

This document is confidential and is proprietary to the American Chemical Society and its authors. Do not copy or disclose without written permission. If you have received this item in error, notify the sender and delete all copies.

Hardener-Dependent Properties of Twice Renewable Epoxy Resins Combining Tailored Lignin Fractions and Recycled BPA

Journal:	<i>ACS Sustainable Chemistry & Engineering</i>
Manuscript ID	sc-2024-02394r.R2
Manuscript Type:	Article
Date Submitted by the Author:	15-May-2024
Complete List of Authors:	Comí, Marc; Flemish Institute for Technological Research, Materials and Chemistry Unit Van Ballaer, Brent; Flemish Institute for Technological Research, Materials and Chemistry Unit Gracia Vitoria, Jaime; Flemish Institute for Technological Research, Materials and Chemistry Unit Parida, Dambarudhar; Flemish Institute for Technological Research, Materials and Chemistry Unit Aerts, Annelore; Flemish Institute for Technological Research, Materials and Chemistry Unit Vanbroekhoven, Karolien; Flemish Institute for Technological Research, Materials and Chemistry Unit Vendamme, Richard; Flemish Institute for Technological Research, Materials and Chemistry Unit

SCHOLARONE™
Manuscripts

Hardener-dependent properties of twice renewable epoxy resins combining tailored lignin fractions and recycled BPA

Marc Comí,^{a*} Brent van Ballaer,^a Jaime Gracia-Vitoria,^a Dambarudhar Parida,^a Annelore Aerts,^a Karolien Vanbroekhoven^a and Richard Vendamme.^{a*}

^a Flemish Institute for Technological Research (VITO N.V.), Boeretang 200, Mol 2400, Belgium.

*Corresponding author. Tel: +32 14 33 69 72; email address: marc.comibonachi@vito.be and richard.vendamme@vito.be

Keywords: Kraft Lignin, Recycling, Coatings, Crosslink Density, Epoxy Resins, Hardener.

Keywords: biobased, sustainable, epoxide, coatings, crosslink density, curing, adhesion

ABSTRACT: The use of bio-sourced and/or recycled raw materials represents a promising strategy for making the polymer industry more renewable. In this context, both biobased lignin fractions and chemically recycled Bisphenol A (r-BPA) have been independently considered as promising renewable alternatives to aromatic fossil monomers. Here, renewable thermosetting epoxies were designed by combining tailored lignin fractions and rBPA, while the influence of several hardeners on the physical structure and properties of the obtained resins was systematically investigated. To do so, the phenolic groups of r-BPA derived from polycarbonate waste and of solvent-extracted Kraft lignin (EKL) were both glycidylated with epichlorohydrin (ECH). This led to the renewable epoxy precursors r-BPA diglycidyl ether (r-DGEBA) and glycidylated extracted Kraft lignin (GEKL), respectively. Twenty different formulations were then designed by tailoring the structural parameters of the resins, such as the hardener length and functionality, the epoxide:hardener (E:H) ratio and the lignin content. The thermomechanical properties were investigated, and the structure-property relationships established, highlighting the excellent and tunable performance of these renewable epoxies. Finally, flexible coatings were produced with lower crosslink density formulations that demonstrated excellent performance, even with 30% of lignin content. Overall, our results show how biobased and recycled aromatic building blocks could be combined for the design of epoxy resins with superior properties, both in sustainable and technical terms.

Introduction

Almost a century after their invention, epoxy resin thermosets still represent a prominent family of versatile and durable synthetic polymers that have found widespread applications in various industries, thanks to their remarkable adhesive properties, excellent electrical insulation, and superior resistance to heat and chemicals. Their ability to form strong, durable bonds with different substrates makes them ideal for applications as diverse as art, automotive, construction, electronics, and aerospace. Their popularity is also based on their ease of molding, low shrinkage during curing, and ability to create a protective barrier against environmental factors, satisfying the advanced specifications expected in adhesives, coatings, and material encapsulation.¹ Despite their advantageous properties, traditional epoxy resins are still derived from glycidylated bisphenol A (BPA), which raises certain issues. At first, BPA is still entirely derived from petroleum feedstocks that are being depleted. Then, BPA is also raising environmental and health concerns for being an endocrine disruptor. These concerns are pushing both academia and industry to develop strategies for enhancing the sustainability of BPA-based epoxy resins, such as i) finding biobased alternative building blocks to (partially) replace BPA in epoxy resin formulations, ii) preventing BPA from ending up in landfill and leaching into the environment, and iii) chemically recycling BPA-based polymers and up-cycling the obtained recycled BPA (r-BPA) toward new high-value applications (e.g., such as coatings).^{2,3}

Plastic chemical depolymerization allows the end-of-life material to be fragmented chemically, efficiently producing the original monomers, which can be purified and used for new applications.⁴ The principal limitations involve the purity of the waste material, solubility, accessibility to the internal structure and capability to break the targeted bonds.^{5, 6} Polycarbonates from transparent screens and plates produced globally in large scale, especially during the COVID restrictions period, represented the perfect material candidates to attempt this chemical recycle methodology.⁷ Thus, our group was motivated to efficiently produce high-quality recycled bisphenol A (r-BPA) from polycarbonate waste, considering previously reported methodologies.^{8-10x} The obtention and repurpose of r-BPA could relax the utilization of fossil-based raw chemicals, promote the recyclability of similar plastics, and consequently, dramatically reduce the BPA environmental impact.¹¹

1
2
3 A complementary strategy to prevent BPA-derived waste could involve using biobased
4 alternatives to produce more sustainable epoxy resin, which is vital for a material industry in
5 continuous expansion.¹ From the perspective of chemical structure similarity with BPA, biobased
6 small molecules such as eugenol and vanillin have been proposed as suitable candidates,¹²⁻¹⁵ but
7 their high obtention price, availability and modification process limit the upscaling production.¹⁶
8 In recent years, lignin biopolymer has attracted significant interest as a biobased candidate due
9 to its three-dimensional structure rich in aromatics and active phenolic groups, which provides
10 rigidity, strength, and reactive points.^{17, 18} Additionally, lignin is the most abundant natural
11 aromatic biopolymer and around 85 % of the total global production is originated as a byproduct
12 from the Kraft pulp process for paper production.^{19, 20} For the time being, the Kraft lignin is
13 regarded as waste and incinerated to partially recuperate the operational energy from the pulp
14 process, which makes the valorization of Kraft lignin into high-value products a suitable biobased
15 alternative to BPA for the production of more sustainable epoxy resins.²¹ To avoid processability
16 issues and to achieve a major resemblance with the BPA molecule, Kraft lignin is generally
17 fractionated to drastically reduce the molecular weight, improve the number of active functional
18 groups, and enhance the solubility.²² This process relies on the hydrolysis of internal ether bonds,
19 such as β -O-4, to produce new aliphatic and phenolic alcohols. An increase of the lignin phenolic
20 content has demonstrated to gratefully assist the epoxidation process, providing more reactivity
21 to the resulting glycidylated biobased monomer.²³
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38

39 Despite the similarities with glycidylated bisphenol A (DGEBA), the utilization of glycidylated
40 lignin (GL) in a resin epoxy formulation present several challenges that must be considered, such
41 as process reproducibility, mixture uniformity, and crosslink contribution. The macromolecular
42 statistical structure and polydispersity of Kraft lignin depends on a large number of parameters,
43 such as the botanical origin (e.g., hardwood vs. softwood), biorefining process, operational batch,
44 fractionation treatment, and functionalization methodology, among others. This affects the
45 replicability of the epoxy resin fabrication, as has been widely reported.^{24, 25} Moreover, in order
46 to avoid phase separation and irregularities on the resulting biobased epoxy resins, the proper
47 selection of formulation mixture is pivotal and presents few limitations commonly related with
48 the dispersion of the GL. These are usually addressed by balancing the biobased content, and the
49
50
51
52
53
54
55
56
57
58
59
60

1
2
3 affinity between the epoxide (BPA, GL, other epoxide compounds) blend with the hardener, since
4 drastic differences in structure (molecular weight, polarity, solubility) typically lead to
5 heterogeneous crosslinks and alter the final properties.²⁶⁻²⁸ The most impacting factor on the
6 material properties is related to the lignin incorporation in a typical crosslink network
7 (BPA:hardener) since the use of this biobased moiety as a partial replacement of BPA will modify
8 the final material properties. The study of systematic alterations in the crosslink density of epoxy
9 resins and understanding its correlation to thermal and mechanical performance is essential. It
10 allows the selection of the best internal crosslink structure for a targeted application.

11
12 The transition to more sustainable epoxy resins with lower carbon footprints should be
13 accompanied by an enhancement of the material's physical properties, understanding the
14 structure-function relation based on the resin composition and benchmarking application tests.
15 Among the numerous functions, lignin-based epoxy resins could provide excellent performances
16 as coatings, where a low CO₂ footprint is crucial, the recyclability is not a primary target and this
17 application is attracting significant attention.²⁹ The remaining phenol groups within lignin serve
18 as effective scavengers of radicals, preventing oxidation reactions, and work as chromophores
19 capable of absorbing UV light, promoting the protection barrier capabilities. While the aliphatic
20 alcohols assist the material-substrate adhesion by forming H-bonds or strong polar attractions to
21 oxide or hydroxyl surfaces.^{30, 31}

22
23 Herein, we have designed and characterized a family of twenty renewable epoxy resins by
24 systematically modulating the structural parameters of the formulations, such as the hardener
25 chemical structures, the epoxide:hardener (E:H) ratios, and the content of extracted Kraft lignin
26 (**EKL**) contents. In order to maximize the renewability of the epoxy resins, a recycled bisphenol A
27 (**r-BPA**, obtained by solvolysis of PC) was combined with extracted Kraft lignin (**EKL**). The
28 functionalization of both compounds using epichlorohydrin (**ECH**) yielded glycidylated kraft lignin
29 (**GEKL**) and bisphenol A diglycidyl ether (**r-DGEBA**) that were combined with linear diamino-based
30 hardeners to synthesize the series of epoxy resin material **Ref1-5** and **ER1-15**. Structural
31 characterization using nuclear magnetic resonance (NMR), Fourier transform infrared (FT-IR), gel
32 permeation chromatography (GPC) and complementary chemical analysis confirmed the quality
33 and reproducibility of the process. The material curing conditions were established after the
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

1
2
3 evaluation of the formulation mixtures thermal behavior by DSC. Thermal and mechanical
4 properties of the final epoxy resin series were investigated using DMA and tensile test analysis.
5 Afterwards, the data extracted was compared to establish a close relationship with the material
6 internal network structure. Finally, a metal coating was selected for application. The coating was
7 prepared and the adhesion of the lignin-based epoxy resins to the substrate was tested. With
8 this study, we have illustrated the combined use of recycled and biobased building blocks to
9 deliver renewable materials with improved properties, anticipating applications in search for
10 alternatives to fossil resources. Moreover, this work allows the prediction of the properties of
11 lignin-based-epoxy resins by simply exchanging some parameters in the formulation that affect
12 the crosslink density of the material which could alter the performance in a designated
13 application.
14
15
16
17
18
19
20
21
22
23

24 **Results and Discussion**

25 **Molecular Design, Synthesis and Characterization of Renewable Epoxy Precursors.**

26
27 The steps followed in the preparation of the epoxide monomers are depicted in **Figure 1** and the
28 complete methodology is described in *Supporting Information, Experimental Procedures (Table*
29 **S1-2** and **Figure S1-3**). As previously reported, polycarbonate waste from transparent screens
30 and panels was selected, washed, treated, and depolymerized.^{9, 10} High purity r-BPA crystals were
31 isolated after precipitation of the depolymerization mixture in toluene. The r-BPA was
32 functionalized with ECH in basic conditions, obtaining r-DGEBA in good yields (> 90 %), as
33 uncolored powder after column purification and dry under vacuum (**Figure 1a**).³²
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

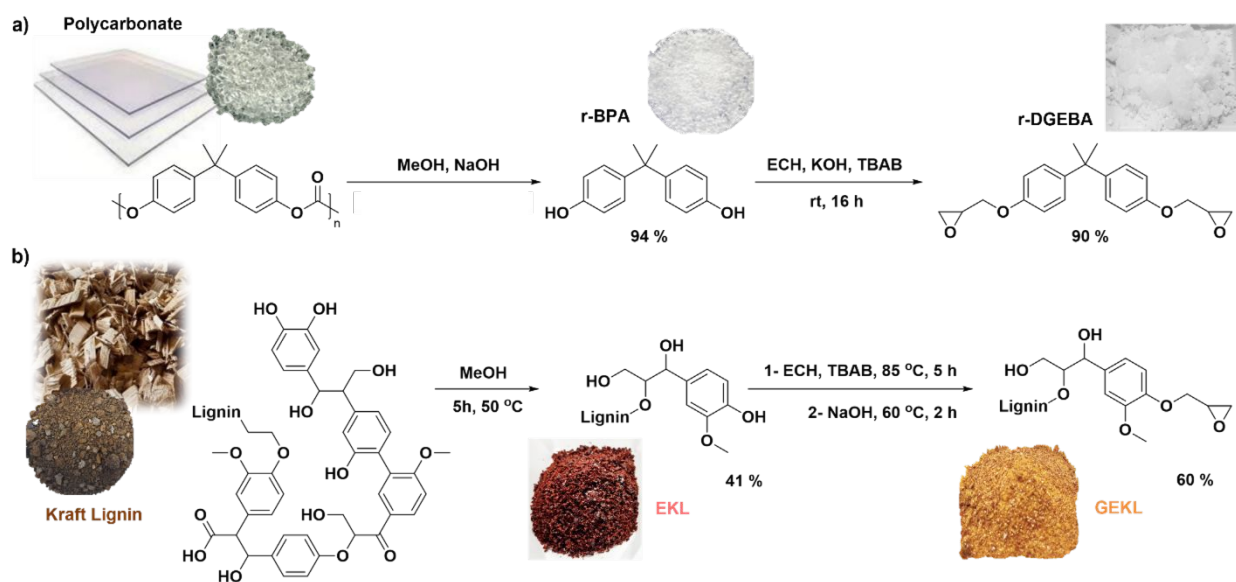


Figure 1. Scheme of the routes used from waste source to epoxide monomers with photographs of the compounds: (a) PC, r-BPA and r-DGEBA, and (b) Kraft Lignin, EKL and GEKL.

As observed in the first part of **Figure 1b**, Kraft lignin was fractionated in methanol at 50 °C and after 5 h, the soluble part (up to 40 %) was isolated, dried, and characterized. This methodology was repeated three times and the extracted Kraft lignin (**EKL1-3**) samples exhibited suitable molar masses (M_n) ranging from 0.95 to 1.15 Kg/mol with values of polydispersity (\mathcal{D}) in all cases close to 2, as summarized in **Table S1**. The hydroxyl content was calculated from the peak integration of the ^{31}P NMR spectra for **EKL1-3** samples, considering the diverse reactivity of each hydroxyl group to the phosphorylating agent.^{33, 34} As shown in **Table S1**, similar results were obtained for the three methanol extraction attempts (**EKL1-3**), which confirms the reliability of the process. Noteworthy, in the **EKL1-3** samples, the phenolic groups were estimated to comprehend the majority of the hydroxyl groups (ranging 60-65 % from the total), benefiting a high further functionalization. For the second part of the process, **EKL1** powder was solubilized and reacted with ECH to produce glycidylated lignin dark syrup, following a similar two-step methodology previously reported.^{28, 35} The dark syrup was precipitated in diethyl ether and dried under vacuum to obtain **GEKL1-3**, as a light brown solid powder (yield ranging 60-63 %). The **GEKL1-3** structures were characterized by ^{31}P NMR and the absence of peaks in the phenolic and carboxylic acid region, between 134-145 ppm (**Figure S1**), confirmed the glycidylation of these functional groups.²⁵ Moreover, FT-IR examination of glycidylated lignin demonstrated a

1
2
3 noticeable reduction in the stretching vibrations of hydroxy groups at approximately 3400 cm^{-1}
4 (as depicted in **Figure S2**), corroborating the phenolic and carboxylic acid modification.
5 Furthermore, a new peak emerged at 905 cm^{-1} , a characteristic asymmetric stretching vibration
6 associated with the C-O-C bonds in epoxide groups. In addition, several new peaks within the
7 1000 to 1250 cm^{-1} range appeared for **GEKL1**, these vibrations were associated with the newly
8 created C-O-glycidyl bonds. The findings aligned with FT-IR spectra of glycidylated lignin
9 compounds previously reported.^{36, 37} Despite the slight increase in the molar mass of **GEKL1-3**
10 after functionalization ($\approx 0.5\text{ kg/mol}$), the polydispersity remained uniform (as shown in **Figure**
11 **S3**). The **GEKL1-3** samples displayed an EEW ranging from 331 to 341 g/eq,²⁸ with almost no ECH-
12 derived impurities, as summarized in **Table S2**.
13
14
15
16
17
18
19
20
21

22 **Design Rationale, Formulation, and Network Development of the Cured Epoxy Resins.**

23

24 Three parameters were selected in order to systematically tune the macromolecular structure of
25 the epoxy materials, as depicted in **Figure 2**: i) the amount of lignin in the formulation (which we
26 further defined as the substitution ratio of r-BADGE by GL), ii) the structure of the hardener, and
27 iii) the epoxy hardener (E:H) ratio.
28
29
30
31

32 i) The first parameter to be modified was the amount of lignin in the mixture, knowing that an
33 excess of rigid and compact moieties of lignin in the formulation of the components could be
34 highly detrimental to the mechanical properties of the epoxy resin. Furthermore, a physical
35 limitation existed during the material preparation, where large amounts of lignin dramatically
36 raised the viscosity of the monomer dispersion. That fact affected the uniformity in the material
37 structure by presenting visible lignin agglomerations (**Image S1a**). Considering these
38 observations, the lignin content in the epoxide monomer mixture was delimited to 0, 10, 20 and
39 30 % (**a**).
40
41
42
43
44
45
46

47 ii) The second parameter to be compared is the hardener structure, particularly the length of the
48 flexible chain between the telechelic amine groups, which was expected to balance the
49 introduction of lignin by conferring ductility to the material. The initial idea of the study was to
50 systematically compare the Jeffamine (Jeff) series D230, D400, and D2000, which all display the
51 same linear structure but with different lengths of flexible middle chains. However, dramatic
52
53
54
55
56
57
58
59
60

phase separation was observed for samples containing Jeff D2000. Despite several attempts to improve the mixture preparation, the uniformity of the obtained materials was poor, especially for specimens containing 20 and 30 % lignin, as shown in **Image S1b**. Therefore, the hardeners selected for the epoxy resin fabrication were 1,6-hexamethylenediamine (HDA), Jeff D230, and Jeff D400 (**b**).

iii) Finally, the E:H ratio was selected as the third design parameter. In an ideal scenario, when E:R ratio = 4:2, every single diamine will react with four epoxide groups, making the hardener fully act as a crosslinking agent of the polymeric system. In order to evaluate the crosslinking capability of the glycidylated lignin, higher amounts of hardener were added to the formulation. This way, it increased the probability of the amine groups reacting only with one epoxide group, allowing the lignin moiety to act partially as a crosslinker. Additionally, this modification enhanced the reaction mixture's fluidity and greatly facilitated the material preparation. The E:H ratios selected were 4:2, 3:2 and 2:2, where 4, 3 or 2 epoxide groups were expected to react for each equivalent of hardener (2 amine groups), respectively (**c**).

Overall, a collection of 20 epoxy bio-resins with differentiated structures were fabricated according to the previously mentioned design parameters: 5 specimens did not contain lignin and were named references (**Ref1-5**), while the 15 remaining samples contain 10-30 % of lignin and were called epoxy resin (**ER1-15**) samples, as represented on **Scheme 2**. The variations on hardener structure, E:H ratio and lignin content for each epoxy resin is summarized in **Table 1**.

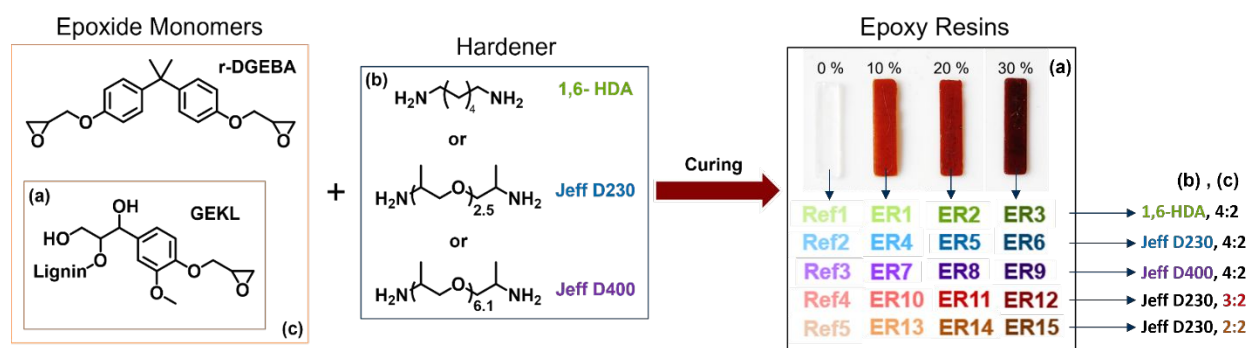


Figure 2. Schematic representation of the parameters altered in the formulation (a) lignin content (0, 10, 20, 30 %), (b) hardener type (1,6-HDA, Jeff D230, Jeff D400) and (c) E:H ratio (4:2, 3:2 and 2:2) leading to the 20 epoxy resins fabricated (**Ref1-5**, **ER1-15**). Photography of **Ref2**, **ER4**, **ER5** and **ER6** epoxy resin samples.

Table 1. Summary of composition, thermal and mechanical parameters from the synthesized epoxy resin specimens.

Epoxy resin	Formulation parameters			DSC	Dynamic Mechanical Analysis				Tensile test		
	GELK (%)	Hardener type	Epo/Hard ratio	T _g (°C)	E' at -25°C (MPa)	E' at 150°C (MPa)	T _g (°C)	v _e (mmol/cm ³)	E _{young} (GPa)	σ _{UTS} (MPa)	ε _{break} (%)
Ref1	0	1,6-HDA	4\2	86	4583.57	54.61	122	5.17	2,2 ± 0,1	79 ± 3	4.6 ± 0,2
ER1	10	1,6-HDA	4\2	91	3437.72	24.01	103	2.27	1,9 ± 0,1	70 ± 3	5.1 ± 0,3
ER2	20	1,6-HDA	4\2	99	4104.29	28.96	108	2.74	2,3 ± 0,1	81 ± 5	4.4 ± 0,2
ER3	30	1,6-HDA	4\2	101	3917.81	25.67	108	2.43	2,4 ± 0,1	86 ± 4	4.2 ± 0,2
Ref2	0	Jeff D230	4\2	82	2961.67	15.26	82	1.45	1,9 ± 0,1	61 ± 2	10.2 ± 0,9
ER4	10	Jeff D230	4\2	83	3291.53	17.75	86	1.68	2,0 ± 0,1	66 ± 2	9.6 ± 0,6
ER5	20	Jeff D230	4\2	83	3766.11	16.45	90	1.56	2,3 ± 0,1	72 ± 3	8.5 ± 0,7
ER6	30	Jeff D230	4\2	80	3522.14	15.90	88	1.51	2,5 ± 0,1	81 ± 4	5.3 ± 0,2
Ref3	0	Jeff D400	4\2	48	3267.29	11.81	47	1.12	1,4 ± 0,1	50 ± 2	19.3 ± 2,0
ER7	10	Jeff D400	4\2	52	3260.82	15.00	50	1.42	1,8 ± 0,1	55 ± 2	15.9 ± 0,7
ER8	20	Jeff D400	4\2	58	3798.01	19.48	53	1.85	2,1 ± 0,1	60 ± 3	12.0 ± 0,9
ER9	30	Jeff D400	4\2	55	3934.80	22.86	54	2.17	2,2 ± 0,2	76 ± 3	10.2 ± 0,7
Ref4	0	Jeff D230	3\2	53	3661.35	10.33	60	0.98	1,8 ± 0,1	57 ± 2	15.4 ± 0,8
ER10	10	Jeff D230	3\2	56	4206.80	12.59	60	1.19	2,0 ± 0,1	61 ± 3	10.6 ± 0,8
ER11	20	Jeff D230	3\2	60	3702.08	13.98	63	1.32	2,2 ± 0,1	66 ± 3	7.7 ± 0,6
ER12	30	Jeff D230	3\2	63	3975.90	14.14	68	1.34	2,3 ± 0,1	76 ± 3	4.5 ± 0,1
Ref5	0	Jeff D230	2\2	34	3336.79	1.86	46	0.18	1,0 ± 0,1	28 ± 1	89.2 ± 5,0
ER13	10	Jeff D230	2\2	33	3555.24	2.87	50	0.27	1,3 ± 0,1	34 ± 1	26.9 ± 0,9
ER14	20	Jeff D230	2\2	34	3795.32	4.95	52	0.47	1,6 ± 0,1	48 ± 1	13.4 ± 0,9
ER15	30	Jeff D230	2\2	39	4341.30	7.65	54	0.72	2,0 ± 0,1	63 ± 2	6.6 ± 0,4

1
2
3 The curing conditions of the precursor mixtures were optimized to obtain fully reacted and
4 homogeneous thermosetting materials. To do so, the curing exotherm of the epoxides-hardener
5 mixtures was first screened by DSC to determine the maximum and the onset temperature of
6 curing. **Figure S9** displays the DSC thermograms of the following systems: (a) different hardeners
7 with r-DGEBA, (b) r-DGEBA: Jeff D230 system, different E:H ratio (top, dash line) and different
8 lignin content (bottom, straight line). The structure of the hardener greatly influences the
9 hardening temperature of the material. Notably, formulations comprising shorter linear
10 hardeners react more quickly and at lower temperatures, which may be related to improved
11 mobility in reactive formulations.
12
13
14
15
16
17
18
19

20 The formulations containing the short linear hardener 1,4-diaminobutane (DAB) consistently
21 displayed somewhat similar thermogram curves, while the onset curing temperature for the Jeff
22 D230 and D400 increased from 55 °C to 69 °C ($\Delta T=14^\circ\text{C}$) and 75 °C ($\Delta T=20^\circ\text{C}$), respectively. In
23 addition, mixtures containing Jeff D230 and D400 as a hardener exhibited a broader exotherm
24 curve than 1,6-HDA mixture, with maximums at 125 °C, 134 °C, and 100 °C respectively. Smaller
25 difference presented the exotherm curves depicted in **Figure S9b**, by exchanging the E:H ratio
26 and lignin content in the formulation seemed to have almost no effect in the onset curing
27 temperatures and modest shift of the curing maximum. In light of the results, the curing
28 conditions summarized in **Table S4** were applied to produce the epoxy resins, following the
29 methodology described in the *Supporting Information*. The resulting samples showed no phase
30 separation or visible defects, as shown in **Figure 2** for **Ref2**, **ER4**, **ER5** and **ER6** samples.
31
32
33
34
35
36
37
38
39
40

41 The samples were characterized by FT-IR and the spectra are included in *Supporting Information*
42 **Figure S4-S8**. All the fabricated samples exhibited the common epoxy resin peaks.³⁸ Broad band
43 above 3400 cm^{-1} , related largely to -OH stretching vibrations for all formulations, although
44 materials **Ref4-5** and **ER10-15** including a major amount of hardener, this band can be overlaid
45 with -NH stretching vibrations from amine groups unreacted. Three peaks assigned to symmetric
46 and asymmetrical C-H stretching for methyl and methylene groups, respectively, appeared for
47 all the samples in the range from 2920 to 2970 cm^{-1} . The region ranging 1600-1700 cm^{-1} and the
48 two intense peaks around 1450 and 1510 cm^{-1} are typically associated with aromatic skeletal
49 vibrations combined with C-H in-plane deformation.^{39,40} Between 1000-1400 cm^{-1} , all the samples
50
51
52
53
54
55
56
57
58
59
60

1
2
3 exhibited a series of peaks related to C-C and C-H linkage vibration in aromatic moieties combined
4 with C-O stretch for secondary alcohol, and including methoxy groups, in the cases of **ER1-15**,
5 which incorporate lignin. The last peak around 830-840 cm^{-1} was assigned to aromatic C-H out-
6 of-plane deformation.⁴¹
7
8
9

10
11 In addition, the thermal analysis by DSC confirmed the complete curing of all the epoxy resins
12 since the thermograms, depicted in **Figure S10-S14**, showed total absence of curing exotherm
13 while exhibiting a clear glass transition, with values of T_g summarized in **Table 1**. In general,
14 results revealed lower T_g by increasing the hardener length for the different materials. This is
15 related to the fact that longer chain moieties in the epoxy resin system provided more mobility
16 at lower temperatures. A similar trend occurred with materials containing large amount of
17 hardener, **Ref4-5** and **ER10-15**, the partial reactivity of the hardener amine groups provided less
18 crosslink points and enhanced the mobility of the epoxy resin structure, decreasing the T_g around
19 30 and 50 $^{\circ}\text{C}$, respectively, in comparison with **Ref2**, **ER4-6** samples. Otherwise, the increment of
20 lignin in the formulation led to a slight increase in the T_g , mainly related with the reduction in
21 chain mobility due to inclusion of the lignin rigid structure.
22
23
24
25
26
27
28
29
30
31

32 33 34 **Epoxy Resins Thermo-Mechanical Profiles and Structure-Property Relationships.**

35
36 The thermo-mechanical properties of the synthesized materials (**Ref1-5** and **ER1-15**, c.f. summary
37 in **Table 1**) were then investigated by DMA in the temperature range (-50 $^{\circ}\text{C}$ to 200 $^{\circ}\text{C}$) to
38 elucidate their structure-property relationships. The thermal range of the analysis was selected
39 to cover the glassy state, thermal transition, and rubbery region for all the samples. The DMA
40 profiles of the epoxy resin illustrating the (a) storage modulus and (b) $\text{Tan } \delta$ /loss modulus are
41 included in **Figure 3** and **Figure S15-S19** (*Supporting Information*). All samples show the typical
42 thermoset thermomechanical curve, where storage modulus (E') presented a glassy region at low
43 temperatures, followed by a thermal transition, which ended in a rubbery plateau. Additionally,
44 all the epoxy resins exhibit only one peak of $\text{Tan } \delta$, that fact confirmed the high homogeneity of
45 the crosslink (no phase separation) in the final material and corroborated the success during the
46 component mixtures and curing methodology. Noteworthy, slightly broader profiles were
47
48
49
50
51
52
53
54
55
56
57
58
59
60

observed in the Tan δ curves due to the increment of the lignin content in the formulation from 0 to 30 % for all groups of epoxy resin fabricated. Besides, as the temperature increases, significant regions of the polymer exhibit cooperative movement, and the dissipated energy escalates, yet concurrently, the material as a whole becomes more susceptible to deformation, and the loss modulus (E'') reaches a peak in the order of 10^2 MPa for all the fabricated epoxy resins, as have been reported in previous studies.²⁵

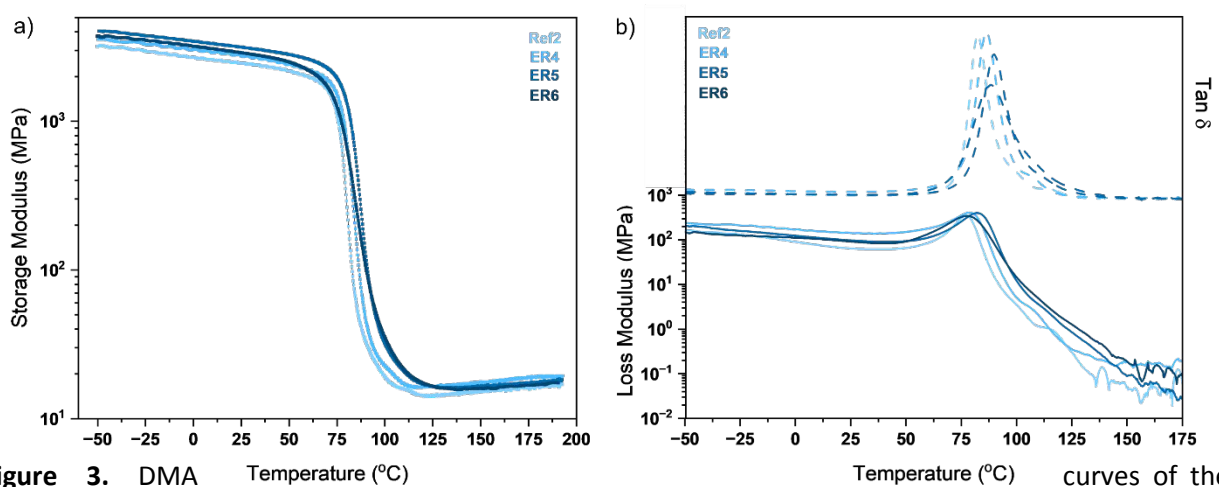


Figure 3. DMA curves of the heating ramp from -50 to 200 $^{\circ}\text{C}$ representing (a) storage modulus and (b) tan δ (dash line) and loss modulus (straight line) for **Ref2**, **ER4**, **ER5**, and **ER6**.

Relevant data such as T_g , E' at glassy stage, E' at rubbery stage, and crosslink density (ν_e) were extracted from the DMA thermograms and summarized in **Table 1**. Given the clarity of the peak definition in all cases, the maximum point of the Tan δ curve was considered as the T_g . Coherent trends (in agreement with previously obtained DSC results) confirmed that hardener with increasing length (1,6-HDA > Jeff D230 > Jeff D400) dramatically influenced the chains mobility and led to lower T_g values. Similarly, by decreasing the E:H ratio from 4:2 to 2:2, it is promoted a partial reactivity of the hardener amine groups, providing the polymer network with a smaller number of crosslink points and including a major quantity of long alkyl chains that enhance the polymer mobility.

Interestingly, the increment of lignin amount (0 to 30%) for the different polymer networks only appeared to alter drastically for the r-DGEBA/1,6-HDA system (**Ref1**, **ER1-3**), where the T_g

1
2
3 dropped 20 °C after incorporating to the material 10 % of lignin (from Ref1 $T_g = 122$ °C to ER1 T_g
4 = 103 °C), which can be explained by the dense crosslink density of **Ref1** being disrupted with the
5 incursion of lignin moieties for **ER1-3**. Despite the previous case, mild fluctuations (0 - 9 °C) of
6 the T_g were observed for the accumulation of lignin (0 – 30 %) in the other epoxy resin groups
7 (**Ref2-5, ER4-15**).

8
9
10
11
12
13 In order to compare the effect in the epoxy resin crosslink structure, the parameters E' at -25 °C
14 (glassy state for all samples), E' at 150 °C (rubbery state for all samples) and v_e at 150 °C were
15 represented in **Figure 4** in two bar graphs, comparing the hardener length **(a)** and the E:H ratio
16 **(b)**, as well as the lignin content in the formulation mixtures. Only slight differences were
17 observed in the glassy state, and all the samples kept a high stiffness expected for glassy
18 thermosetting polymers with values of E' above 3×10^3 MPa.²⁸ On the contrary, in the rubbery
19 state (defined here at 150 °C to facilitate the comparison), epoxy resin containing 1,6-HDA as a
20 crosslinking agent (**Ref1, ER1-3**), clearly were able to store more energy elastically than epoxy
21 resins with longer hardener, as depicted in **Figure 4a**. The same trend was observed by increasing
22 the quantity of Jeff D230 in the formulation (**Figure 4b**), with a remarkable drop in E' in the range
23 of 10-15 MPa, by comparing samples with E:H ratio 4:2 (**Ref2, ER4-6**) with samples E:H ratio 2:2
24 (**Ref5, ER13-15**). This fact can be related with the addition of a major number of long hardener
25 linear chains and decreasing the hardener reactivity per amine group, which give more mobility
26 to the system at high temperatures. It is precisely this enhanced polymer mobility in the rubbery
27 state that allowed to evaluate deeply the contribution of lignin in the material network. As shown
28 in **Figure 4a**, the incorporation of lignin to the flexible network that uses Jeff D400, resulted in
29 the continuous increase of the crosslink density, raising the v_e value from 0.77 mmol/cm³ for **Ref3**
30 (0 % lignin) to 1.28 mmol/cm³ for **ER9** (30 % lignin). The opposite case occurred for epoxy resins
31 using the shortest hardener 1,6-HDA (**Ref1**); after small lignin inclusion (10 %, **ER1**), E' and
32 consequently the crosslink density dropped drastically (around 30 MPa and 3 mmol/cm³), which
33 was attributed to a lignin disruption in the already compact original network for **Ref1**. Increasing
34 the lignin content to 20 % seemed to improve slightly the crosslink density from 2.3 (**ER1**) to 2.7
35 mmol/cm³ (**ER2**) without achieving **Ref1** v_e initial values (5.2 mmol/cm³), and further lignin
36 incorporation to 30 % for **ER3** collapsed again the system decreasing E' by 3.3 MPa. Epoxy resins
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

Ref2, ER4, ER5, and ER6 using Jeff D230 as a hardener at an E:H ratio 4:2, exhibited a particular behavior; the system improved with 10 % lignin (**ER4**), while by increasing the lignin amount (20-30 %) was slightly detrimental for the crosslink system (**ER5-6**). Furthermore, as shown in **Figure 4b**, the addition of up to 30 % lignin increases the crosslink density for the formulations based on Jeff D230 with E:H ratios of 3:2 and 2:2. This is emphasized when comparing **Ref5**, with the lowest crosslink density ($v_e = 0.2 \text{ mmol/cm}^3$) to **ER15** with a 40 % higher crosslink density ($v_e = 0.7 \text{ mmol/cm}^3$) and 30 % lignin. These observations can help us adjust the formulation of the lignin-based epoxy resins to improve the material internal structure and, at the same time, enhance the biobased content.

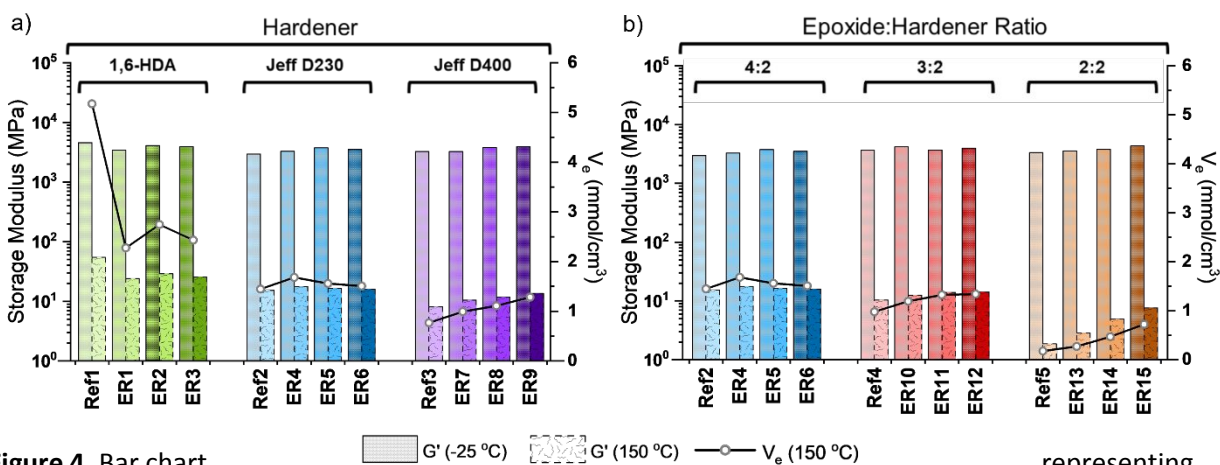
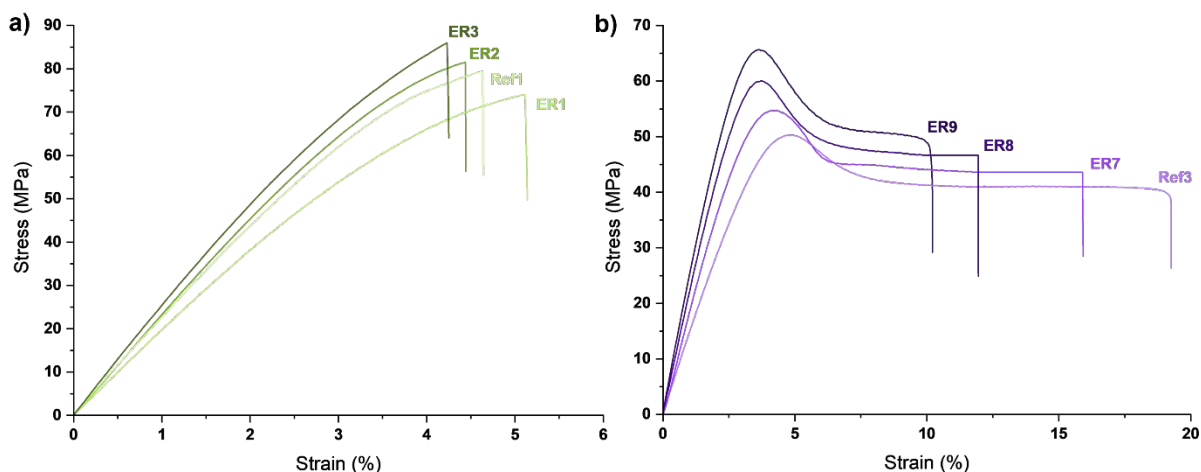


Figure 4. Bar chart representing storage modulus (E') at glassy region (-25 °C), storage modulus (E') at rubbery plateau and crosslink density (150 °C) versus epoxy resin samples with (a) different hardener and (b) different E:H ratio.

To further evaluate the mechanical properties of the lignin-based epoxy resins at large strains, tensile tests were carried out. Stress-strain curves are presented in **Figure 5** and **Figure S20-S24 (Supporting Information)**, and the data is summarized in **Table 1**. The stress-strain curves are very distinctive for each group of epoxy resins. As expected, they behave differently at room temperature upon mechanical strength depending on the hardener structure, E:H ratio, and lignin content in the formulation mixtures. Epoxy resins using 1,6-HDA as a crosslink agent (**Ref1, ER1-3**) exhibited a pronounced elastic response before break characteristic of brittle materials (**Figure 5a**), while samples containing Jeff D400 moieties (**Ref3, ER7-9**) displayed an initial elastic region, followed by an elastic limit point of maximum stress (yield point) that ultimately leads to

1
2
3 a plastic deformation before break, typical for ductile materials (**Figure 5b**). Similar trends were
4 observed by decreasing the E:H ratio in epoxy resins based on Jeff D230 and by reducing the
5 lignin content in the formulations; therefore, for clarity in the material comparison, the data
6 extracted from the stress-strain curves was depicted in **Figure 6**. High Young Modulus values in
7 the 1.0-2.5 GPa range were obtained, which are common results for epoxy resins containing
8 linear hardeners. Interestingly, by exchanging the crosslinking agent in lignin-based samples from
9 1,6-HDA (**ER1-3**) to Jeff D230 (**ER4-6**), the elastic modulus remained constant or slightly increasing
10 instead of decreasing, as can be observed in **Figure 6a**, passing from **Ref1** (2.2 GPa) to **Ref2** (1.9
11 GPa). This can be related with the contribution of lignin to the crosslink density, and for rigid
12 reference networks (**Ref1**) this seemed to be detrimental. In contrast, lignin addition improved
13 more flexible networks (**Ref2-3**), as have been mentioned in the DMA discussion. Identical
14 observation appeared in **Figure 6b**, with a small particularity, epoxy resins using 1,6-HDA as
15 hardener (**Ref1, ER1-3**) not only exhibited the highest σ_{UTS} values (70-86 MPa) but also were the
16 only samples that maximum stress and fracture of the sample coincided. Increasing the length of
17 the hardener to Jeff D400 (**Ref3, ER7-9**) promoted the network flexibility, decreasing the elastic
18 modulus between 0.1-0.2 GPa and the σ_{UTS} values from 6 to 12 MPa, in comparison with epoxy
19 resins fabricated from Jeff D230 (**Ref2, ER4-6**). Remarkable was the ability of dissipating the stress
20 applied via plastic deformation, as depicted in **Figure 6c**, especially in lignin-based epoxy resins
21 fabricated with Jeff D400 (**ER7-9**), showing values of deformation before failure above 10 %, even
22 with 30 % of lignin content.



1
2
3 **Figure 5.** Stress-strain curves at 5 mm/min for a) **Ref1, ER1, ER2, and ER3**, and b) **Ref3, ER7, ER8, and ER9**.
4
5
6
7

8 In comparison with **Ref2, ER4, ER5, and ER6**, the reduction of r-DGEBA: Jeff D230 ratio (from 4:2
9 to 3:2 and 2:2, samples **Ref4-5, ER10-15**) led to materials with inferior elastic modulus, lower
10 elastic limit, but enhanced the plastic response and the deformation to fracture, as observed in
11 **Figure 6d-f**. These results agreed with previously mentioned statements that defended the
12 increase in ductility of the materials by decreasing E:H ratio in their formulation, which provided
13 lower crosslink density structure for the fabricated epoxy resins. The last parameter to evaluate
14 was the effect of the lignin content on the tensile performance of the epoxy resin. Mostly all the
15 systems behaved similarly, by increasing the lignin content from 0 to 30 %, the material became
16 rigid, which increases the Young's modulus and the maximum stress, therefore reducing the
17 plastic deformation before break. Noteworthy, the difference in the mechanical properties by
18 exchanging the lignin amount in the formulation were greater for epoxy resins with more flexible
19 network, such as **Ref3, ER7-9 and Ref5, ER13-15**. Therefore, it confirmed the premise that lignin
20 inclusion was beneficial or detrimental depending on the crosslink density of the reference r-
21 DGEBA : hardener network, while elastic behavior was reduced from **Ref1 to ER1**, was increased
22 from **Ref2 to ER4, Ref3 to ER7, Ref4 to ER11 and Ref5 to ER13** by only increasing 10 % lignin
23 content in comparison with the reference system. This large comparison verified the mechanical
24 behavior previously observed and gave an idea of the performance expected for each epoxy resin
25 system in a real-life application.
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

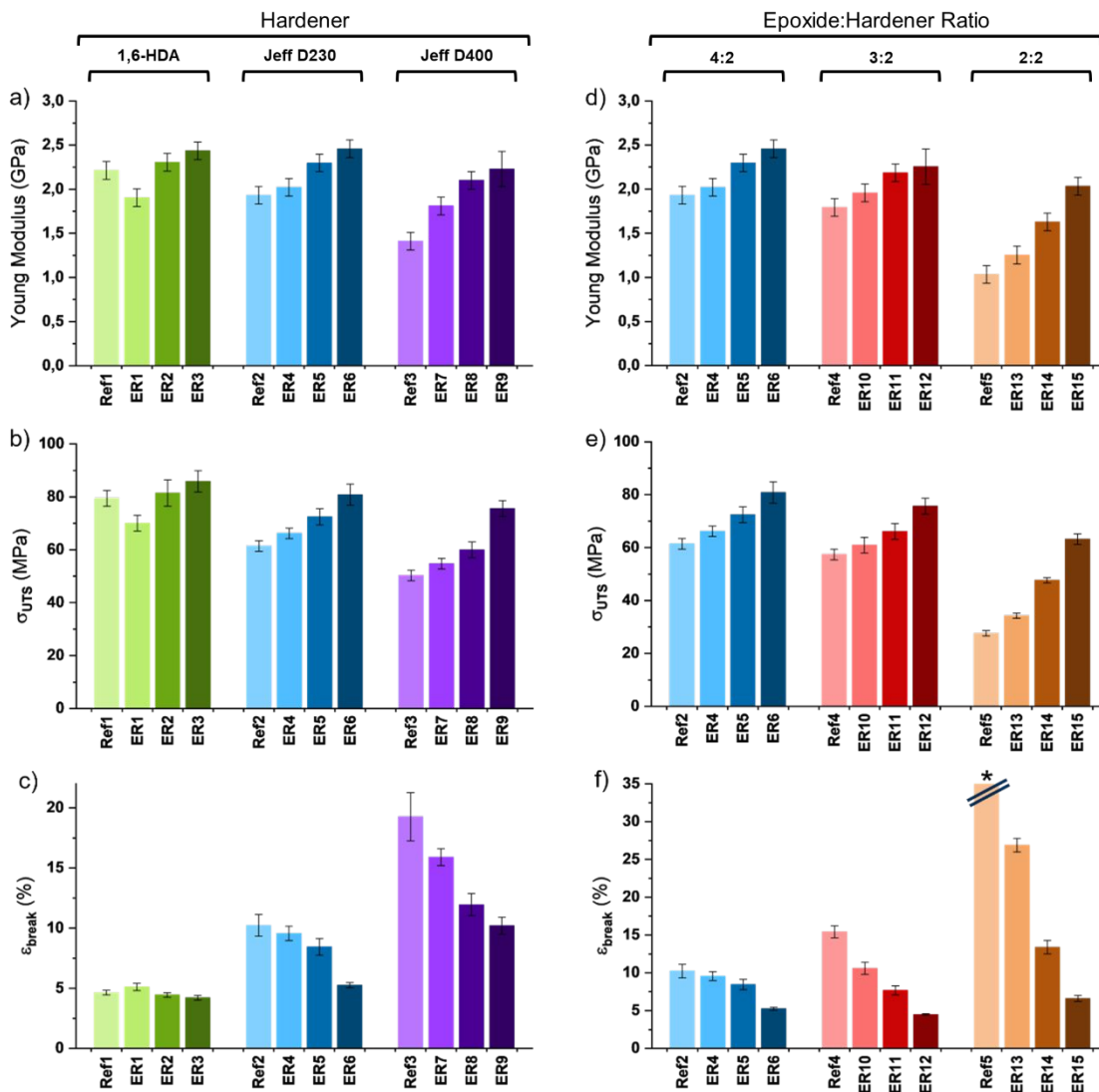


Figure 6. Bar chart representing Young's Modulus (a,d), the ultimate tensile strength (b,e) and fracture deformation (c,f) versus epoxy resin samples with (a,b,c) different hardener and (d,e,f) different E:H ratio. (*) $\epsilon_{\text{break}} = 89.2 \pm 5.0$ % for Ref5.

Coating Fabrication and Cross Hatch Test

In order to evaluate the role the hardener plays for a specific application, the epoxy resin formulations presented in **Table 1** were coated on steel substrates at a constant flow rate. The coated plates were then thermally cured according to the conditions summarized in **Table S4**, producing a series of smooth, transparent, and amber-colored coatings as shown in **Tables S5-S9** (*Supporting Information*). The coatings had thicknesses ranging from 80-110 μm , displayed a

1
2
3 homogeneous and transparent appearance, glossy surface, and were without visible defects. The
4 color of the coatings was directly related with the lignin content, generally varying from full
5 transparent at 0 %, yellowish at 10 %, golden at 20 % and brown at 30 %. Besides, the E:H ratio
6
7 influenced the volume of hardener used to disperse the lignin and for that reason coatings
8
9 presented a lighter coloration by using 3:2 and 2:2 E:H ratio, respectively, instead of 4:2 ratio.
10
11

12
13 Additionally, the mechanical stability of the coatings on the substrate was analyzed by the surface
14 crosshatch test. The methodology involves two different steps; first, the scratch step, where two
15 perpendicular series of cuts were applied on the coating surface using a special utility knife with
16 multiple parallel sharp blades, and second, the peeling step, which requires the adhesion of a
17 tape on the crosshatch surface for specific period of time and further fast removal in a
18 determined angle. The pictures of the coatings after scratch, after peeling, and the value ISO
19 attributed after the crosshatch test are summarized in **Table S5-S9**.
20
21
22
23
24
25

26
27 The final results are compared in **Figure 7**. Considering that ISO value 0 (green), a perfect
28 adhesion in steel substrate, and ISO value 5 (maroon), an incompatible union coating-substrate,
29 remarkable trends related to the structure of the hardener, the lignin content, and the E:H ratio
30 were extracted by comparing the different coating formulations. Better adhesion coating-
31 substrate was achieved by increasing the length of the hardener, 1,6-HAD < Jeff D230 < Jeff D400,
32 as shown in **Figure 7a**. This fact was attributed to the reduced crosslink density of the epoxy resin
33 observed by DMA, yielding coatings with enhanced flexibility which allowed an improved
34 resistance during the surface test. A similar tendency was observed by decreasing 4:2 to 2:2 the
35 E:H ratio in the formulation, as a result, better adhesion was obtained for the coatings presenting
36 more relaxed internal structure with an incremented quantity of hardener Jeff-D230 in the final
37 material, as observed in **Figure 7b**. Interestingly, the influence between the formulation's lignin
38 content and the resulting coatings' adhesion properties depended on how well the lignin
39 interacted with the original r-DGEBA/hardener network. Consistent with what was previously
40 mentioned in the thermal and mechanical properties section, the increased incorporation of
41 lignin in r-DGEBA/Jeff D230 systems seems to have a dramatic effect on crosslink networks with
42 shorter and fully reacted hardener (**ER4 > ER5 > ER6**). On the other hand, minor impacts on the
43 adhesion coating-substrate quality were observed by including lignin to relaxed r-DGEBA/Jeff
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

D400 networks (**ER7**, **ER8** and **ER9**) and with formulations of r-DGEBA/Jeff D230 partially reacted (**ER13**, **ER14** and **ER15**). These results suggest that an accurate balance between hardener structure and ratio, as well as lignin content in the coating formulation could be determinant for a suitable coating-substrate adhesion.

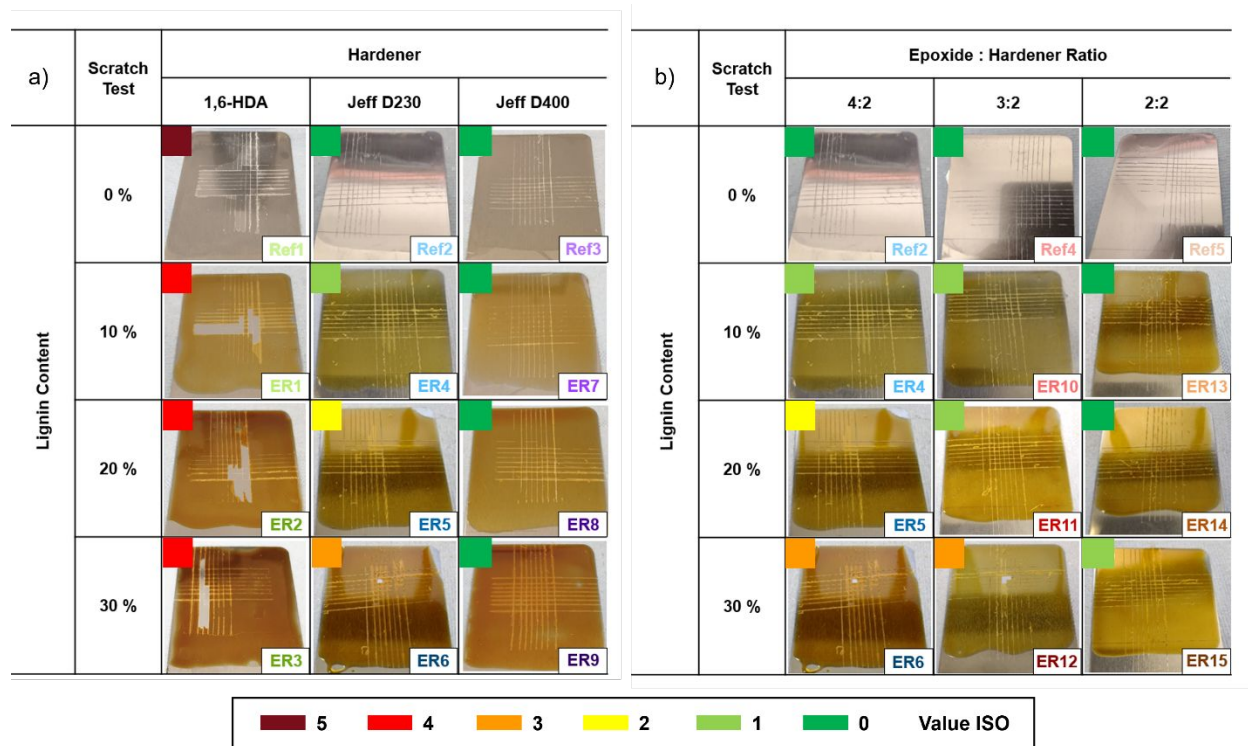


Figure 7. Surface scratch test of epoxy resin coatings with (a) different hardener and (b) different E:H ratio. Value ISO where 0 represent best adhesion and 5 represent worst adhesion coating/substrate.

CONCLUSIONS

In summary, **EKL** and **r-BPA** as waste-derived compounds have been used to produce **GEKL** and **r-BADGE**, respectively, using simple, efficient, and reproducible upcycling processes. We have characterized the epoxide monomer structures and tested thermally with different hardeners in order to evaluate the curing conditions and the uniformity of the final materials. Twenty epoxy resins were fabricated (**Ref1-5**, **ER1-15**) with different formulations by exchanging hardener structure (1,6-HDA, Jeff D230 and Jeff D400), E:H ratio (4:2, 3:2 and 2:2) and lignin content (0, 10, 20 and 30 %). Full curing was confirmed by the absence of exotherm in the DSC thermograms,

1
2
3 and the epoxy resins fabricated were characterized by FT-IR and DMA. The thermomechanical
4 analysis revealed clear thermoset thermograms for all materials, with high storage modulus at
5 glassy state ($-25\text{ }^{\circ}\text{C}$, $E' > 3\text{ GPa}$), followed by thermal transition and a final rubbery plateau. The
6 crosslink density of the epoxy resins was determined at $150\text{ }^{\circ}\text{C}$, showing clear trends between
7 formulations, such as a reduction of v_e by increasing the length of the hardener structure or by
8 decreasing the E:H ratio, for these cases, the samples exhibited lower T_g 's and E' at rubbery state.
9 Incrementing the lignin content altered differently the crosslink density of the materials, for
10 networks using 1,6-HDA as a crosslinking agent, the lignin contribution was detrimental, while
11 for systems containing a longer hardener or lower E:H ratio have experienced certain
12 improvement by adding lignin. To further compare the mechanical behavior at standard
13 conditions, tensile tests were performed. Except for the epoxy resins using 1,6-HDA as hardener
14 that were clearly rigid with elastic responses that broke upon stress, all the other samples
15 exhibited an elastic response, followed by a maximum in stress leading to a plastic dissipation
16 before fracture. In general, using longer hardener or decreasing the E:H ratio in the formulation
17 yielded epoxy resins with a smaller Young's modulus and lower σ_{UTS} while keeping plastic
18 response to higher deformations before break. Finally, coatings on steel substrate were produced
19 from the 20 different formulations, applying the previous knowledge of curing, and evaluating
20 their appearance and adhesion properties.
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35

36
37 The results extracted from the coating cross hatch tests confirmed that epoxy resins containing
38 structures with lower crosslink density, due to the use of longer chain hardeners or a major
39 amount of them, improved the adhesion of the coating. Additionally, these flexible systems can
40 easily endure the addition of lignin (up to 20 %) and maintain their properties. This study provides
41 an extensive comparison of how the final properties of lignin-based epoxy resins can be altered
42 and predicted through exchanging formulation parameters related with the hardener, which
43 ultimately will be the component that greatly affects the crosslink density of the covalent
44 network and influences the performance of the material in specific applications.
45
46
47
48
49
50
51
52
53
54

55 ASSOCIATED CONTENT
56
57
58
59
60

Supporting Information: Information on general experimental details, synthetic procedures, epoxy resin fabrication, curing conditions, characterization, spectroscopic data, thermal, mechanical, and adhesion properties.

AUTHOR INFORMATION

Corresponding Author

*Email: marc.comibonachi@vito.be

*Email: richard.vendamme@vito.be

ACKNOWLEDGMENT

The authors gratefully acknowledge the research work done in LIGNICOAT and Cyclops projects. The LIGNICOAT project has received funding from the Bio-Based Industries Joint Undertaking under the European Union's Horizon 2020 research and innovation programme under the Grant Agreement No. 101023342. The JU receives support from the European Union's Horizon 2020 research and innovation programme and the Bio-based Industries Consortium. The Moonshot project CYCLOPS HBC.2021.0584 has received financial support of the Flemish Government and Flanders Innovation & Entrepreneurship (VLAIO).

REFERENCES

- (1) Liu, J.; Wang, S.; Peng, Y.; Zhu, J.; Zhao, W.; Liu, X. Advances in sustainable thermosetting resins: From renewable feedstock to high performance and recyclability. *Progress in polymer science*, **2021**, *113*, 101353. DOI: 10.1016/j.progpolymsci.2020.101353
- (2) Gonçalves, F. A.; Santos, M.; Cernadas, T.; Ferreira, P.; Alves, P. Advances in the development of biobased epoxy resins: insight into more sustainable materials and future applications. *International Materials Reviews*, **2022**, *67*, 2, 119-149. DOI: 10.1080/09506608.2021.1915936
- (3) Lu, X.; Gu, X. A sustainable lignin-based epoxy resin: Its preparation and combustion behaviors. *Industrial Crops and Products*, **2023**, *192*, 116151. DOI: 10.1016/j.indcrop.2022.116151
- (4) Jiang, T.-W.; Reddy, K. S. K.; Chen, Y.-C.; Wang, M.-W.; Chang, H.-C.; Abu-Omar, M. M.; Lin, C.-H. Recycling waste polycarbonate to bisphenol A-based oligoesters as epoxy-curing agents, and degrading epoxy thermosets and carbon fiber composites into useful chemicals. *ACS Sustainable Chemistry & Engineering* **2022**, *10*, 7, 2429-2440. DOI: 10.1016/j.jobab.2024.01.003
- (5) Yu, E.; Jan, K.; Chen, W.-T. Separation and Solvent Based Material Recycling of Polycarbonate from Electronic Waste. *ACS Sustainable Chemistry & Engineering* **2023**, *11*, 34, 12759-12770. DOI: 10.1021/acssuschemeng.3c03152
- (6) Romani, A.; Levi, M.; Pearce, J. M. Recycled polycarbonate and polycarbonate/acrylonitrile butadiene styrene feedstocks for circular economy product applications with fused granular fabrication-

1
2
3 based additive manufacturing. *Sustainable Materials and Technologies*, **2023**, *38*, e00730. DOI:
4 10.2139/ssrn.4508039

5 (7) Parida, D.; Aerts, A.; Vanbroekhoven, K.; Van Dael, M.; Mitta, H.; Li, L.; Eevers, W.; Van Geem, K.
6 M.; Feghali, E.; Elst, K. Monomer recycling of polyethylene terephthalate, polycarbonate and polyethers:
7 scalable processes to achieve high carbon circularity. *Progress in Polymer Science*, **2023**, 101783. DOI:
8 10.1016/j.progpolymsci.2023.101783.

9 (8) Hu, L.-C.; Oku, A.; Yamada, E. Alkali-catalyzed methanolysis of polycarbonate. A study on recycling
10 of bisphenol A and dimethyl carbonate. *Polymer*, **1998**, *39* (16), 3841-3845. DOI: 10.1016/S0032-
11 3861(97)10298-1

12 (9) Liu, F.-S.; Li, Z.; Yu, S.-T.; Cui, X.; Xie, C.-X.; Ge, X.-P. Methanolysis and hydrolysis of polycarbonate
13 under moderate conditions. *Journal of Polymers and the Environment*, **2009**, *17*, 208-211. DOI:
14 10.1007/s10924-009-0140-0

15 (10) Kim, J. G. Chemical recycling of poly (bisphenol A carbonate). *Polymer Chemistry*, **2020**, *11* (30),
16 4830-4849. DOI: 10.1039/C9PY01927H

17 (11) Zhou, X.; Zhai, Y.; Ren, K.; Cheng, Z.; Shen, X.; Zhang, T.; Bai, Y.; Jia, Y.; Hong, J. Life cycle
18 assessment of polycarbonate production: Proposed optimization toward sustainability. *Resources,*
19 *Conservation and Recycling*, **2023**, *189*, 106765. DOI: 10.1016/j.resconrec.2022.106765

20 (12) Verdugo, P.; Santiago, D.; De la Flor, S.; Serra, À. A Biobased Epoxy Vitrimer with Dual Relaxation
21 Mechanism: A Promising Material for Renewable, Reusable, and Recyclable Adhesives and Composites.
22 *ACS Sustainable Chemistry & Engineering* **2024**, *12*, 15, 5965-5978. DOI:
23 10.1021/acssuschemeng.4c00205.

24 (13) Kalita, D. J.; Tarnavchyk, I.; Kalita, H.; Chisholm, B. J.; Webster, D. C. Novel bio-based epoxy resins
25 from eugenol derived copolymers as an alternative to DGEBA resin. *Progress in Organic Coatings* **2023**,
26 *178*, 107471. DOI: 10.1016/j.porgcoat.2023.107471.

27 (14) Chen, C.-H.; Tung, S.-H.; Jeng, R.-J.; Abu-Omar, M. M.; Lin, C.-H. A facile strategy to achieve fully
28 bio-based epoxy thermosets from eugenol. *Green chemistry* **2019**, *21*, 16, 4475-4488. DOI:
29 10.1039/C9GC01184F

30 (15) Fang, Z.; Nikafshar, S.; Hegg, E. L.; Nejad, M. Biobased divanillin as a precursor for formulating
31 biobased epoxy resin. *ACS sustainable chemistry & engineering* **2020**, *8*, 24, 9095-9103. DOI:
32 10.1021/acssuschemeng.8b02419

33 (16) Martinez-Hernandez, E.; Cui, X.; Scown, C. D.; Amezcua-Allieri, M. A.; Aburto, J.; Simmons, B. A.
34 Techno-economic and greenhouse gas analyses of lignin valorization to eugenol and phenolic products in
35 integrated ethanol biorefineries. *Biofuels, Bioproducts and Biorefining* **2019**, *13*, 4, 978-993. DOI:
36 10.1002/bbb.1989

37 (17) Pappa, C.; Feghali, E.; Vanbroekhoven, K.; Triantafyllidis, K. S. Recent advances in epoxy resins and
38 composites derived from lignin and related bio-oils. *Current Opinion in Green and Sustainable Chemistry*,
39 **2022**, 100687. DOI: 10.1016/j.cogsc.2022.100687

40 (18) Lu, X.; Gu, X. A review on lignin-based epoxy resins: Lignin effects on their synthesis and
41 properties. *International Journal of Biological Macromolecules*, **2023**, 229, 778-790. DOI:
42 10.1016/j.ijbiomac.2022.12.322

43 (19) Dessbesell, L.; Paleologou, M.; Leitch, M.; Pulkki, R.; Xu, C. C. Global lignin supply overview and
44 kraft lignin potential as an alternative for petroleum-based polymers. *Renewable and Sustainable Energy*
45 *Reviews*, **2020**, *123*, 109768. DOI: 10.1016/j.rser.2020.109768

46 (20) Sethupathy, S.; Morales, G. M.; Gao, L.; Wang, H.; Yang, B.; Jiang, J.; Sun, J.; Zhu, D. Lignin
47 valorization: Status, challenges and opportunities. *Bioresource Technology* **2022**, *347*, 126696. DOI:
48 10.1016/j.biortech.2022.126696

49 (21) Lawoko, M.; Samec, J. S. Kraft lignin valorization: Biofuels and thermoset materials in focus.
50 *Current Opinion in Green and Sustainable Chemistry*, **2022**, 100738. DOI: 10.1016/j.cogsc.2022.100738

- 1
2
3 (22) Zou, S.-L.; Xiao, L.-P.; Li, X.-Y.; Yin, W.-Z.; Sun, R.-C. Lignin-based composites with enhanced
4 mechanical properties by acetone fractionation and epoxidation modification. *Iscience*, **2023**, *26*, 3. DOI:
5 10.1016/j.isci.2023.106187
6
7 (23) Gioia, C.; Lo Re, G.; Lawoko, M.; Berglund, L. Tunable thermosetting epoxies based on fractionated
8 and well-characterized lignins. *Journal of the American Chemical Society*, **2018**, *140*, 11, 4054-4061. DOI:
9 10.1021/jacs.7b13620
10
11 (24) Silau, H.; Melas, A.; Dam-Johansen, K.; Wu, H.; Daugaard, A. E.; Høj, M. Solvent Fractionation and
12 Depolymerization Provide Liquid Lignin Fractions Exploited as Bio-based Aromatic Building Blocks in
13 Epoxies. *ACS Sustainable Chemistry & Engineering*, **2023**, *11*, 4, 1591-1597. DOI:
14 10.1021/acssuschemeng.2c06668
15
16 (25) Gioia, C.; Colonna, M.; Tagami, A.; Medina, L.; Sevastyanova, O.; Berglund, L. A.; Lawoko, M.
17 Lignin-Based Epoxy Resins: Unravelling the Relationship between Structure and Material Properties.
18 *Biomacromolecules*, **2020**, *21*, 5, 1920-1928. DOI: 10.1021/acs.biomac.0c00057.
19
20 (26) Tang, R.; Xue, B.; Tan, J.; Guan, Y.; Wen, J.; Li, X.; Zhao, W. Regulating lignin-based epoxy vitrimer
21 performance by fine-tuning the lignin structure. *ACS Applied Polymer Materials*, **2022**, *4*, 2, 1117-1125.
22 DOI: 10.1021/acsapm.1c01541
23
24 (27) Li, X.-Y.; Xiao, L.-P.; Zou, S.-L.; Xu, Q.; Wang, Q.; Lv, Y.-H.; Sun, R.-C. Preparation and
25 Characterization of Bisphenol A-Based Thermosetting Epoxies Based on Modified Lignin. *ACS Applied*
26 *Polymer Materials*, **2023**, *5*, 5, 3611-3621. DOI: 10.1021/acsapm.3c00262
27
28 (28) Xue, B.; Tang, R.; Xue, D.; Guan, Y.; Sun, Y.; Zhao, W.; Tan, J.; Li, X. Sustainable alternative for
29 bisphenol A epoxy resin high-performance and recyclable lignin-based epoxy vitrimers. *Industrial Crops*
30 *and Products*, **2021**, *168*, 113583. DOI: 10.1016/j.indcrop.2021.113583.
31
32 (29) Sreejaya, M.; Sankar, R. J.; Ramanunni, K.; Pillai, N. P.; Ramkumar, K.; Anuvinda, P.; Meenakshi,
33 V.; Sadanandan, S. Lignin-based organic coatings and their applications: A review. *Materials Today:*
34 *Proceedings*, **2022**, *60*, 494-501. DOI: 10.1021/acssuschemeng.3c00889
35
36 (30) Boarino, A.; Charmillot, J.; Figueirêdo, M. B.; Le, T. T. H.; Carrara, N.; Klok, H.-A. Ductile, High-
37 Lignin-Content Thermoset Films and Coatings. *ACS Sustainable Chemistry & Engineering*, **2023**. DOI:
38 10.1021/acssuschemeng.3c03030.
39
40 (31) Thys, M.; Kaya, G. E.; Soetemans, L.; Van Assche, G.; Bourbigot, S.; Baytekin, B.; Vendamme, R.;
41 Van den Brande, N. Bioaromatic-Associated Multifunctionality in Lignin-Containing Reversible Elastomers.
42 *ACS Applied Polymer Materials*, **2023**, *5* (8), 5846-5856. DOI: 10.1021/acsapm.3c00491.
43
44 (32) Zhou, Y.; Jiang, C.; Zhang, Y.; Liang, Z.; Liu, W.; Wang, L.; Luo, C.; Zhong, T.; Sun, Y.; Zhao, L.; et al.
45 Structural Optimization and Biological Evaluation of Substituted Bisphenol A Derivatives as β -Amyloid
46 Peptide Aggregation Inhibitors. *Journal of Medicinal Chemistry*, **2010**, *53* (15), 5449-5466. DOI:
47 10.1021/jm1000584.
48
49 (33) Meng, X.; Crestini, C.; Ben, H.; Hao, N.; Pu, Y.; Ragauskas, A. J.; Argyropoulos, D. S. Determination
50 of hydroxyl groups in biorefinery resources via quantitative 31P NMR spectroscopy. *Nature Protocols*,
51 **2019**, *14* (9), 2627-2647. DOI: 10.1038/s41596-019-0191-1.
52
53 (34) Gracia-Vitoria, J.; Rubens, M.; Feghali, E.; Adriaensens, P.; Vanbroekhoven, K.; Vendamme, R. Low-
54 field benchtop versus high-field NMR for routine 31P analysis of lignin, a comparative study. *Industrial*
55 *Crops and Products*, **2022**, *176*, 114405. DOI: 10.1016/j.indcrop.2021.114405
56
57 (35) Zhao, S.; Abu-Omar, M. M. Renewable Thermoplastics Based on Lignin-Derived Polyphenols.
58 *Macromolecules*, **2017**, *50* (9), 3573-3581. DOI: 10.1021/acs.macromol.7b00064.
59
60 (36) Over, L. C.; Grau, E.; Grelier, S.; Meier, M. A. R.; Cramail, H. Synthesis and Characterization of
Epoxy Thermosetting Polymers from Glycidylated Organosolv Lignin and Bisphenol A. *Macromolecular*
Chemistry and Physics, **2017**, *218* (4), 1600411. DOI: 10.1002/macp.201600411.

1
2
3 (37) Xin, J.; Li, M.; Li, R.; Wolcott, M. P.; Zhang, J. Green Epoxy Resin System Based on Lignin and Tung
4 Oil and Its Application in Epoxy Asphalt. *ACS Sustainable Chemistry & Engineering*, **2016**, *4* (5), 2754-2761.
5 DOI: 10.1021/acssuschemeng.6b00256.

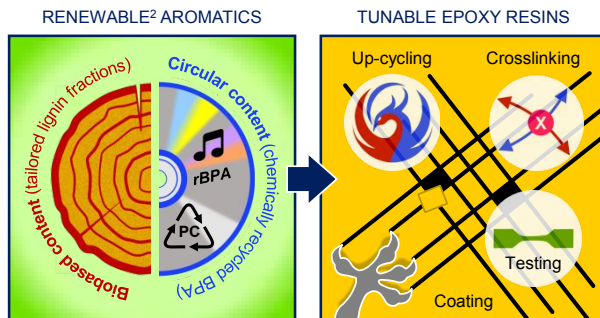
6 (38) Sabu, M.; Bementa, E.; Jaya Vinse Ruban, Y.; Ginil Mon, S. A novel analysis of the dielectric
7 properties of hybrid epoxy composites. *Advanced Composites and Hybrid Materials*, **2020**, *3*, 325-335.
8 DOI: 10.1007/s42114-020-00166-0

9 (39) Prado, R.; Erdocia, X.; De Gregorio, G. F.; Labidi, J.; Welton, T. Willow lignin oxidation and
10 depolymerization under low cost ionic liquid. *ACS Sustainable Chemistry & Engineering*, **2016**, *4*, 10, 5277-
11 5288. DOI: 10.1021/acssuschemeng.6b00642

12 (40) García, A.; Erdocia, X.; Alriols, M. G.; Labidi, J. Effect of ultrasound treatment on the
13 physicochemical properties of alkaline lignin. *Chemical Engineering and Processing: Process*
14 *Intensification*, **2012**, *62*, 150-158. DOI: 10.1016/j.cep.2012.07.011

15 (41) Gordobil, O.; Delucis, R.; Egüés, I.; Labidi, J. Kraft lignin as filler in PLA to improve ductility and
16 thermal properties. *Industrial Crops and Products*, **2015**, *72*, 46-53. DOI:
17 10.1016/j.indcrop.2015.01.0553.
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

Graphical Abstract (TOC)



Synopsis:

This study investigates the combined sustainable use of recycled and biobased building blocks to deliver renewable materials with improved properties.