U.P.B. Sci. Bull., Series B, Vol. 85, Iss. 1, 2023 ISSN 1454-2331

SYNTHESIS AND THERMO-MECHANICAL CHARACTERIZATION OF VANILLIN-BASED POLYBENZOXAZINES WITH COMPLEX ARCHITECTURE

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Bio-based benzoxazine monomers with complex architecture were developed by reacting natural occurring phenols vanillin and eugenol with paraformaldehyde and branched polyethyleneimine. The chemical structure of the synthesized monomers was characterized by FT-IR and ^{1}H-NMR spectroscopy while the formation of the oxazine ring along the macromolecular backbone of oligomeric PEI reactant was proved by GPC. The resulting monomers exhibited low polymerization temperatures in the range of 166-218°C as shown by DSC analysis. The corresponding polybenzoxazines were further characterized in terms of thermal and mechanical properties by employing TGA and nanoindentation methods while the surface characteristics were evaluated through Contact angle measurements.

Keywords: bio-based thermoset, benzoxazines, nanomechanical properties

1. Introduction

Polybenzoxazines, as a new versatile class of thermoset resins are widely known due to numerous unique properties such as dimensional stability, chemical resistance, increased char yield, low flammability, hydrophobic character, low shrinkage, and superior mechanical properties [1]. In contrast with their reduced crosslinking density, the increased values for Tg results as a consequence of the extensive hydrogen bonding network assembled between pendant hydroxyl groups of the polymeric backbone [2]. Advantageously, three-dimensional polybenzoxazine networks can be easily obtained by thermal activated ring opening polymerization of oxazine monomers without the support of any catalyst [3].

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The versatility of polybenzoxazines reside in the remarkable molecular design flexibility based on which limitations such as brittleness and elevated curing temperatures can be tailored. Over the last years, the development of new bio-based polymeric polybenzoxazines employing various natural reactants such as guaiacol [4], vanillin [5], eugenol [6], cardanol [7], furfuryl amine [8], salicylaldehyde [9] have encouraged the researchers to extent the applicability of thermoset materials towards a sustainable development of the industrial field.

Vanillin and eugenol are natural occurring phenols which have recently become an attractive resource for the development of numerous polymeric materials [10,11]. These aromatic compounds decorated with a methoxy group in ortho position have resembling chemical structures which however differentiate through the functional groups present on the para position of the aromatic ring thus, vanillin has a free formyl group while eugenol has an allyl group.

Over the last years, several bio-based benzoxazine were developed employing these natural phenols. Periyasamy et all. [12] have synthesized vanillin and eugenol based benzoxazines with polymerization temperature similar with the commercial petrol-based resins and the authors have successfully demonstrated the participation of the functional groups from the phenolic structure in the crosslinking process. Up to now, based on the rich existing library of natural reactants, polybenzoxazines with interesting features such as antifouling [13], flame-retardant [14], anticorrosive [9] and superhydrophobic properties [15] were developed as an alternative to the petroleum-based thermosets. However, there are still some deficiencies such as high polymerization temperatures, and brittleness that need to be improved.

Recently, Nebhani group [16] expanded the library of nitrogen enriched polybenzoxazine structures by employing eugenol and polyethyleneimine structures as raw materials showing that the polymerization process takes place slightly above 200°C. However, the effect of the para-alkyl and alkoxy substituents of the phenolic structures on the thermo-mechanical properties of the thermosets needs to be further investigated as they highly influence the crosslinking process. In this study, plant-based phenols such as vanillin and eugenol were employed in the synthesis of bio-based benzoxazine monomers in order to develop renewable polybenzoxazines and moreover, the influence of the naturally occurring phenolic chemical structure on the thermal and mechanical properties of the final materials was thoroughly investigated.

2. Materials and methods

2.1 Materials

Eugenol (≥98%) (Eu); Vanillin (≥98%) (V); Paraformaldehyde, powder 95% (PFA); Polyethyleneimine, branched average Mn 600~g/mol by GPC (PEI); sodium hydroxide ≥97.0% (NaOH), pellets and chloroform were used as received from Sigma Aldrich, and magnesium sulfate anhydrous was purchased from Alfa Aesar. All the compounds were used without further purifications.

2.2 Methods

^{1}H NMR spectra to confirm the chemical structure of synthesized monomers were acquired using $CDCl_3$ as a solvent on a Bruker Advance III HD 600 MHz spectrometer, corresponding to the resonance frequency of 600.12 MHz.

Complementary to ^{1}H NMR, The Fourier Transform Infrared Spectrometry (FT-IR) spectra were measured with a Bruker VERTEX 70 spectrometer in total attenuated reflection mode (ATR) by employing a Ge crystal while 32 scans were recorded per spectrum at a 4 cm^{-1} resolution in the 400-4000 cm^{-1} domain.

The molecular weight and polydispersity index of the benzoxazine monomers were evaluated through Gel Permeation Chromatography (GPC) on a Rapid HPLC System - Jasco LC4000 system equipped with a PSS column (TSK gel G3000HHR; 7.8 mm I.D. × 30 cm; detection limit 60 000 Da) using a flow rate of 1 mL/min at room temperature with Tetrahydrofuran (THF) as eluent and polystyrene (PS) as standard.

Non-isothermal Differential Scanning Calorimetry (DSC) thermograms were recorded on a Netzsch 204 F1 Phoenix equipment. Monomer samples with a mass around 10 mg were subjected to heat with a rate of 10°C/min in aluminum crucibles from room temperature to 300°C in a nitrogen flow rate of 20 mL/min.

Thermogravimetric analyses (TGA) were performed on a TG 209 F1 Libra instrument by heating the samples with a heating rate of 10°C/min in the temperature range 20-700°C under nitrogen atmosphere (20 mL/min) by using a Platinum/Rhodium crucible.

Contact angle measurements under static conditions were done on a DSA100E (KRUSS GMBH) equipment by employing Sessile drop method. Water and ethylene glycol drops with a volume of ~2 μL were deposited on the thermoset samples at room temperature and the reported results comprise the average of three measurements by using Young Laplace fitting method.

The mechanical properties at microscale expressed as micro-elastic modulus (E) and micro-hardness (H) were evaluated by nanoindentation using a Nano Indenter G200 system, through the method of continuous stiffness measurement (CSM).

3. Results and discussions

3.1 The synthesis of bio-based benzoxazine monomers

As shown in Fig. 1, two bio-based benzoxazine monomers namely Eu-PEI-Bz and V-PEI-Bz were synthesized by Mannich condensation reaction between eugenol and vanillin as natural phenolic reactants, paraformaldehyde, and PEI . For each benzoxazine monomer, 5.7 g (37.5 mmol) of vanillin and 6.15 g (37.5 mmol), respectively of eugenol as naturally derived phenolic compound, 2 g (2.5 mmol) of PEI and 2.25 g (75 mmol) of paraformaldehyde in excess were reacted for 8 h at 70°C employing chloroform as solvent. The crude product was then cooled to room temperature and subjected to purification by filtration. Then the organic layer was washed several times with 0.1M NaOH solution and deionized water. After that, the product was dried over anhydrous $MgSO_4$, and the solvent was removed under pressure leading to viscous products with a reaction yield around 72%.

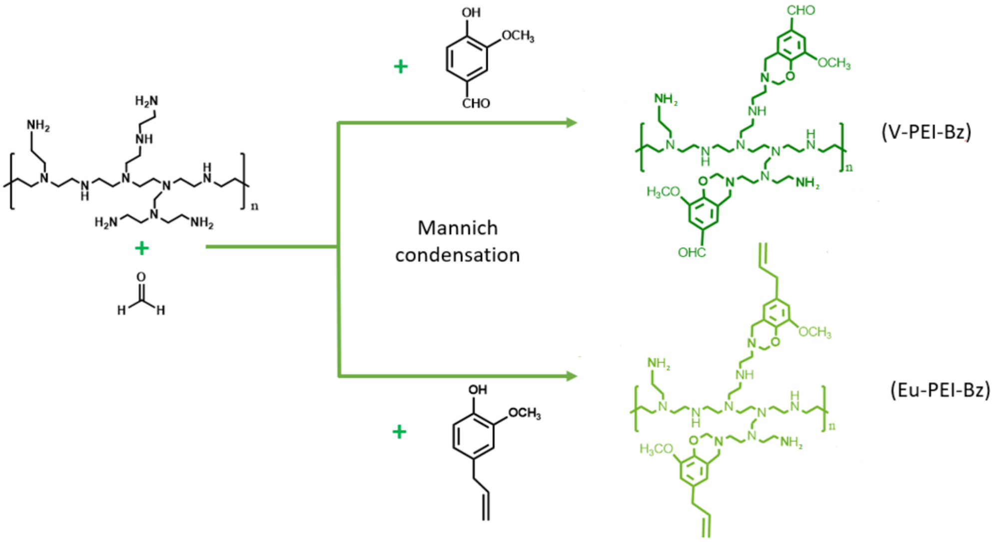

Fig. 1. The synthesis reaction pathways for V-PEI-Bz and Eu-PEI-Bz bio based benzoxazine monomers

3.2 Benzoxazine monomers polymerization

To assess the thermo-mechanical properties of the synthesized thermosets, the monomers were subjected to thermal activated ring opening polymerization. Firstly, the V-PEI-Bz and Eu-PEI-Bz monomers were heated at 50°C for 24h under reduced pressure to remove the residual solvent and at the same time to reduce the formation of micro voids within the material. After that, the monomers were step cured in a convection oven by gradually increasing the temperature from 80 to 120°C within 5 hours.

3.3 FT-IR and ^{1}H NMR spectroscopy

The chemical structure of bio-based benzoxazine monomers was confirmed by FT-IR and ^{1}H-NMR analysis. As shown in the FT-IR spectrum from Figs. 2 and 3, the typical signal for the benzene ring attached to the benzoxazine functionality is present on each spectrum for both V-PEI-Bz (900 cm^{-1}) and Eu-PEI-Bz (916 cm^{-1}) monomers. The asymmetric stretching vibration of the C-O-C group from the oxazine ring was recorded at 1222 cm^{-1} for both monomers [5] and the symmetric and asymmetric stretching vibration of the C-N-C group were recorded for V-PEI-Bz at 1089 cm^{-1} and 1585 cm^{-1} and for Eu-PEI-Bz at 1150 cm^{-1} and 1593 cm^{-1}.

The weak absorption signal between 2830-3032 cm^{-1} marked on each monomer spectrum is assigned to the CH_2 alkyl groups from the oxazine ring and the CH aromatic groups. However, there is a slight difference between the two monomers. In the case of eugenol-based benzoxazine monomer, the intensity is higher may be due to the presence of the allyl functionalities from the *para* position. Apart from that, the absence of any signal characteristic for the phenol functionality in the region of 3000-3200 cm^{-1} confirms the success of the condensation reaction.

The synthesis of the benzoxazine monomers was further confirmed through ^{1}H-NMR and the spectra are depicted in Fig. 2 and 3.

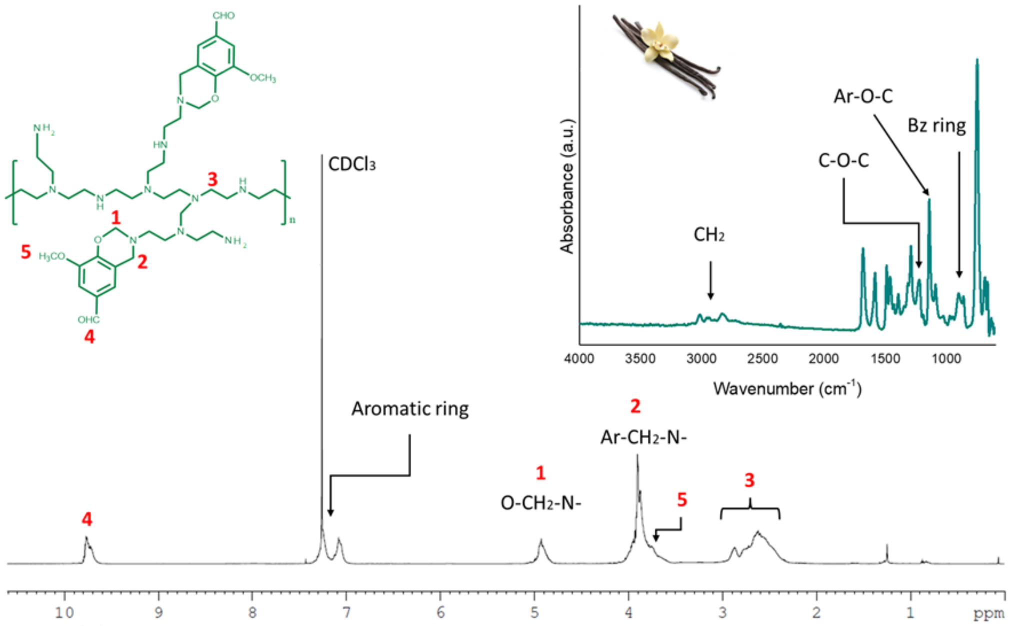

Fig. 2. FT-IR and ^{1}H NMR analysis for V-PEI-Bz

Both monomers, V-PEI-Bz and Eu-PEI-Bz display characteristic signals for benzoxazine structure at ~3.9 ppm (Ar-CH_2-N) and ~4.8 ppm (O-CH_2-N). In the case of Eu-PEI-Bz, the signals from ~5.9, ~5.1 and ~3.3 ppm are assigned to the protons from the characteristic allyl functionality of eugenol [17]. The formyl group from vanillin backbone display resonance at ~9.8 ppm. For both monomers, the methoxy group signals from ~3.9 ppm overlaps with the benzoxazine characteristic peak from the same region.

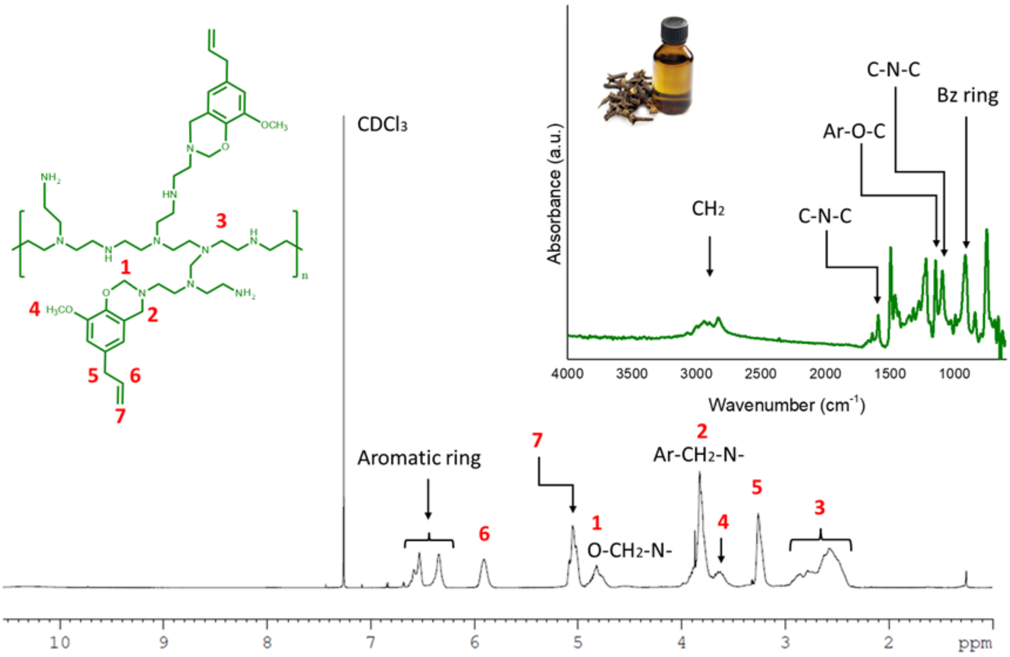

Fig. 3. FT-IR and ^{1}H NMR analysis for Eu-PEI-Bz monomer

The resonance signal at 2.5-3 ppm defines the characteristic protons of the structural unit of the amine reactant (PEI) and the signals for the aromatic protons can be noticed around ~6.5-7 ppm for both monomers. Moreover, the percentage for closed oxazine ring functionalization was determined from the ^{1}H-NMR spectra by the subsequent equation:

$$Ring\ content\ (\%) = \frac{\frac{I}{2}}{\frac{I'}{4}+\frac{I}{2}} \times 100 \qquad [18]$$

where I is the integrated intensity of the methylene protons of O–CH$_2$–N group in the benzoxazine ring and I′ is the integrated intensity of the ethylene protons of N-(CH$_2$)n-N. Thus, the ^{1}H-NMR data showed that only 28% of the available primary amine groups from the PEI structure were converted into oxazine rings (Table 1).

3.4 Differential scanning calorimetry (DSC) and Gel permeation chromatography (GPC)

The curing behavior for Eu-PEI-Bz and V-PEI-Bz monomers was analyzed using Differential Scanning Calorimetry and the corresponding thermograms are represented in Fig. 4. Both monomers are viscous at room temperature and no melting transition was recorded thus, both thermograms exhibit one single exothermic peak in the temperature range of 166-218°C. The low curing temperature (Table 1) recorded for the Eu-PEI-Bz may be a consequence of the participation in the crosslinking process of the allyl group present in the chemical structure of the phenol employed.

Vanillin and Eugenol are both ortho-methoxy-para-substituted phenols with resembling chemical structure. Despite that, when converted into reactive monomers, the properties of each compound are different due to the only difference between them. Eugenol has an allyl group in the *para* position while vanillin has a formyl group. It was already proven that benzoxazines synthesized from *p*-substituted phenols with electron withdrawing groups [19] tend to polymerize at lower temperature.

As depicted by the DSC thermograms from Fig. 4, eugenol-based benzoxazine monomer polymerizes at a significantly lower temperature in comparison with vanillin monomer. We can assume that a possible synergistic effect exerted between the allyl group and the multiple amino functionalities may catalyze the ring opening polymerization reaction which takes place at a considerably lower temperature as compared with various eugenol-based benzoxazine monomers existing in the literature (200-260°C) [20,21].

Although the formyl group from vanillin structure tends to undergo decarboxylation reaction, its influence over the polymerization process is not significant thus in this case only the aldehyde groups are involved in the crosslinking process of the novel benzoxazine monomers.

However, there is a significant difference between the maximum temperature for the ring opening polymerization reaction which can be ascribed to the different chemical structure of the phenolic reactants [22]. Previous studies have demonstrated that a low curing enthalpy can be associated with a reduced concentration of oxazine functionality [23]. The lower concentration of oxazine functionalities may be a consequence of the oligomeric nature of PEI thus, the long backbone of the amine reactant can induce a dilution effect over the polymerization reaction. Polyethylene imine also possesses numerous primary, secondary and tertiary amine groups from which it is widely known that only primary amines participate in the oxazine ring formation.

The reduced content of benzoxazine groups may be a consequence of a steric hinderance effect exerted by the branched architecture of the polyethyleneimine reactant which could hinder the phenols to form benzoxazine functionality along the macromolecular chain [24] as shown also by the ^{1}H-NMR results. Furthermore, the molecular weight of the new bio-based monomers was evaluated through GPC and the corresponding values are listed in Table 1. Considering the Mn for PEI 600g/mol it can be assumed that for each monomer, an average of 6-7 oxazine functionalities were formed along one structural unit of PEI. These results are in agreement with the DSC analyses, where the reduced curing enthalpy denoted a low amount of benzoxazine rings.

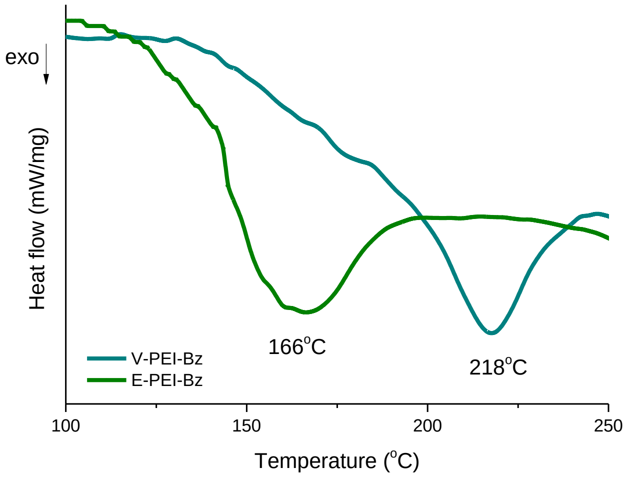

Fig. 4. DSC thermograms of bio-based benzoxazine monomers

Table 1

Curing reaction characteristics monitored through Differential scanning calorimetry and Molecular weight determination for bio-based benzoxazine monomers

Sample	ΔH (J/g)	T_{max} (°C)	M_p (g/mol) *	M_n (g/mol) *	M_w (g/mol) *	I_d (M_n/ M_w) *	Oxazine ring content (%)**
Eu-PEI-Bz	72.62	217.6	2239	1915	2214	1.08	28.2
V-PEI-Bz	75.28	166.3	2227	1905	2199	1.08	28.7

** Determined by GPC according to polystyrene standards ** from ^{1}H-NMR results*

3.5 Thermogravimetric analysis (TGA)

The thermal stability of the cross-linked benzoxazine resins along with the decomposition behavior were determined through thermogravimetric analysis under nitrogen atmosphere and the corresponding parameters are listed in Table 2.

As it can be seen form the thermograms depicted in Fig. 5, both monomers exhibit a multiple stage and broad degradation process. This fact can be attributed to the additional functionalities such as methoxy, allyl and aldehyde groups present on the phenolic reactants. However, V-PEI-PBz has a significant reduced thermal stability in comparison with its eugenol based analogous due to its aldehyde functionality which suffer decarboxylation reactions during heating [5]. The broad allure for the TGA curves denotes that for both polybenzoxazines resins the thermal degradation occurs with a slow rate [25]. The thermal degradation in the interval corresponding to the mass loss for $T_{d10\%}$ is attributed to the chain scission of the ethylene units from PEI reactant backbone [5].

Both monomers display the main degradation step at temperatures above 250°C and the weight loss in this interval is due to the Mannich base degradation along with the breaking of the crosslinked network [5].

The limiting oxygen index (LOI) is a parameter that determines the flame retardancy characteristics of a material. This can be calculated by employing the char yield from TGA with the help of the Van Krevelen and Hoftyzer equation:

$$LOI = 17.5 + 0.4[CY] \text{ [26]}$$

Both bio-based thermosets possess a char yield around 31.8-32.4 which determines LOI values ~30. These parameters suggest that the synthesized thermosets display self-extinguishing properties and can be used as fire-retardant materials.

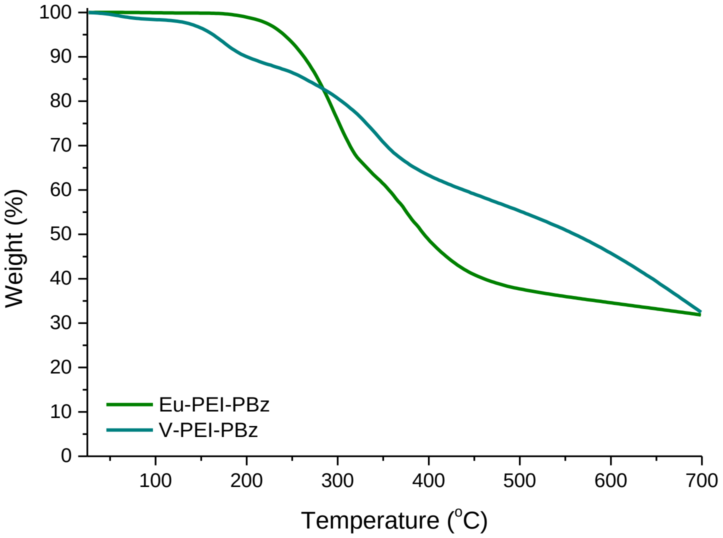

Fig. 5. TGA thermograms of crosslinked biobased benzoxazines under N_2 atmosphere

Table 2

Thermal stability parameters obtained for crosslinked bio-based thermosets

Sample	$T_{d3\%}$(°C)	$T_{d5\%}$(°C)	$T_{d10\%}$(°C)	Char yield (%)	LOI	Tmax(°C)	
Eu-PEI-PBz	227.4	240.9	263.0	31.8	30.2	278.9	365.0
V-PEI-PBz	143.6	163.0	200.5	32.4	30.5	296.8	374.6

3.6 Nanoindentation measurements

The nanoindentation technique was used to evaluate the nanomechanical properties such as hardness, stiffness, and elastic modulus of the final bio-based polybenzoxazine materials. In comparison with the classical mechanical tests, nanoindentation technique represents a more suitable and precise method to evaluate the properties of a thermoset which may present structural defects such as micro voids after curing which can further affect the overall performances of the final materials [27]. Young's modulus (E) and hardness (H) were calculated based on the load versus displacement curves according to the Oliver–Pharr method [28] and the average values for these parameters are presented in Fig. 6.

As it can be clearly noticed, there are significant differences in terms of mechanical features between the two biobased polybenzoxazines as the only structural difference between the synthesized thermosets derives from the *para* substituents of the phenolic groups.

The superior properties in terms of hardness and stiffness encountered in the case of eugenol-based polybenzoxazine may be a consequence of the supplementary participation of the allyl functionality in the monomer`s crosslinking process. During the polymerization, the CH_2=CH active group from eugenol structure may form covalent bonds as triggered eighter by temperature or by the numerous active species present in the system leading to a more stable network in terms of mechanical properties.

Nevertheless, the formyl substituent present in the case of vanillin-based benzoxazine will generate an increased number of hydrogen interactions upon curing which are less stable in comparison with covalent interactions. Not only this may be the reason for poor nanomechanical features but also the chemical instability of the formaldehyde group over the polymerization temperature range which may form structural defects within the material through decarboxylation reaction that will further alter the mechanical features.

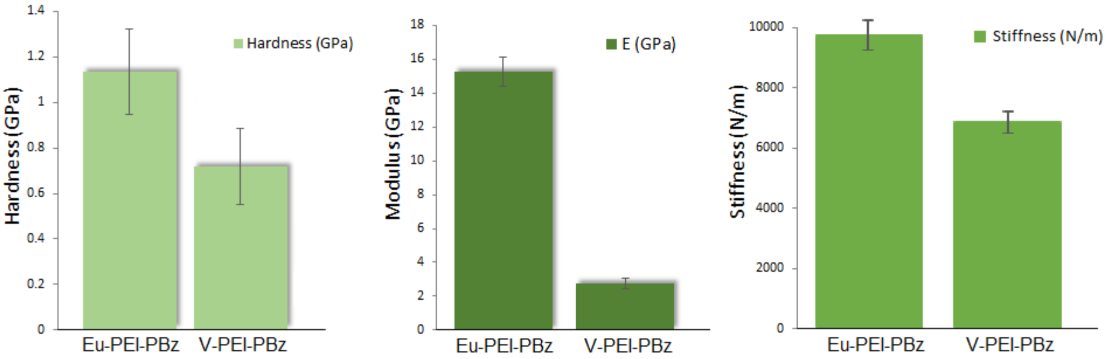

Fig. 6. Nanomechanical properties of biobased polybenzoxazines

3.7 Contact angle measurements (CA)

The surface characteristics were evaluated with the aid of contact angle measurement by using water and ethylene glycol as probing liquids and the corresponding results are presented in Table 3. The high content of polar functionalities located on the PEI backbone such as primary and secondary amines along with the OH groups formed through ring opening polymerization strongly affects the wetting properties of the bio-based thermosets which consequently exhibit a hydrophilic character.

The slight shift towards hydrophobic behavior observed in the case of V-PEI-PBz (Fig. 7) represents a consequence of the presence of the formyl group from vanillin structure which leads to intra and intermolecular hydrogen [29] bonding formation during polymerization, thus improving the surface characteristics of the final materials. The high density of hydrogen bonds formed in the crosslinked network of polybenzoxazine resins usually determines low surface free energy values and such values are associated with hydrophobic surfaces [17].

Table 3

Static contact angle values obtained for bio-based polybenzoxazines

Sample	CA water (°)	CA EG (°)	Surface free energy (mN/m)
Eu-PEI-PBz	73.34 (±2.92)	41.29 (±2.94)	38.49
V-PEI-PBz	77.99 (±2.84)	53.12 (±1.07)	31.06

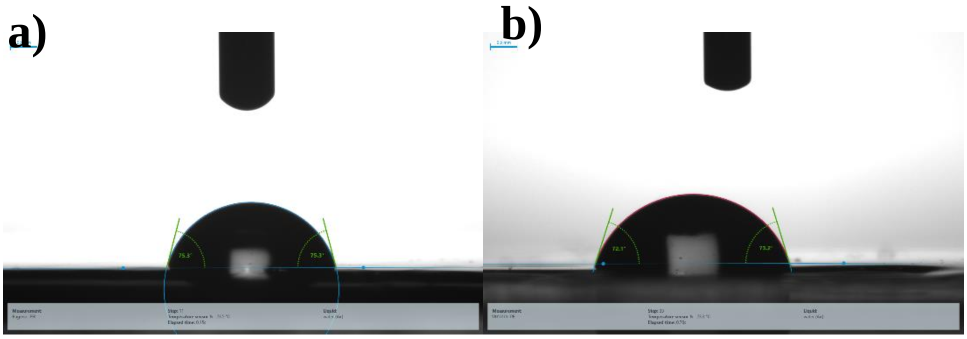

Fig. 7. Contact angle measurements of a) EU-PEI-PBz and b) V-PEI-PBz using water as probing liquid

4. Conclusions

The present study addressed the synthesis of new bio-based benzoxazine monomers grafted on branched polyethyleneimine backbones by employing natural phenolic reactants. Moreover, the study approached the differences brought by the functional groups that differentiate the chemical structures of the naturally derived eugenol and vanillin phenols.

It was shown that the curing characteristics of each monomer are strongly dependent on the chemical structure of the phenolic reactant. The final eugenol and vanillin based polybenzoxazines exhibited lower curing temperatures and superior nanomechanical properties. Both thermosets exhibit high char yield along with increased values for LOI parameter and therefore the synthesized bio-polybenzoxazines could be successfully employed as fire-resistant materials.

Acknowledgement

The contact angle, GPC and nanoindentation measurements were possible due to European Regional Development Fund through Project No. P_36_611, MySMIS code 107066, INOVABIOMED.

REFERENCES

1. Lligadas, G.; Tüzün, A.; Ronda, J.C.; Galià, M.; Cádiz, V. Polybenzoxazines: new players in the bio-based polymer arena. Polymer Chemistry **2014**, 5, 6636-6644, doi:10.1039/C4PY00914B.
2. Ghosh, N.N.; Kiskan, B.; Yagci, Y. Polybenzoxazines—New high performance thermosetting resins: Synthesis and properties. Progress in Polymer Science **2007**, 32, 1344-1391, doi:https://doi.org/10.1016/j.progpolymsci.2007.07.002.
3. Hamerton, I.; McNamara, L.T.; Howlin, B.J.; Smith, P.A.; Cross, P.; Ward, S. Examining the initiation of the polymerization mechanism and network development in aromatic polybenzoxazines. Macromolecules **2013**, 46, 5117-5132, doi:10.1021/ma401014h.
4. Yang, R.; Han, M.; Hao, B.; Zhang, K. Biobased high-performance tri-furan functional bis-benzoxazine resin derived from renewable guaiacol, furfural and furfurylamine. European Polymer Journal **2020**, 131, 109706, doi:https://doi.org/10.1016/j.eurpolymj.2020.109706.
5. Sini, N.K.; Bijwe, J.; Varma, I.K. Thermal behaviour of bis-benzoxazines derived from renewable feed stock 'vanillin'. Polymer Degradation and Stability **2014**, 109, 270-277, doi:https://doi.org/10.1016/j.polymdegradstab.2014.07.015.
6. Dumas, L.; Bonnaud, L.; Olivier, M.; Poorteman, M.; Dubois, P. Eugenol-based benzoxazine: from straight synthesis to taming of the network properties. Journal of Materials Chemistry A **2015**, 3, 6012-6018, doi:10.1039/C4TA06636G.
7. Bai, W.; Lin, H.; Chen, K.; Xu, J.; Chen, J.; Zhang, X.; Zeng, R.; Lin, J.; Xu, Y. Eco-friendly stable cardanol-based benzoxazine modified superhydrophobic cotton fabrics for oil–water separation. Separation and Purification Technology **2020**, 253, 117545, doi:https://doi.org/10.1016/j.seppur.2020.117545.
8. Wang, X.; Niu, H.; Huang, J.; Song, L.; Hu, Y. A desoxyanisoin- and furfurylamine-derived high-performance benzoxazine thermoset with high glass transition temperature and excellent anti-flammability. Polymer Degradation and Stability **2021**, 189, 109604, doi:https://doi.org/10.1016/j.polymdegradstab.2021.109604.
9. Aly, K.I.; Mohamed, M.G.; Younis, O.; Mahross, M.H.; Abdel-Hakim, M.; Sayed, M.M. Salicylaldehyde azine-functionalized polybenzoxazine: Synthesis, characterization, and its nanocomposites as coatings for inhibiting the mild steel corrosion. Progress in Organic Coatings **2020**, 138, 105385, doi:https://doi.org/10.1016/j.porgcoat.2019.105385.
10. Fache, M.; Darroman, E.; Besse, V.; Auvergne, R.; Caillol, S.; Boutevin, B. Vanillin, a promising biobased building-block for monomer synthesis. Green Chemistry **2014**, 16, 1987-1998, doi:10.1039/C3GC42613K.
11. Molina-Gutiérrez, S.; Manseri, A.; Ladmiral, V.; Bongiovanni, R.; Caillol, S.; Lacroix-Desmazes, P. Eugenol: a promising building block for synthesis of radically polymerizable monomers. Macromolecular Chemistry and Physics **2019**, 220, doi:10.1002/macp.201900179.

12. Periyasamy, T.; Asrafali, S.P.; Muthusamy, S. New benzoxazines containing polyhedral oligomeric silsesquioxane from eugenol, guaiacol and vanillin. New Journal of Chemistry **2015**, 39, 1691-1702, doi:10.1039/C4NJ02047B.
13. Deng, Y.; Xia, L.; Song, G.-L.; Zhao, Y.; Zhang, Y.; Xu, Y.; Zheng, D. Development of a curcumin-based antifouling and anticorrosion sustainable polybenzoxazine resin composite coating. Composites Part B: Engineering **2021**, 225, 109263, doi:https://doi.org/10.1016/j.compositesb.2021.109263.
14. Machado, I.; Shaer, C.; Hurdle, K.; Calado, V.; Ishida, H. Towards the development of green flame retardancy by polybenzoxazines. Progress in Polymer Science **2021**, 121, 101435, doi:https://doi.org/10.1016/j.progpolymsci.2021.101435.
15. Wang, L.; Yuan, M.; Zhao, Y.; Guo, Z.; Lu, X.; Xin, Z. Fabrication of superhydrophobic bio-based polybenzoxazine/hexagonal boron nitride composite coating for corrosion protection. Progress in Organic Coatings **2022**, 167, 106863, doi:https://doi.org/10.1016/j.porgcoat.2022.106863.
16. Sharma, P.; Nebhani, L. Expanding the library of nitrogen enriched polybenzoxazine thermosets prepared from side-chain type benzoxazines functionalized with polyethylenimine. European Polymer Journal **2021**, 155, 110542, doi:https://doi.org/10.1016/j.eurpolymj.2021.110542.
17. Yao, H.; Lu, X.; Xin, Z.; Li, X.; Chen, C.; Cao, Y. Two novel eugenol-based difunctional benzoxazines: Synthesis and properties. Colloids and Surfaces A: Physicochemical and Engineering Aspects **2021**, 616, 126209, doi:https://doi.org/10.1016/j.colsurfa.2021.126209.
18. Deepak Singh, D., Sharma, P., Nebhani, L., Tuning the architecture and performance of multifarious benzoxazine resin based on guaiacol and polyethylenimine, European Polymer Journal **2020**, 135, 109848, doi:https://doi.org/10.1016/j.eurpolymj.2020.109848
19. Ohashi, S.; Iguchi, D.; Heyl, T.R.; Froimowicz, P.; Ishida, H. Quantitative studies on the p-substituent effect of the phenolic component on the polymerization of benzoxazines. Polymer Chemistry **2018**, 9, 4194-4204, doi:10.1039/C8PY00760H.
20. Dumas, L.; Bonnaud, L.; Olivier, M.; Poorteman, M.; Dubois, P. Bio-based high performance thermosets: Stabilization and reinforcement of eugenol-based benzoxazine networks with BMI and CNT. European Polymer Journal **2015**, 67, 494-502, doi:https://doi.org/10.1016/j.eurpolymj.2014.11.030.
21. Thirukumaran, P.; Shakila, A.; Muthusamy, S. Synthesis and characterization of novel bio-based benzoxazines from eugenol. RSC Advances **2014**, 4, 7959-7966, doi:10.1039/C3RA46582A.
22. Lu, G.; Dai, J.; Liu, J.; Tian, S.; Xu, Y.; Teng, N.; Liu, X. A new sight into bio-based polybenzoxazine: from tunable thermal and mechanical properties to excellent marine antifouling performance. ACS Omega **2020**, 5, 3763-3773, doi:10.1021/acsomega.0c00025.
23. Dai, J.; Teng, N.; Shen, X.; Liu, Y.; Cao, L.; Zhu, J.; Liu, X. Synthesis of biobased benzoxazines suitable for vacuum-assisted resin transfer molding process via introduction of soft silicon segment. Industrial & Engineering Chemistry Research **2018**, 57, 3091-3102, doi:10.1021/acs.iecr.7b04716.
24. Agag, T.; Geiger, S.; Alhassan, S.M.; Qutubuddin, S.; Ishida, H. Low-viscosity polyether-based main-chain benzoxazine polymers: precursors for flexible thermosetting polymers. Macromolecules **2010**, 43, 7122-7127, doi:10.1021/ma1014337.
25. Van, A.; Chiou, K.; Ishida, H. Use of renewable resource vanillin for the preparation of benzoxazine resin and reactive monomeric surfactant containing oxazine ring. Polymer **2014**, 55, 1443-1451, doi:https://doi.org/10.1016/j.polymer.2014.01.041.
26. van Krevelen, D.W. Some basic aspects of flame resistance of polymeric materials. Polymer **1975**, 16, 615-620, doi:https://doi.org/10.1016/0032-3861(75)90157-3.

27. Zhang, H.; Li, X.; Qian, W.; Zhu, J.; Chen, B.; Yang, J.; Xia, Y. Characterization of mechanical properties of epoxy/nanohybrid composites by nanoindentation. Nanotechnology Reviews **2020**, 9, 28-40, doi:doi:10.1515/ntrev-2020-0003.
28. Oliver, W.C.; Pharr, G.M. An improved technique for determining hardness and elastic modulus using load and displacement sensing indentation experiments. Journal of Materials Research **1992**, 7, 1564-1583, doi:10.1557/JMR.1992.1564.
29. Trejo-Machin, A.; Puchot, L.; Verge, P. Design and Synthesis of Bio-Based Benzoxazines. Synthetic Resins**,** InTechOpen, **march 2018**, p. 53-69, DOI: 10.5772/intechopen.76104