24 h. The possibility of polymerizing the resins at low temperature for longer duration, has been credited to the presence of catalytic functionalities, and autocatalytic nature of oxazine polymerization.[53] In addition, enthalpy of polymerization observed for **G-pei** resins was very low (36 to 74 J/g). Consequently, the approach can be considered to lower the polymerization temperature, and enhance the processability of bio-based benzoxazines.

The presence of multiple oxazine rings and polar groups in side-chain type benzoxazine-functionalized polyethylenimine resins, is expected to alter the flow behaviour of resins. It is to be noted that the **G-pei** resins were found to be highly viscous, and difficult to process or cast at room temperature. In order to investigate the processing window, rheological behaviour of the **G-pei** resins has been studied and temperature sweep experiments have been performed. The

variation in complex viscosity of resins with respect to temperature has been presented as **Figure 8(i).** As can be seen from the plot, on increasing the temperature to 100°C, resins achieved minimum possible viscosity and remains unaltered till 150°C, except for **G-pei(8:1)**, where increase in the viscosity was visible from 130°C. The gelation, observed as a cross over point of storage and loss modulus plots with respect to temperature, is presented in **Figure 8(ii)-(vi).** Loss modulus which is indicative of the viscous portion of the resin, initially decreases as temperature rises to 100°C, and remains unaltered until cross linking in the linear polymer chains is initiated which occurs above 150°C. Storage modulus which represents the elastic portion, decreases at a much faster rate with increase in temperature, as well as increases at a relatively faster rate as cross-linking is initiated. The gelation was observed at temperatures below 200°C for all resins and supports the curing parameters obtained from DSC studies. It is to be noted, a hump in storage modulus plot was observed near 100°C and the same is reflected in the DSC traces, as a shift in the baseline. The processing window defined as the difference in liquefaction and gelation temperature was found to be sufficiently broad to fabricate or cast the specimens at high temperatures. Based on the rheological behaviour and DSC results, the resins were processed at temperature $\sim100^{\circ}$C for 24 h, to prepare specimens for analysis of surface property, thermal and adhesion performance. Moreover, the processing of the resins was additionally attempted at 150°C, in order to reduce the polymerization time, however, the accelerated polymerization conditions led to the formation of voids in the cured specimens.
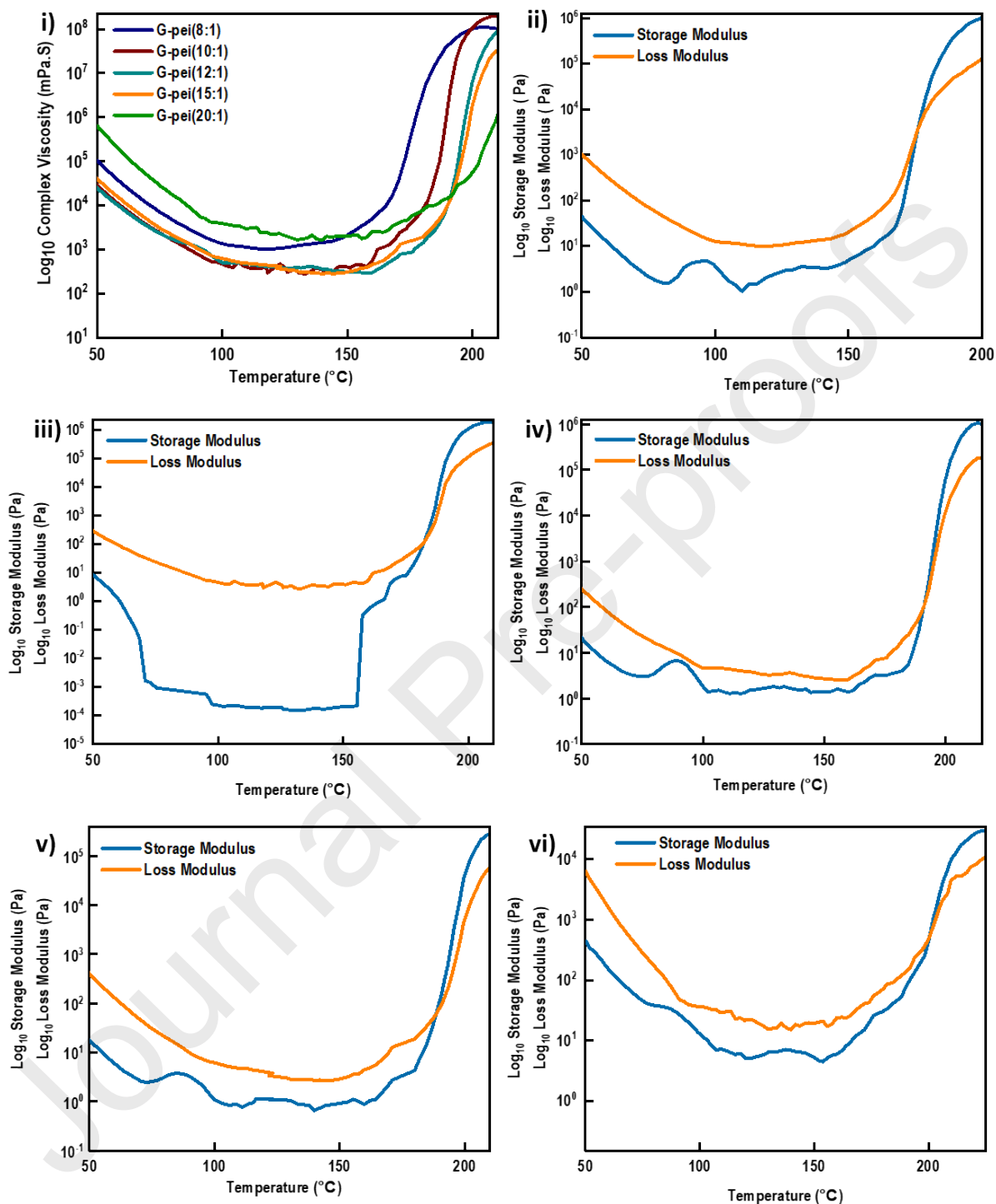
Figure 8. Rheological behaviour of **G-pei** resins obtained from temperature sweep experiments:

i) variation of complex viscosity with respect to temperature. Storage-loss modulus plots with

respect to temperature for resins designated as ii) G-pei (8:1), iii) G-pei (10:1), iv) G-pei (12:1), v) G-pei (15:1) and vi) G-pei (20:1)

Bio-based thermosets prepared using side-chain type guaiacol based benzoxazine-functionalized polyethylenimine resins were characterized using FTIR spectroscopy, and the spectra are presented in supplementary section as **Figure S16**. It is well known, that oxazine rings undergoes thermally accelerated ring opening polymerization to generate functional groups such as –OH and >N-,[54] which further participates in six-membered intramolecular hydrogen bonding and this interaction has been credited for the advance performance of polybenzoxazine thermosets. Polybenzoxazine network in the thermosets prepared using **G-pei** resins, was characterized by the appearance of a strong absorption band at ~3230 cm^{-1}, attributed to the O-H groups. In addition, a significant reduction in the intensity of the characteristic oxazine peaks appearing at ~929 cm^{-1}, ~1240 cm^{-1} and~ 1050 cm^{-1} was observed.

Presence of polar groups, is expected to influence the surface property of thermosets, prepared using **G-pei** resins, and the same was investigated by performing contact angle measurements. In the measurement, distilled water was used as a probing liquid, and the images captured to determine the contact angle of the cured specimens, are presented as **Figure 9**. In addition, the contact angle (CA) values using dimethylformamide as a probing liquid were also obtained, which were then utilized to calculate surface free energy (SFE) values. Contact angle and surface free energy values for the specimens are tabulated in supplementary section as **Table S4.** It is to be noted, that polybenzoxazines are usually hydrophobic in nature, in spite of the presence of

hydroxyl and tertiary amine groups which are generated after polymerization. As already mentioned, these groups participates in the six-membered intramolecular hydrogen. Thermosets prepared in the present work were found to be hydrophilic in nature (CA is less than 90°). In addition, thermosets exhibited high surface energy values (> 35 mN/m) and has been attributed to the presence of amine groups and phenolic structures, which then confer polarity to the network.
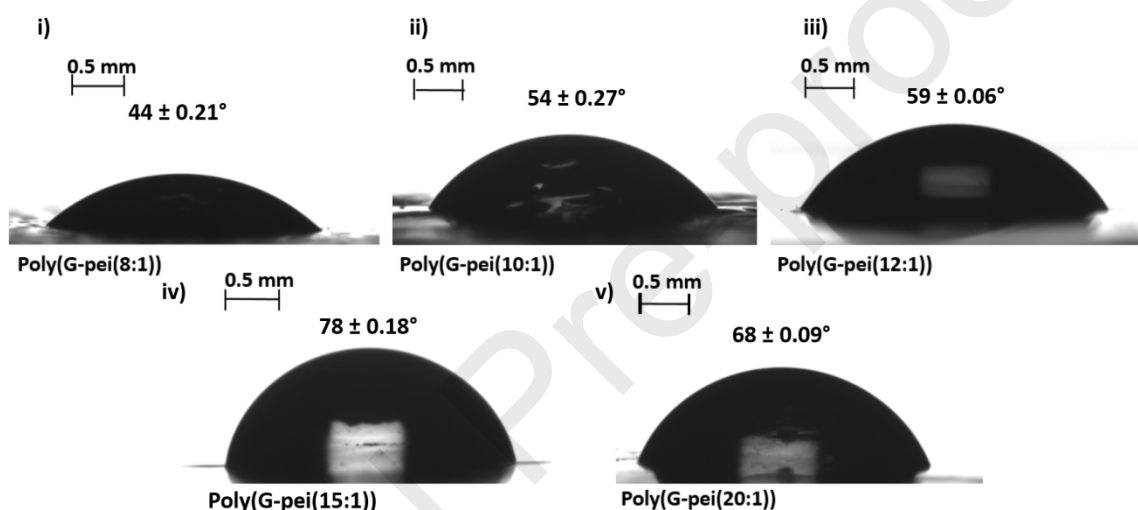
Figure 9. Images captured (distilled water as probe liquid) for contact angle measurements on the surface of cured specimens, prepared using side-chain type guaiacol based benzoxazine-functionalized polyethylenimine resins (**G-pei**).

3.3 Adhesive performance of side-chain type guaiacol based benzoxazine-functionalized polyethylenimine resins, (G-pei)

Adhesive strength is governed by a combination of factors which includes, ability of the resin to wet the substrate, substrate roughness, thickness of the adhesive, and type of failure.[55] Additionally, dense network of the polymer plays a vital role in determining the lap shear strength

27

(LSS). Adhesive strength of thermosets prepared using **G-pei** resins was determined according to

ASTM standard D1002. The procedure involves lapping of a small area (1.5 cm × 1.5 cm) of

stainless steel plates, adhered due to the polymerization of resin in the overlapped area, and was

followed by the quantification of lap shear strength in tensile mode. Lap shear strength values

for thermosets prepared from **G-pei** resins are tabulated in **Table 2**. The representative load-

displacement plots for specimens prepared using **G-pei** resins are presented in supplementary

section as **Figure S17.**

Table 2. Lap shear strength of thermosets **(poly(G-pei)),** prepared from various side-chain type

G-pei resins.

Specimen Designation	LSS value (Kg/cm^2)
Poly(G-pei(8:1))	32 ± 2
Poly(G-pei(10:1))	49 ± 7
Poly(G-pei(12:1))	25 ± 5
Poly(G-pei(15:1))	22 ± 2
Poly(G-pei(20:1))	Not determined due to brittle nature

On comparing the results, LSS values for thermosets obtained from resins designated as **G-**

pei(8:1) and **G-pei(10:1),** are significantly higher. This is credited to the primary amine groups

available with the resins, which may interact with the surface of the substrate, thereby improving

the wettability of the resin and consequently, adhesion performance. Further, adhesive

performance of the thermoset prepared using **G-pei(10:1)** resin, is superior than thermoset

obtained from **G-pei(8:1)**, and is attributed to relatively higher cross-link density in the former, as the resin exhibits relatively higher percentage of oxazine functionalities. Similarly, cross-link density in thermosets prepared using **G-pei(12:1)** and **G-pei(15:1)** resins, is expected to be relatively high, however, the LSS values observed for their respective thermosets are lower. Furthermore, LSS value could not be determined for thermoset obtained from **G-pei(20:1)** resin, in view of its highly brittle nature. This can be considered as a result of reduced fraction of primary amine groups in the resin, as these polar groups are responsible for improving the resin wettability with the substrate. In addition, the anomaly can be explained in terms of the possibility in types of cross-links within the thermoset. Multiple oxazine rings, depending on their proximity, can undergo polymerization, generating intramolecular or intermolecular cross-links. Intramolecular cross-links are generated from the linkage of oxazine moieties belonging to the same entity, whereas the intermolecular cross-links are produced from the linkage of oxazine moieties belonging to different polymerizable entity. Unquestionably, intermolecular cross-links between the polymer chains, will contribute more in enhancing the strength of thermoset. The percentage of oxazine functionalization as well as the proximity of oxazine rings in **G-pei(12:1)** and **G-pei(15:1)** resins is high. Consequently, during polymerization, intermolecular cross-links are compromised over intramolecular cross-links, which is then reflected in relatively lower LSS values of its respective thermosets.

3.4 Thermal performance of thermosets (poly(G-pei)), obtained from side-chain type guaiacol based benzoxazine-functionalized polyethylenimine resins

Multiple oxazine rings in **G-pei** resins are expected to result in extensively cross-linked thermoset and subsequently high thermal performance. In order to investigate the same, the thermal

performance of thermosets was analyzed using thermogravimetric analysis and the thermogravimetric and derivative thermogravimetric (TG-DTG) traces are presented as **Figure 10.** TG traces reveals that the thermosets undergoes single step degradation, and was further evidenced from the analysis of their respective derivative plots. Parameters for evaluation of thermal stability, such as temperatures at which 5% mass loss, 10% mass loss, maximum mass loss occurs and char content (at 800°C) are tabulated in **Table 3**. Overall, it can be observed, that thermosets exhibit $T_{5\%}$ > 260°C, $T_{10\%}$ >290°C, and T_{max} > 300°C. In addition, the char yield of the material was found to be in in the range of 39 to 50 %. On comparing the results, thermoset designated as **poly(G-pei(20:1),** demonstrated relatively higher thermal stability with T_{max} ~342°C and char yield ~50 %. Furthermore, thermal performance of thermosets was found to increase with increase in aromatic character, which in combination with the extensive cross-linking, has contributed in the immobilization of the polymeric chains, thereby enhancing the thermal performance of material. In addition, glass transition temperature (T_g) for thermosets has been obtained from DSC traces, as temperatures at which shift in the heat capacity is observed, and are presented in the supplementary section as **Figure S18**. DSC traces reveals that T_g for all thermosets was found to be approximately ~122°C and is attributed to the similarity in network as well as extent of cross-linking.[40]

One of the several interesting features of polybenzoxazines is, high char yield, which makes these materials qualify for flame retardant standards. Char layer, act as an insulation which prevents heat to reach the remaining polymer, thereby retarding the oxidative degradation. It can be seen that thermosets prepared in the present work exhibited significant char yield and is expected to show flame retardancy. In order to adjudge the same, van Krevelen equation has been utilized

to obtain Limiting Oxygen Index (LOI) value, which is defined as the amount of oxygen (%) sufficient to maintain the combustion of material and is related to char residue (CR) as, LOI = 17.5 + 0.4 × CR[56]. Accordingly, LOI values has been calculated for thermosets and have been tabulated in **Table 3.** It can be seen that all thermosets exhibit LOI above 30. On comparing, **poly(G-pei(20:1))** thermoset demonstrated relatively higher LOI value (LOI ~ 37), due to high char yield (~50%).
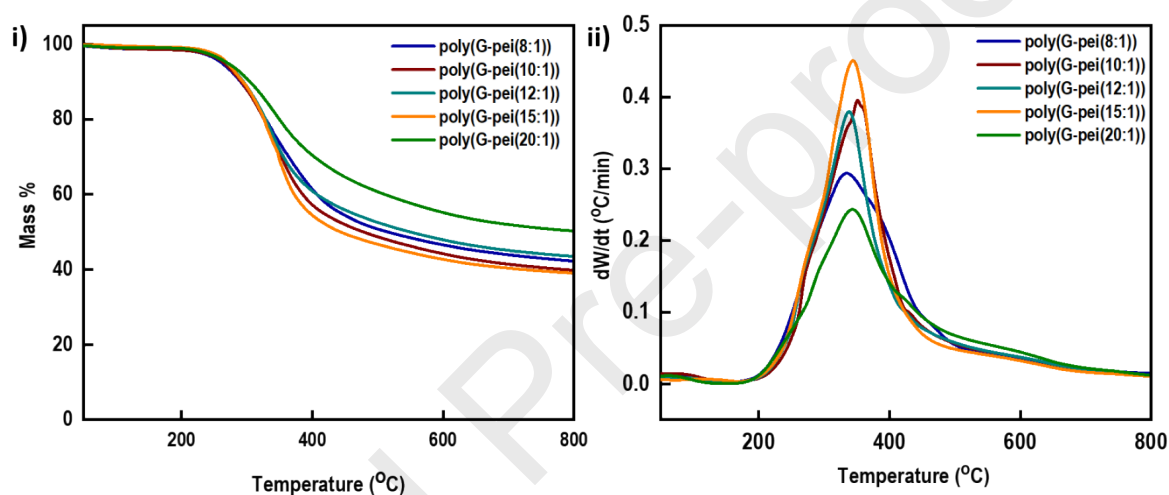
Figure 10. i) TG and ii) DTG traces of **poly(G-pei)** thermosets prepared using side-chain type guaiacol based benzoxazine-functionalized polyethylenimine resins.

Table 3. Thermal parameters for **poly(G-pei)** thermosets prepared using side-chain type guaiacol based benzoxazine-functionalized polyethylenimine resins.

Specimen Designation	$T_{5\%}$ (°C)	$T_{10\%}$ (°C)	T_{max} (°C)	Char Yield (%)	LOI
Poly(G-pei(8:1))	261	290	334	42	34
Poly(G-pei(10:1))	265	291	339	40	33

Poly(G-pei(12:1))	269	294	340	43	35
Poly(G-pei(15:1))	270	294	338	39	33
Poly(G-pei(20:1))	270	304	342	50	37

4. Conclusion

Side-chain type guaiacol based benzoxazine-functionalized polyethylenimine resins (**G-pei**), were synthesized using guaiacol, paraformaldehyde and polyethylenimine (PEI). In view of the oligomeric nature of amine co reactant, reaction completion time was optimized, by monitoring the characteristic oxazine signals in FTIR and ^{1}H-NMR spectra of the reaction content, recorded at different time intervals. Evolution of oxazine functionalization was monitored at different time intervals, and it was concluded that 8 h of reaction time, was sufficient to synthesize resins in appreciable yields (~70%). As the absolute amount of reactive primary amines in PEI is not defined, the architecture of side-chain type benzoxazine-functionalized polyethylenimine (**G-pei**) resins, was tuned by varying the reactants (Phenol: Amine: Paraformaldehyde) stoichiometry from **2:1:4** to **20:1:40**, which resulted in series of resins comprising of oxazine functionalities, Mannich bases and polar groups. Percentage of oxazine functionalization was calculated for the resins, and was found to increase with increase in reactants stoichiometry. DSC studies revealed that oxazine functionalities in the resins undergoes ring opening polymerization at low temperatures (<200°C), which was credited to the accelerating potential of primary amine groups as well as phenolic structure of Mannich bases. Rheological behaviour of the resins displayed significant reduction in the complex viscosity at 100°C, and was thus considered appropriate for processing of resins. Influence of polar groups on the surface property of thermosets, was studied

by performing contact angle measurements, which revealed their hydrophilic nature. Side-chain type benzoxazine functional resins were additionally evaluated for adhesive performance, which was found to be highest for **poly(G-pei(10:1)) thermoset** with LSS value ~ 49 ± 7 Kg/cm$^{2.}$. This was credited to the presence of amine groups which improved the wettability of resin with substrate, and the dense network provided by polymerization of multiple oxazine rings. Thermogravimetric analysis revealed that thermosets demonstrates single step degradation and exhibit $T_{5\%} > 260^{\circ}C$, $T_{10\%} > 290^{\circ}C$, and $T_{max} > 300^{\circ}C$. Comparison of the results showed, that thermal parameters for **poly(G-pei(20:1))** thermoset were relatively highest, and was attributed to higher aromatic character, as well as extensive cross-linking, both of which contributed in the immobilization of the polymeric chains. In addition, similarity in network as well as extent of cross-linking, resulted in similar glass transition values for thermosets. Limiting oxygen index (LOI) value was calculated for cured specimens, using Van krevelan equation and was found to be highest for thermoset designated as **poly(G-pei(20:1)).** It is worth mentioning, that the thermosets obtained in the present work are enriched with nitrogen and may prove useful in CO_2 sequestration applications.

Acknowledgement

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Tuning the architecture and performance of multifarious benzoxazine resin based on guaiacol and polyethylenimine

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Conflict of interest

The authors declare no conflict of interest.

Tuning the architecture of guaiacol based multifunctional benzoxazine resins and performance of multifarious structures of bio-based polybenzoxazine thermosets

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Graphical Abstract
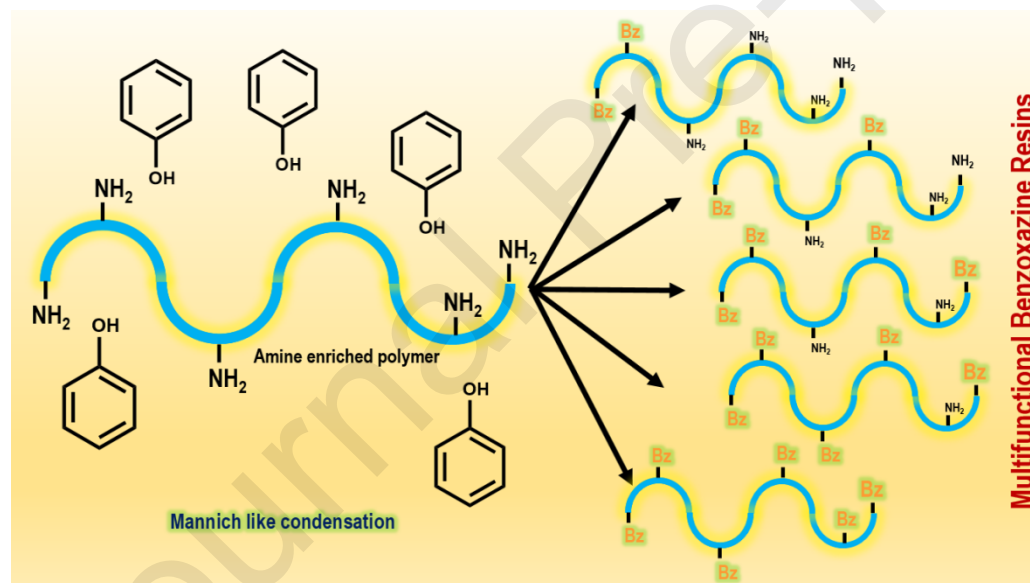
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Highlights

1. Side-chain type benzoxazine-functionalized polyethylenimine resins have been prepared.

2. Reactants stoichiometry has been varied resulting in a series of functionalized resins.

3. Resins have been processed at low temperature, 100°C for 24h.

4. Cured specimens exhibited maximum degradation temperature (T_{max}) above 300°C.

5. Adhesion performance of resins has been credited to the polar groups.