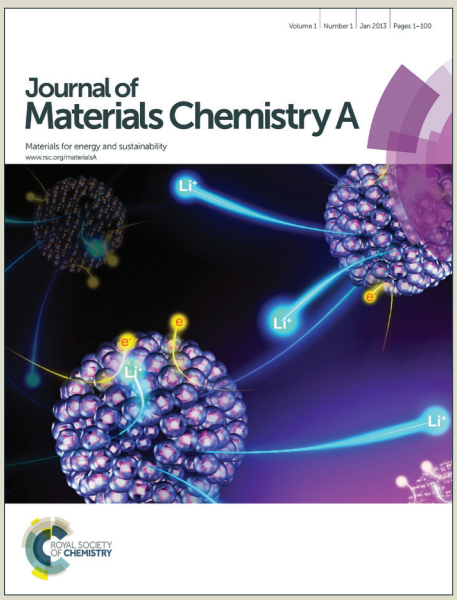
Journal of Materials Chemistry A

Accepted Manuscript



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Eugenol-based benzoxazine: from straight synthesis to taming of the network properties

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Abstract

Mixed benzoxazine precursors were synthesized using a blend of eugenol, a natural renewable product, and phenol. The structures of these mixed benzoxazine precursors with different phenol:eugenol compositions were attested by ^{1}H NMR. Their polymerization and degradation were investigated and monitored by DSC and TGA and showed an enhancement of the crosslinking ability with the phenol content. Depending on its relative content, the phenol moiety proved to limit the thermal degradation of the bis-benzoxazine "hybrid" monomer and allowed the formation of crosslinked networks with high thermomechanical stabilities. The properties of the networks were closely dependent on the phenol : eugenol ratio, which allowed for an adjustment of the crosslinking density and a fine tuning of the glass transition temperature (T_g) within a wide temperature range. A comparison between the polymerized hybrid precursors and blend of two pure monomers displaying the same overall composition showed the same material properties increasing the tune-ability of the system. The eugenol/phenol combination for the preparation of mixed/hybrid benzoxazines or corresponding blends clearly paves the way to new sustainable high performance bio-based materials.

Keywords: Benzoxazine, bio-based, eugenol, tune-ability, hybrid precursor, blend

Introduction

Benzoxazine resins represent a class of thermosets currently benefiting some renewed interest because they can provide a highly competitive combination of properties compared with more classical thermoset materials such as epoxy or phenolic resins. Their popularization in material science was driven by Ishida in the 90's introducing a solventless synthesis.[1, 2] Their major advantages are a near-zero volume shrinkage during curing, low water absorption, a high char yield upon burning, a low coefficient of thermal expansion, easy thermal curing without the need of hardeners or catalysts and, for some benzoxazines, the glass transition temperature (T_g) can be higher than the curing temperature.[3-6]. Nevertheless, the main interesting characteristic of benzoxazines is their straight and easy synthesis by a Mannich-like condensation of three compounds: a phenol, an amine and formaldehyde. As a consequence, the great versatility of monomer molecular design allows for readily tailoring a large range of properties and adding specific functionalities.[7] The number of newly synthesized monomers is therefore constantly increasing. However, a particular interest for both academics and industrials is driven on benzoxazines based on renewable organic materials, for the development of environmentally friendly and sustainable polymers.[8] Bio-based benzoxazines have already been synthesized using various bio-sourced components such as diphenolic acids,[9] cardanol,[10, 11] furfurylamine,[12-14] stearylamine, guaiacol[13, 14]. Interestingly, a short review on bio-based benzoxazine has been published very recently.[15] Eugenol (4-allyl-2-methoxyphenol) has also attracted some attention for preparing different bio-based bis-benzoxazines, the properties of these resins appeared to be quite limited, with a glass transition temperature not higher than 140°C if they are not combined to appropriate comonomers.[16-19] Additionaly, except an article,[17] the first studies of eugenol-based benzoxazine did not mention the drastic thermal degradation of the eugenol-based monomers during the curing procedure. However, eugenol still present a high potential for green chemistry due to its realistic availability and low production cost.[20] Indeed, eugenol is the main component (80 wt%) of clove essential oil and is relatively cheap (*ca.* 5 $.kg^{-1}). Its molecular structure is based on a tri-substituted benzene on which the *ortho* and *para* positions are occupied by a methoxy and an allyl group respectively. It is known that the preferential site for the ring opening polymerization of benzoxazines being the *ortho* position, however the *para* position shows also some ability to react.[21-23] As the two mentioned positions are hindered, the polymerisation of eugenol-based benzoxazines is theoretically not likely to occur. Additionally, although the allyl function is readily attractive for copolymerization, its thermal reactivity to enhance the homopolymerisation of eugenol-based benzoxazine is not effective or sufficient to allow the formation of highly crosslinked networks. Contrariwise, and taking into advantage the thermal stability of the allyl function, the allylic group of eugenol-based benzoxazine has been readily used to enhance the crosslinking density of benzoxazine networks using a

copolymerzation with bismaleimide, which proceeds at temperature lower than the ring opening polymerization of benzoxazine ring and can lead to improved network properties.[17]

In this paper we propose the preparation of mixed/"hybrid" benzoxazine monomers showing both eugenol and phenolic moieties, leading to additional potential polymerization sites. The influence of the eugenol content on the crosslinking ability of the bio-based precursors has been investigated. The properties of the so-polymerized compositions were found to be easily tuneable through the eugenol content.

Experimental

Materials

The following chemicals were purchased from Aldrich and used without any further purification: 1,4-phenylenediamine (99%), eugenol (99%), phenol (99%) and paraformaldéhyde (95%). Technical chloroform and diméthylsulfoxyde (DMSO) were purchased from VWR and used as received.

Characterization

The ^{1}H NMR spectra were recorded with a NMR spectrometer (Bruker, 500 MHz), using deuterated dimethylsulfoxide (DMSO-d_6) as solvent and the chemical shift was calibrated by setting the chemical shift of DMSO as 2.50 ppm.

Size Exclusion Chromatography (SEC) was performed in $CHCl_3$ at 35 °C using a Polymer Laboratories liquid chromatograph equipped with a PL-DG802 degasser, an isocratic HPLC pump LC 1120 with a flow rate of 1 ml/min, a differential refractive index detector ERMA 7517, and two PL gel Mixed-B 10 µm columns. PS standards were used for calibration.

Calorimetric studies were carried out at a heating rate of 10 °C/min using a differential scanning calorimeter (DSC Q200 from TA Instruments) under a nitrogen flow of 50 mL/min. An Indium standard was used for calibration.

Thermogravimetric analysis (TGA) was used to study the anaerobic thermal degradation of the precursor blends and cured systems. Approximately 10 mg of the sample was submitted to a temperature ramp from 25 to 1000°C at a heating rate of 10°C/min under a nitrogen flow of 60 mL/min. All TGA experiments were performed by using a TGA Q50 device from TA Instruments.

Thermo-mechanical properties were investigated using a dynamic mechanical thermal analysis (DMTA) apparatus (DMA 2980 Dynamical Mechanical Analyzer from TA Instruments). Specimens (70x12x3 mm^3) were tested in a dual cantilever configuration with a dual cantilever length of 35 mm. The thermal transitions were studied in the temperature range of 25-370 °C at a heating rate of 3 °C/min and at a fixed frequency of 1 Hz. An amplitude of 18 µm was used corresponding to a strain of 0.043 %. One representative sample was used for the measurements.

Sol-gel analyses were performed with DMSO. About 1 g of polymerized sample was accurately weighed (w_i) and introduced in a balloon equipped with a reflux. A large excess (100 mL) of solvent was then introduced and heated at 200°C for 12h to allow the complete extraction of the soluble part. Swollen samples were extracted and the solvent was then evaporated under vacuum for 48h at 200 °C to determine the weight of dried gel (w_{dg}) *i.e.* the weight of insolubles:

$$\% \, gel = \frac{w_{dg}}{w_i} \times 100$$

Preparation and characterization of the eugenol-based benzoxazine, PE-pPDA (1 : 1)

The PE-pPDA (1 : 1) synthesis has been adapted from a procedure reported by Ishida *et al.*[2] Eugenol 30.67 g (1.85 10^{-1} mol), phenol 17.58 g (1.85 10^{-1} mol) and paraformaldehyde in excess 25.72 g (8.14 10^{-1} mol) were introduced in a beaker at 50 °C. The mixture was stirred with a mechanical stirrer leading to the formation of a homogeneous white solution. 20 g of 1,4-phenylenediamine (1.85 10^{-1} mol), finely powdered, was then added into the beaker and immersed in an oil bath preheated at 120 °C. The addition of the diamine leads to the gelation of the mixture resulting from the condensation of the aromatic diamine and formaldehyde and the subsequent formation of a triazine network.[24, 25] At this temperature, the triaza compound reacts quickly with eugenol and phenol and the gel is destroyed in a couple of minutes. The mixture was then allowed to react for 25 min under continuous stirring. The crude reaction product was then dissolved in $CHCl_3$ (~150 mL) and filtered in order to remove the residual insolubles (0.2 g) issuing from unreacted triaza compound. The solvent was then evaporated on a large aluminium surface in a vacuum oven at 140 °C for 10 min. A vitrified dark-orange resin was obtained (weight yield ~ 93 %). The PE-pPDA (1 : 1) precursor was characterized by a T_g of ~5 °C, and enthalpy of polymerization equal to 280 J.g^{-1} occurring at a T_{Peak} of 240 °C.

Preparation of PE-pPDA (x : 2-x)

Each benzoxazine with different phenol : eugenol (P : E) ratios (x : 2-x) was prepared according to the procedure previously described. Only the amount of phenol and eugenol were adjusted in order to prepare benzoxazines with P : E molar ratio of 1.2 : 0.8; 1.4 : 0.6; 1.6 : 0.4 and 1.8 : 0.2. In all cases, a dark orange vitrified resin was obtained with a weight yield higher than 92 % and a residual insoluble proportion lower than 0.4 wt%.

Preparation of P-pPDA, E-pPDA and their blend

The details of the synthesis procedure of "single component" monomers based on either phenol (P-pPDA) or eugenol (E-pPDA) can be found elsewhere.[17, 26] The two precursors were blended in the molten state at 140°C, which is facilitated by the low viscosity of the E-pPDA.

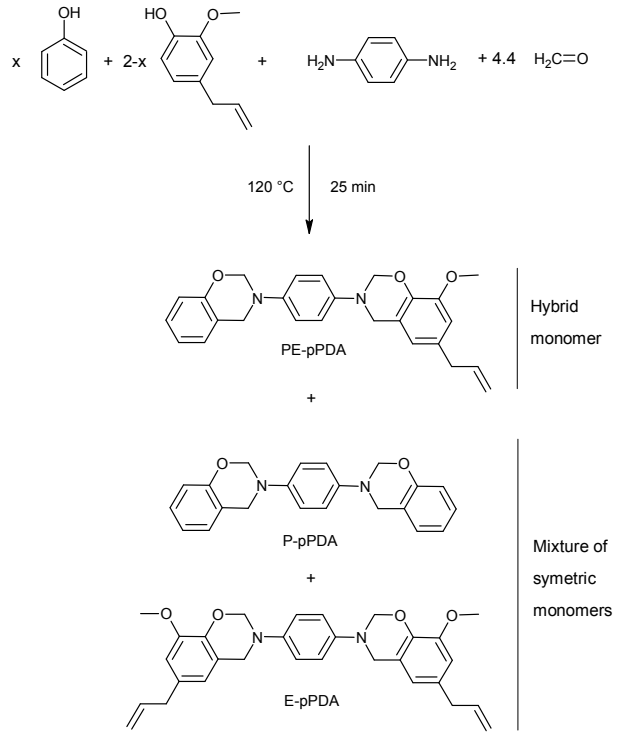
Curing procedure

Each precursor or blend was introduced in a stainless steel 80x12x3 mm^3 mould, melted, further degassed in a vacuum oven at 140 °C for 10 min, and then step cured in an air-circulating oven according to the following cycle: 1h at 160 °C, 2h at 180 °C, 2h at 200 °C, and 30 min at 220 °C. Temperatures of the step cure were determined in order to avoid a thermal degradation which can occur simultaneously to the polymerization if the temperature is rapidly increased at elevated values. Afterwards, the samples were allowed to slowly cool down to room temperature before unmolding.

Results and Discussion

Synthesis and characterization of PE-pPDA precursors

PE-pPDA precursors were successfully prepared by a solventless synthesis from eugenol, phenol and 1,4-phenylene diamine with an easy and scalable procedure according to the reaction depicted in Scheme 1.



Scheme 1 One pot synthesis of PE-pPDA precursors.

The structures of the new benzoxazines were investigated by ^{1}H NMR as shown in Figure 1. The attribution of peaks was based on the analysis of ^{1}H NMR spectra of reagents and on similar benzoxazine derivatives.[16, 17] The presence of characteristic peaks around 4.5 and 5.3 ppm corresponding to the Ph-CH_2-N and O-CH_2-N of oxazine ring, respectively, attests for the formation of the benzoxazine ring.[27] Interestingly, these signals are split into two well defined peaks, which correspond to both parts of the molecule, *i.e.,* the benzoxazine ring formed with phenol (b' and c') and eugenol (b and c). Additional aromatic peaks labelled *a, d, e, d', e', f', g'* and the presence of the singlet *f* at 3.67 ppm corresponding to the O-CH_3 and the doublet *g* at 3.23 ppm attributed to the methylene of the allyl function attest for the formation of the desired benzoxazine structure.

The right matching of all integrals and the presence of peaks *i* and *h* at 5.0 and 5.9 ppm with relative intensities of 2 and 1, respectively, support the successful benzoxazine synthesis without loss of the allyl group. Additionally, some residual traces of unreacted eugenol can also be found through the signal located at 3.76 ppm corresponding to the O-CH_3 group of the eugenol molecule. This light amount of unreacted eugenol can be correlated to the incomplete reaction of the triaza compound, the amount can however be neglected regarding the low intensity of the signal. The evolution of the distribution of the intensity of peaks c and c' compared to the eugenol initial content matches relatively well the theoretical values as shown in Tab. 1 and illustrated in the zoom part of Fig. 1. The only divergent integral ratio is observed for the PE-pPDA (1.8 : 0.2), but this discrepancy may arise from a low signal intensity superimposed with a broadening signal.

Tab. 1. Composition of bio-based PE-pPDA and verification by ^{1}H NMR

PE-pPDA (x : 2-x)	% C_{Bio}	c' : c integrals ratio	
		exp.	theor.
1 : 1	53.8	1 : 1.02	1 : 1
1.2 : 0.8	47.6	1 : 0.7	1 : 0,67
1.4 : 0.6	41.0	1 : 0.5	1 : 0,43
1.6 : 0.4	33.9	1 : 0.24	1 : 0,25
1.8 : 0.2	26.3	1 : 0.05	1 : 0,11

Indeed, as can be seen in Fig. 1, the broadening signals localized in the area of methylenic protons of the benzoxazine ring (c, c', d and d') increases when the eugenol content becomes lower. This broadening is attributed to the presence of some oligomers which are formed during the synthesis and the drying process.[26] As a result, an increase of the eugenol content into the molecule seems to decrease beneficially the risk of oligomerization during synthesis.

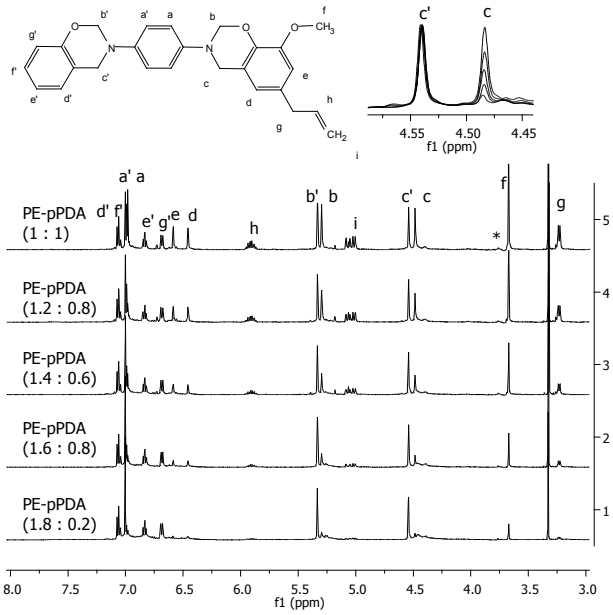


Fig. 1^{1}H NMR spectra of PE-pPDA precursors in DMSO-d_6 normalised by the intensity of peak c' and zoom over the area of methylene protons. Residual methyl of eugenol labelled *.

PE-pPDA precursors were further analysed by SEC in $CHCl_3$ (Fig. 2). These results complete the ^{1}H NMR analysis and bring forward the formation of different monomers. Indeed, a PE-pPDA precursor is comprised of a mixture of pure P-pPDA and E-pPDA with a certain proportion of hybrid monomers, *i.e.,* which contain both an eugenol and a phenol parts as shown by the appearance of 3 major elution peaks instead of the expected two peaks associated to pure E-pPDA (17.6 min) and P-pPDA (18.7 min). However, it should be noted that the accurate concentration of each species cannot be estimated from the chromatograms. Indeed, as the chemical structure of each monomer varies, the response of the refractive index detector is not proportional to the concentration only. Back to the results, the blend of the two initial benzoxazine monomers (P-pPDA + E-pPDA) with a molar ratio of 1:1 only showed two main elution peaks. The chromatograms also suggested an increase of the

oligomer content with the decreasing proportion of eugenol into PE-pPDA with the emergence of other signals at lower elution time but their proportion cannot be accurately determined.

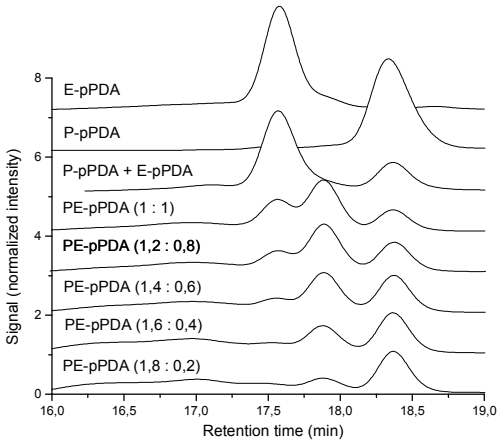


Fig. 2 SEC chromatograms of benzoxazine precursors normalized by the total signal area. Solvent : $CHCl_3$

The properties and reactivity of PE-pPDA precursors were further characterized by DSC. Fig. 3 shows the evolution of the curing exotherm depending on the P:E ratio. As clearly evidenced, an increase of the eugenol content shifts the exotherm peak to higher temperatures whereas the peak width is reduced. It appears from these observations that a larger window of processability for the eugenol-rich benzoxazines is achieved. Additionally, there is no evidence for the reaction of allylic group for the studied temperature range. This result is in accordance with the ones obtained for the pure eugenol-based benzoxazine E-pPDA where the allyl function was found to not be polymerized nor post-cured before the thermal degradation of the eugenol moiety.[17] The preservation of the allyl function can be considered of prime interest for a possible post-functionnalization or co-curing with an appropriate comonomer.

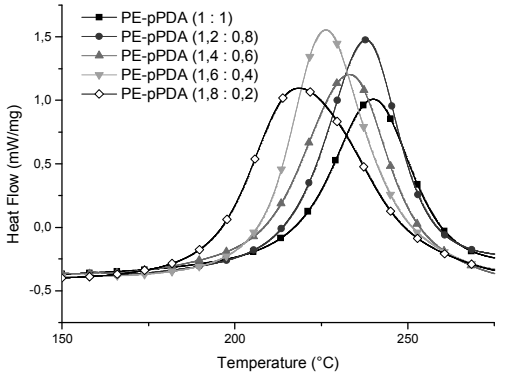


Fig. 3. DSC curing exotherms of PE-pPDA (x : 2-x) precursors

A deeper study of the polymerization enthalpy values highlights the beneficial effect of the phenol moiety to the polymerizability of PE-pPDA (x:2-x) precursors (Tab. 2). Indeed, the curing enthalpy value per mole of benzoxazine cycle increased with the phenol content from 58 kJ/mol until it reached a threshold of 72 kJ/mol when the phenol/eugenol ratio becomes higher than 1.4 : 0.6. The value of 72 kJ/mol is quite interesting as it corresponds to the theoretical enthalpy of polymerization of a benzoxazine cycle, which is of 73 kJ/mol. [28] The decreasing enthalpy observed when the eugenol content increases can be explained by a lower polymerizability of the eugenol-rich precursors. This result is consistent with the lower reactivity of the eugenol moiety as the preferential polymerization sites, *i.e.,* the *ortho* and *para* ones are not free but occupied by the oxymethylene and the allyl function respectively. Moreover, with increasing the content of phenol moiety, which exhibits free *ortho* and *para* positions, the ring opening polymerization of the benzoxazine cycles with a structure containing both eugenol and phenol seems to be favoured.

Tab. 2 Evolution of the thermal properties of PE-pPDA (x : 2-x) precursors.

PE-pPDA (x : 2-x)	T_g^{ini} (°C)	ΔH (J/g)	ΔH (kJ/mol) of benzoxazine cycle
1 : 1	5	280	58
1.2 : 0.8	10	335	67
1.4 : 0.6	15	370	71
1.6 : 0.4	21	385	72
1.8 : 0.2	32	400	72

In addition, Tab. 2 shows the evolution of the glass transition temperature of each precursor combination. Interestingly, an increase of the eugenol content significantly reduces the value of the T_g increasing even more the processing window of this kind of resin precursor. This decrease of T_g may be due to the extra free volume provided by the oxymethylene and allyl function.

Another interesting feature provided by the presence of the phenol moiety into the benzoxazine structure is the greater thermal stability of the precursor. Indeed, while the pure E-pPDA monomer undergoes a dramatic thermal degradation within the curing temperature range with a weight loss of nearly 40% at 300°C, the increasing content of phenol in the PE-pPDA precursor drastically limits the degradation which becomes negligible when the P:E ratio reaches 1,4 : 0.6 (Fig. 4). The polymerization can therefore become predominant at these temperatures and stabilizes the weaker eugenol part.

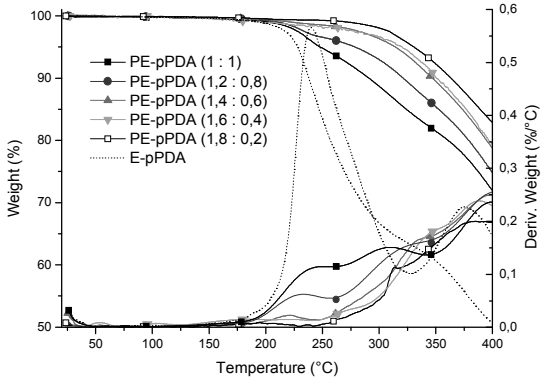


Fig.4. TGA profiles of PE-pPDA and E-pPDA precursors recorded under nitrogen upon the curing temperature range

Properties of the cured PE-pPDA

The cured samples were characterized after curing, without any additional treatment, i.e. the possible soluble fraction due to low polymerization degree of eugenol moiety was not extracted. The

properties are thus those of the entire samples. The evolution of the glass transition temperatures of the cured PE-pPDA with different compositions is depicted in Fig. 5. The T_g increased proportionally with the phenol content from 120 °C to 220°C for the ratio P:E of (1:1) to (1.8:0.2), respectively. More precisely, the glass transition temperature has a linear dependence (R^2 = 0.991) with the proportion of phenol moiety into the PE-pPDA polymers for the studied P:E ratios.

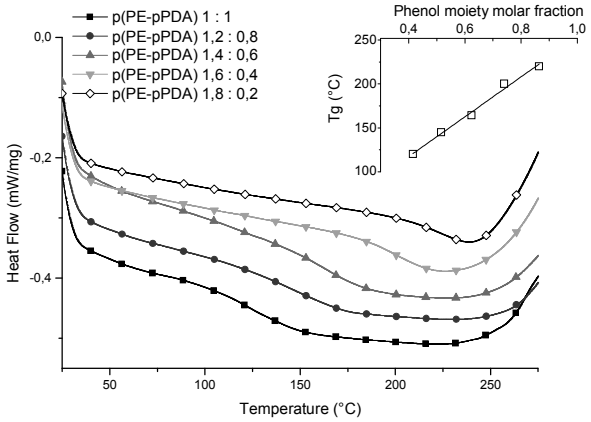


Fig. 7. Evolution of the glass transition temperature of cured PE-pPDA-resins with different P:E ratios

The T_g relationship with respect to the composition follows in this case a Gordon and Taylor simplified model based on additivity and can be expressed as follows: [29]

$$T_g = \sum_i \omega_i . T_{gi}$$

were ω_i is the weight fraction of component *i* and T_{gi} the T_g of the pure components *i*.

The determination of each T_{gi} by this model leads roughly to a T_g of 250°C for the pure p(P-pPDA) and 25°C for the p(E-pPDA). If the first value is slightly overestimating measured values by nearly 20°C, the low T_g value for the p(E-pPDA) is quite well representative for the poor polymerizability and crosslinkability of the E-pPDA precursor as previously discussed. The very low extrapolated T_g of pure p(E-pPDA) would imply that the functionality of the eugenol moiety should be near zero, even in the case of PE-pPDA precursors. In other words, the benzoxazine ring mounted on eugenol will not be involved in the formation of the active segment of the network. This remark is not in accordance with referenced data for benzoxazine synthesized with eugenol and diamines, where the authors argue a polymerizability of both the benzoxazine ring and the allyl function.[16] Even if the diamine used is quite different in our case, the properties of the polymerized samples are clearly driven by the rate of benzoxazine ring attached to the phenol while the benzoxazine ring attached to the eugenol seems to be inactive. The inaptitude of eugenol benzoxazine ring to polymerize even with additional free polymerizable positions provided by the phenol moiety is further supported by swelling tests.

Tab. 3. Average calculated functionality and % gel calculated by swelling measurements.

p(PE-pPDA) (x : 2-x)	f_{ave}	% gel
1 : 1	2	0
1.2 : 0.8	2.4	80
1.4 : 0.6	2.8	100
1.6 : 0.4	3.2	100
1.8 : 0.2	3.6	100

As evidenced in Tab. 3, the polymerized PE-pPDA (1:1) remained entirely soluble meaning that the polymer was not crosslinked. As a result, both the allyl function and the eugenol-based benzoxazine ring were not involved in the polymerization. The calculated average functionality f_{ave}, *i.e.,* the number of covalent links formed by the molecule, for this composition is 2 if we consider that the eugenol moiety presents a functionality of zero. The functionality is in this case not sufficient to form a three dimensional network. In addition, when the phenol content increases, the gel fraction increases until it reaches 100% meaning that there are enough active benzoxazine rings to link all precursors to the network if the P:E ratio is higher than the critical value of (1.4 : 0.6). The average functionality for this composition is equal to 2.8. Actually, this value is near 3.0, meaning that, in average, almost all precursors can form crosslinking points. A further increase of phenol content leads to an increase of the average functionality of precursors and thus to a higher crosslinking density. The determination of the gel content tends thus to prove that the eugenol moiety cannot be significantly involved into the crosslinking mechanism.

Back to the analysis of the polymerized samples, the crosslinking density was further estimated by DMA. Based on the rubber elasticity theory, the value of the storage modulus G' taken in the rubbery state is proportional to the crosslinking density.[30] Fig. 8. shows the variation of the thermomechanical properties of each p(PE-pPDA) composition. As can be clearly seen, a plateau appears after the glass transition when the ratio of phenol in p(PE-pPDA) is higher than 1.4 : 0.6. The value of the storage modulus in the rubbery area increased with the proportion of phenol traducing a higher crosslinking density. For lower phenol content, G' did not form a real plateau as the samples flow with the temperature. In addition, the temperature at the maximum of the tan δ peak, associated to the T_g increased gradually with the phenol content of the resin, but the linearity is in this case not well established. This light divergence from the DSC measurements may arise from the difference of the solicitation type. Nonetheless, the thermomechanical stability can be tailored by the P:E ratio and covers a range from 150°C to 220°C. For the phenol-rich content, the thermomechanical behaviour is very close to the one of the pure p(P-pPDA) The networks are thus very similar. This observation shows again that the crosslinking of the PE-pPDA precursors is driven by the phenolic moiety.

In addition, Fig. 8 highlights an interesting phenomenon: a blend composed of pure P-pPDA and E-pPDA polymerized in stoichiometric ratio, shows a similar behaviour compared to the polymerized hybrid monomer p(PE-pPDA) 1 : 1. This result extends further the tune-ability of the studied system with a possible adjustment of the properties by the addition of a specific

pure monomer. The hybrid precursor properties follow thus the same rules as for blends.

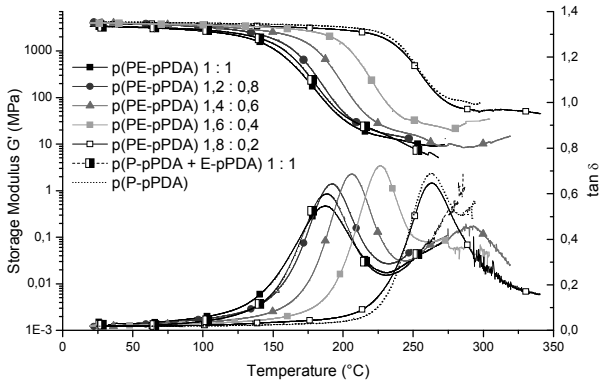


Fig. 8. Temperature dependence of the storage modulus G' and tan δ for different benzoxazine compositions.

Thermal stabilities of the polybenzoxazines were investigated by TGA (Fig. 9). As clearly evidenced, an increase of the phenol content in the benzoxazines leads to an improved thermal stability and char ability. Indeed, the temperature $T_{5\%}$ corresponding to the weight loss of 5% is shifted from 300 °C to 340°C for the P:E ratio of 1:1 and 1.8:0.2, respectively. The charring ability is also progressively increased from 45 to 52% for the same studied compositions. This enhancement of thermal properties may be associated to higher aromatic contents and crosslinking densities in the phenol-rich compositions while the eugenol moieties can be considered as the weakest part with the oxymethylene and allyl function.[17] However, all the polymers present a relatively high thermal stability with char yields around 50% which let expect improved fire properties.[31] Additionally, a similarity of the behavior of the hybrid polybenzoxazine PE-pPDA (1:1) and the stoichiometric blend of P-pPDA and E-pPDA is again observed. The thermal stability is thus governed by the phenol content of each polybenzoxazine.

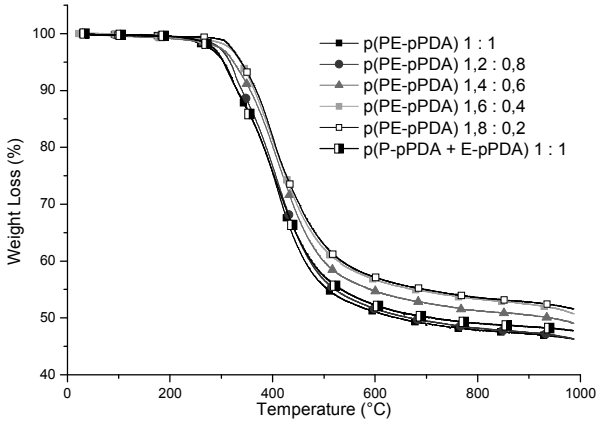


Fig. 9. TGA anaerobic profiles of different polymerized benzoxazines compositions.

Conclusions

The use of eugenol, a renewable natural product, for the synthesis of hybrid Phenol:Eugenol benzoxazine precursors (PE-pPDA) allows the preparation of different crosslinked matrices exhibiting a wide range of properties. Our study demonstrates that the introduction of an eugenol part into a benzoxazine molecule based on a diamine and phenol, facilitates the solventless synthesis while the eugenol content can be used to monitor the crosslink density and the resulting properties of the bio-based network. Interestingly enough, direct blending of both pure Eugenol (E-pPDA) and pure Phenol (P-pPDA) based benzoxazine monomers, similar results to hybrid precursor (PE-pPDA) ones are obtained allowing to enlarge the possibilities of modulation of the system. These results also point out the weakness of eugenol monomer which cannot be used alone for the preparation of crosslinkable benzoxazines due to its ortho and para substitutions actually limiting the polymerizability of the attached benzoxazine ring and leading to a partial thermal degradation during curing. The degradation process needs a deeper investigation far beyond the scope of this paper. To conclude, new bio-based thermosetting matrices can be thus prepared and allow the covering of a large range of properties, which can be tuned by the ratio of bio-based carbons.

Acknowledgements

The authors wish to thank the "Région Wallonne" for the financial support in the framework of the ECOTAC project from the "Pôle de Compétitivité SKYWIN". MATERIA NOVA and CIRMAP thank the European Community for general support in the framework of the 7th Framework research project "IASS", the ''Belgian Federal Government Office Policy of Science (SSTC)'' for its support in the framework of the PAI-6/27 and the ''Région Wallonne'' in the framework of the ''Programme excellence FLYCOAT''.

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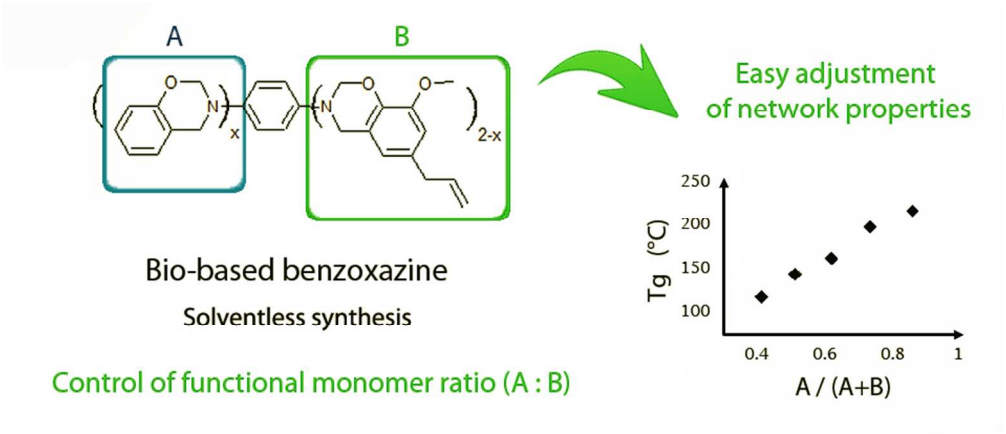

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