

Deliverable report

D3.2 Comparison of properties of available lignin sources and derivatives for selected applications.

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Verified (WP leader)	25/04/2023	Karolien Vanbroekhoven
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D3.2 A Comparison of properties of available lignin sources and derivatives for selected applications

Working Group 3

1 Introduction – how to compare and correlate properties of lignin and its derivatives to selected applications?

Since a lot of different applications are possible with lignin as described in D3.1., one of the major points to decide where it makes sense to use lignin is linked to its properties. Besides the properties of the lignin, also the integration in the value chain and markets is crucial to make its use a success for specific industrial applications as discussed in working group 4.

Based on interactive discussions with WG3 and WG4, the different applications and taskforces defined in WG3 have been narrowed down to specific industrial relevant needs and potential for market introduction in the upcoming years.

The scope of this deliverable is to provide insight for these defined applications and make the link between using all different types of lignin resources available (technical lignins, hydrolysis lignins and lignin oils) and their end use in terms of material properties and define existing gaps to get the community to align on for the future.

- Downselection from 7 taskforces to 6 defined applications

Specific taskforces with defined taskforce leaders were initiated and organized as reported in D3.1. Based on those applications, a link was made to the development of the value chains and therefore a downselection to 6 defined applications was agreed upon. Different members of lignocost were involved to contribute to the work to build specific info for each selected application.

Table 2: Linking taskforces and applications to value chains – prioritize end uses.

Taskforces (WG 3)	Value chain (WG 4)	Compound				Lead
TF1	VC 1	A.1. Phenol-Formaldehyde (PF) resins	polymeric lignin* oligomeric lignin lignin oil	Lignin is replacing (up 40-50 wt.%) of petroleum phenol in the phenol-formaldehyde resin	Particle boards, wood panels,	Kostas
TF1	VC 2	A.2. Polyurethanes		Lignin utilized as bio-polyol to replace (partially or completely) isocyanates,	foams (rigid, soft), adhesives, ...	Filomena
TF1	VC4	A.3. Epoxy resins (polymers)		Lignin is replacing petroleum derived bisphenol A and/or cross-linking agent	All applications of glassy and rubbery epoxy polymers	Elias
TF5	VC 3	D.1. Bitumen	road constructions, roofing	Richard
TF4	VC2	D.2. Polymeric blends (eg rencomm, DOMTAR)		Beata
TF7	VC4	D.1. carbon fibers	carbonized lignin	composites for automotive, aerospace,...	Omid

- Detailed info for 4 defined applications:
 - Based on the prioritisation above, 4 defined lignin-based applications have been detailed for lignin structure -property relations with the end-use, i.e. for epoxies, phenolic resins, PU and polymeric blends; the case for epoxies has been detailed below.
 - The 2 remaining applications, i.e. bitumen and carbon fibers have been more elaborated in the value chain approach of working group 4 and will be detailed there in Deliverable reports D4.1-D4.3.

2 Approach and suggestions

Among the polymer materials containing aromatic rings, bis-phenol A (BPA) based epoxy resins have been widely produced compared with other thermosets because their properties can be tailored to suit a different applications such as coatings, composites, adhesives and the electronics industry. BPA-derived epoxy resins also called bisphenol A diglycidyl ether (BADGE) constitute 75% of the market of liquid epoxy resins (LER). Epoxy resins are polyethers usually obtained by reacting polyols or more generally a component comprising hydroxyl groups with epichlorohydrin (ECH). Commonly epoxy resins are cross-linked with various curing agents such as amines, anhydrides, alcohols etc. Epoxy resins are sold in the market as liquids or solids. According to several market reports, the global epoxy resins market can be estimated to around 11 to 12 billion USD in 2021 [1,2]. The market volume was valued between 3.5 to 5 MT in 2020-2021 [3,4].

The main drawback in using epoxy resins is that their main constituent BPA is toxic and carcinogenic [5]. To this end, investing in the production of next generation epoxy thermosets from renewable aromatic bio-polymers or bio-based monomers, such as lignin and the derived phenolics, is crucial towards sustainability and circular (bio)economy [6,7]. Lignin has already been successfully incorporated in a variety of thermosets and thermoplastics with the attention to epoxy resins being spurred only in the last years.

Lignin, due to its phenolic nature and high functionality, can be utilized as a reactive filler in epoxy resins, replacing the commonly used petrochemical curing agents. Due to its reactive surface groups like hydroxyls (and carboxyls), lignin can react with the epoxy rings of the resins and promote ring opening polymerization. An extensive review of the literature was written in the framework of this deliverable [8]. The different types of

lignins along with their properties as well as the resulting lignin epoxy material characterization are summarized in the table below (references listed in the reference section).

Reference	Type of lignin/ bio-oil	Type of functionalization	EEW (gr/eq.)	Epoxy Pre-polymer	Curing agent	Lignin (wt.%)	Substitution (wt.%) *	Properties of lignin-epoxy polymers/composites					
								T _g (°C)	Residual mass (%)	T _g (°C)	Tensile strength (MPa)	Tensile Modulus, E (GPa)	Storage Modulus (GPa, Troom)
[20]	Kraft Lignin (Indulin AT)	-	-	1,3-Glycerol diglycidyl ether	-	20-50	-	-	-	66	37	2.7	-
[20]	Kraft Lignin (Indulin AT)	-	-	1,3-Glycerol diglycidyl ether	Pyrogallol	24-30	-	-	-	63	87	3.6	-
[21]	Organosolv (corn stover)	Glycidylation	343	-	Cardolite GX-3090	-	-	241	-	181	-	-	1.4
[21]	Hardwood Kraft	Glycidylation	614	-	Cardolite GX-3090	-	-	245	-	173	-	-	1.3
[23]	enzymatic hydrolyzed lignin (corn straw)	-	-	Bisphenol A epoxy resin (WR5618)	Polyamide (TY-200)	5	-	-	-	-	-	-	-
[24]	Lignin (oil balm empty fruit bunches black liquor)	-	-	Diglycidyl ether of bisphenol A (DGEBA)	Isophorone diamine (IPD)	15-30	-	284 (14,10%)	16.7 (at 800oC)	-	13.6	0.45	-
[26]	Hardwood Kraft Lignin	-	-	LR200	LE20	15-30	-	-	-	-	-	-	-
[26]	Hardwood Kraft Lignin	-	-	LR200	LE20	15-30	-	-	-	-	-	-	-
[26]	Hardwood Kraft Lignin	-	-	LR200	LE20	15-30	-	-	-	-	-	-	-
[26]	Hardwood Kraft Lignin	-	-	LR200	LE20	15-30	-	-	-	-	-	-	-
[31]	Kraft lignin	Amination	-	Diglycidyl ether of bisphenol A (DGEBA)	Triethylene tetramine (TETA)	0.8-1.2	-	-	-	110-125	-	-	-
[32]	Kraft lignin (spruce)	Amination	-	Diglycidyl Ether of Bisphenol A (Epon 828)	-	12.9	-	309.8	-	158	86.7	3.029	-
[33]	steam exploded methanol-soluble lignin (cedar)	Glycidylation	337.5	-	TD2131	63.3	(100 / -)	293	40.6 (800oC)	-	-	-	-
[33]	steam exploded methanol-soluble lignin (cedar)	Glycidylation	337.5	-	Methanol-soluble lignin	88.2	(100 / -)	296	40.9 (800oC)	-	-	-	-
[33]	steam exploded methanol-soluble lignin (cedar)	-	-	Diglycidyl Ether of Bisphenol A (EP828)	Methanol-soluble lignin	34.2	(- / 100)	326	22.5 (800oC)	-	-	-	-
[34]	LignoBoost™ softwood kraft lignin	Glycidylation	367.5	Araldite® LY1564	Aradur®3486	-	(2-10 / -)	303-325	13.7-22.6 (at 500oC)	-	61.3-66.2	3.09-3.36	-
[35]	LignoBoost™ kraft lignin (spruce)	Glycidylation	256-370	-	Jeffamine D-2000	33.3-41.8	(100 / -)	-	-	-50 - (-52)	1.2 - 5	0.006-0.1	0.013-0.156
[36]	Kraft lignin (spruce)	Glycidylation	208	-	Jeffamine D-400	66	(100 / -)	-	-	60	66	0.0017	3.2
[36]	Kraft lignin (eucalyptus)	Glycidylation	196	-	Jeffamine D-400	64-66	(100 / -)	-	-	73	56-59	0.0014-0.0016	1.9-2.2
[36]	Kraft lignin (spruce)	Glycidylation	208	-	Jeffamine D-2000	33	(100 / -)	-	-	-50	1.2	0.006	0.009-0.034
[36]	Kraft lignin (eucalyptus)	Glycidylation	196	-	Jeffamine D-2000	30-31	(100 / -)	-	-	-49 - (-51)	1-1.4	0.0034-0.0057	0.013
[38]	Industrial pre-hydrolyzed lignin	Glycidylation	434-666	Bisphenol-A diglycidyl ether (BADGE)	Jeffamine D-400	5-15	-	336.8	-	4.8	8.1	0.0038	0.021
[41]	Organosolv (beechwood)	Glycidylation	312.5	Bisphenol-A diglycidyl ether	Isophorone diamine (IPD)	8-42	(0-50 / -)	318-284	-	121-138	26-36	182-192	1.07-2.02
[42]	LignoBoost Kraft lignin	Fractionation in Methanol	-	Epoxydized vegetable (soybean, linseed) oil	Praximer 1074	6-22.2	-	315	40 (800oC)	0	4	0.0138	-
[46]	Kraft lignin	Fractionation in Methanol and Glycidylation	-	-	Phthalic anhydride	-	-	257.1	-25	-	-	-	-
[64]	Hardwood pyrolysis bio-oil	Fast pyrolysis and Glycidylation	-	EPON 828	Diethylenetriamine (DETA)	-	(0-50 / -)	120	-20%	44-53	-	-	-
[65]	Fast pyrolysis bio-oil derived from hardwood	Fast pyrolysis and Glycidylation	314	-	Jeffamine T-403	-	-	-	-	89-92	-	-	1.88
[68]	native wood lignin (P. radiata)	hydrogenolysis and glycidylation	324-451	Bisphenol A diglycidyl ether (BADGE)	Diethylenetriamine (DETA)	17-67	-	-	-	74-108	-	2.4-3.8	2.6-3.7
[67]	Organosolv hardwood	catalytic depolymerization and glycidylation	537	-	Diethylenetriamine (DETA)	-	(100 / -)	228	23	-	-	-	-
[67]	Kraft softwood	catalytic depolymerization and glycidylation	768	-	Diethylenetriamine (DETA)	-	(100 / -)	252	33	-	-	-	-

* First value refers to wt.% substitution of epoxy prepolymer, the second value refers to wt.% substitution of curing agent

The tables shows that there is still a big lack of characterization of lignins as well as the epoxy materials using common methods of characterization. Indeed a lot of publications focus on the synthesis part and not on the

characterization which is the main key to advance the understanding the relationship between properties of lignin and the performance of the materials. In addition, the enrichment of lignin surface with epoxides via glycidylation is the selected method for preparing bio-based phenolic epoxy prepolymers while amination or further hydroxylation of the surface may lead to reactive substitutes of curing agents as the intrinsic hydroxyls/carboxylic groups of lignin are not sufficient to compensate the reactivity of poly-amines or other classical curing agents. Technical lignins, organosolv lignins, and lignin oils have all been used to make epoxy resins. Nevertheless, with the lack of common thermomechanical characterization of the lignins as well as the final epoxy material, it is very difficult to decide which type of lignin is performing the best. Although, the measured values indicate that the epoxy-lignin composites may offer similar or even improved thermo-mechanical properties compared to the pristine epoxy polymers, and can provide new ones such as UV blocking and antioxidant, antibacterial and flame retardant properties. Moreover, the values are very broad to cover a lot of applications depending on the desired properties. One should finally note that technical lignins have the advantage of being available and relatively cheaper than the other types of lignin while their incorporation into epoxy materials in high percentages is limited to their low solubility dictated by their highly condensed structures. While on the other hand, in a longer term trajectory, lignin oils produced by pyrolysis or hydrogenolysis can be added in higher percentages in weight in epoxy materials while their cost and availability in big volumes still needs innovative trajectories with national, regional and European initiatives to be able to go from lab scale (TRL 4) to pilot scale (TRL 5-6).

3 Conclusions and outlook

Whereas a lot of work has been done as described in literature, and compiled in this task and deliverable report; still a lot of gaps exist as described below:



www.lignocost.eu | CA17128 - Establishment of a Pan-European Network on the Sustainable Valorisation of Lignin

Identified gaps:

- Not always the articles consider simultaneously the lignin and application properties (materials, chemicals etc.) – Hard to establish a relationship;
- For several applications, only recent articles start to report lignin properties (e.g. hydroxyl index);
- Attention must be taken when comparing the properties obtained by different techniques/methodologies (e.g. molecular weight determination).

It would be interesting to search for articles with more complete information.

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