Electronic Supporting Information

Valorisation of Technical Lignin in Rigid Polyurethane Foam: A Critical Evaluation on Trends, Guidelines and Future Perspectives

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S.1. Rigid Polyurethane Foams (RPUF)

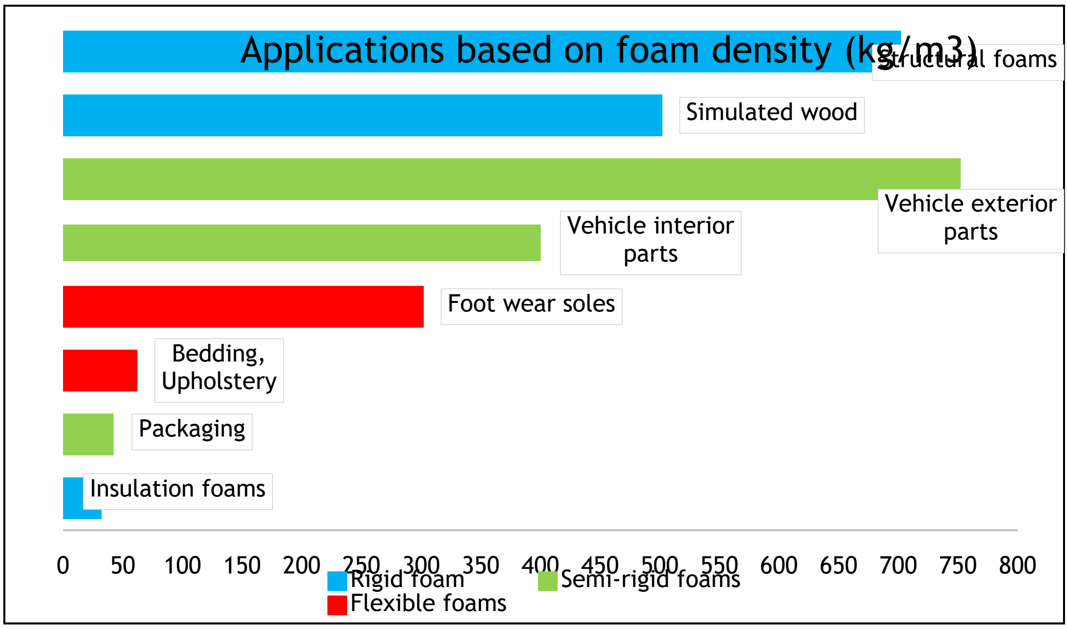

Figure S.1 Polyurethane foam applications with respect to its density [1-4]

S.2. Rudiments in Formulation of RPUF

The polyols used in RPUF are chosen to have a hydroxyl value of 250-1000 mg KOH/g, a functionality of 3.0-8.0 and a Mw of 150-1,200 Da [5]. For example, Voranol ™ 446 from **Table 1** is a sucrose-glycerine initiated polyether polyol with a functionality of 4.5 and a hydroxyl value of 446 mg KOH/g which means it has an average Mw of 566 Da [6]. Polyether polyols for RPUF are manufactured by reacting propylene oxide (PO) with an initiator, illustrated with glycerine [7]. Propylene oxide polyols largely terminate (95%) with secondary hydroxyl groups and are less reactive than primary hydroxyl groups [1]. The final product, however, is not a discrete Mw but has a multimodal distribution around the desired Mw plus a mixture of diols (PPG) and monols produced as side reactions during the oxypropoxylation [7].

In a typical RPUF formulation, polyols which are polymers with two or more hydroxyl groups per molecule and they are selected by their characteristic chemical and physical properties such as *molecular weight (Mw), average functionality (f), hydroxyl value (OHv), acid value (Av) and the viscosity*. They are interrelated by the following formula

$$Mw = \frac{f\ x\ 56100}{(OHv\ + Av)} \qquad \text{(A.I)}$$

where *f***,** the average functionality is the total moles of hydroxyl groups divided by the total moles of polyol; *OHv*, the hydroxyl value is the weight of KOH in mg that will neutralise the acetic anhydride capable of reacting with 1g of polyol [5]; and *Av*, the acid value is defined as the weight of KOH in mg, that neutralises the acid on 1 g of polyol [5], it is usually ignored if below a value of around 1 mg KOH/g.

Polyols are highly viscous in nature and exhibit properties depending on their OHv, f, and Mw [8]. Polyols are produced from a wider range of precursor biomolecules and chemical pathways mainly yielding three kinds of polyols; namely; short, aliphatic and aromatic polyols. The precursors or initiators are selected depending upon the chain architecture, functionality, molecular weight and are chemically modified to afford particular requirements of the application [7].

Isocyanates are compounds with -NCO functional groups, particularly reactive towards nucleophiles such as amines, alcohols, carboxylic acids, thiols, water, urea, and urethane [9]. Polymeric isocyanates or Polyisocyanates (denoted by 'p' in pMDI) are a mixture of dimers and trimers generating cyclic structures that provides rigidity and stability to the RPUF [10]. Hence, aromatic diisocyanates are frequently used in RPUF production as they enable crosslinking during foaming and gelling reactions, thereby controlling the rigidity and heat resistance of the foams. pMDI in **Table 1** is a mixture of aromatic compounds containing on average around 2.7 isocyanate groups per molecule (functionality of 2.7) which are particularly reactive towards nucleophiles such as amines, alcohols, carboxylic acids, thiols, water, urea, and urethane [9].

The isocyanate index for a formulation is a measure of the excess isocyanate used relative to the theoretical amount required to react with all the hydroxyl groups. For example, in **Table 1**, pMDI has an index of 103 (or 1.03) indicates a 3% excess of isocyanate [11]. An efficient method to calculate the Isocyanate index is using the concept of the equivalent number of reacting groups taking account of the available number of hydroxyl groups in the polyol as well as the water added in the formulation [12]. Typically, polyurethane foams have an index from 90 - 130 [13], whereas Polyisocyanurate (PIR) foams have a higher index above 180 [14-15].

S.3. ASTM and ISO Standards used for Raw Materials and Physical Properties of RPUF

Table S.1 ASTM and ISO standards used for determination of characteristic parameters of polyols used in RPUF

ASTM Standard	ISO standard	Key parameters / characteristics
ASTM D4273	ISO 14900	Hydroxyl number
ASTM D7253		Acid value
ASTM D 6437		Alkaline value
ASTM D4878		Viscosity
ASTM D4890		Colour
ASTM D4672	ISO 14897	Water content
ASTM D4670		Suspended matter
ASTM D4662		Acid and Alkalinity Numbers of Polyols
ASTM D4671	ISO 17710	Unsaturation of Polyols
ASTM D4669		Specific Gravity
ASTM D4273		Primary Hydroxyl Content of Polyether Polyols
ASTM D6979	ISO 25761	Basicity in Polyols, Expressed as Percent Nitrogen
ASTM D4875		Polymerized Ethylene Oxide Content of Polyether Polyols
ASTM D6342	ISO 15063	Hydroxyl number by NIR spectroscopy

Table S.2. ASTM and ISO standards used for determination / measurements of physical properties of RPUF

ASTM Standard	ISO standard	Description
ASTM D1622	ISO 845	Density
ASTM C518	ISO 8301	Thermal conductivity measurements
ASTM D2856	ISO 4590	Closed Cell Content
ASTM E96	ISO 1663	Water vapour permeance

ASTM D2126	ISO 2796	Dimensional stability
ASTM D1621	ISO 844	Compression properties
ASTM D1623	ISO 1926	Tensile Strength
ASTM D2842	ISO 2896	Water absorption
ASTM C1303	ISO 2440	Ageing
	ISO 6187	Friability
ASTM D7487		Foam cup test
ASTM C1338	ISO 846	Fungi resistance
ASTM D3576		Cell size
ASTM D3014		Fire resistance
ASTM D5113		Adhesive attack
ASTM C1029	ISO 8873	Spray foam
	ISO 4898	Thermal insulation products for buildings
ASTM C1289		PIR Thermal Insulation Board
ASTM E1730		Structural Sandwich Panel Cores
Other tests		
ASTM E-84	AS1530.3, DIN 4102-1, BS 476-7	Small scale fire tests
	ISO 13785-2	
	FM 4880,	
	LPS 1181, AS5113:2016, BS8414,	Large scale fire tests
	DIN 4201-20	

S.4. Summary of Lignin Incorporated RPUF Included in the Review

Table S.3 Reported data on physical properties of lignin incorporated RPUF

Approach	Lignin type	Polyol	Lignin% w/w in polyol	NCO index	Density (kg/m^3)	Thermal conductivity (mW/m.K)	Compressive strength (MPa) Parallel to foam rise	Compressive strength (MPa) Perpendicular to rise	Compressive modulus (MPa) Parallel to foam rise	Compressive modulus (MPa) Perpendicular to foam rise	Tg (°C)	References
Direct Incorporation	KL	Voranol™ 360, glycerol	0	110	36.2	25.6	0.18	0.16	4.8	3.6	131	Hayati et al. [16]a
			2.5		38.6	24.7	0.14	0.12	4.5	3.5	133	
			5		40.1	24.7	0.15	0.13	4.5	3.52	135	
			10		38.8	25.2	0.15	0.15	4.3	4.1	145	
Direct Incorporation	KL	Stepanpol ™ PS2352, glycerol	0	110	42.6	34.5	0.24	0.26	7.5	6.4	155	Haridevan et al. [17]
			0.5		44.5	22.6	0.25	0.26	5.8	5.7	155	
			1		44.3	23	0.3	0.29	7.4	7.2	158	

			6		44	23.5	0.3	0.19	8.5	4.5	167	
Direct incorporation	KL	Voranol ™ 270	0	1.1	116	NR	0.5	NR	NR	NR	NR	Pan and Saddler [18]
			23		100		0.24					
			46		70		0.23					
			55		80		0.2					
			64		83		0.1					
Direct incorporation	HL	PEG-400	0	105	120	NR	0.47	NR	NR	NR	NR	Xue et al. [19]
			9		85		0.28					
			18		70		0.18					
			27		60		0.07					
			36		52		0.06					
			45		50		0.05					
Direct incorporation	Softwood lignin	JEFFOL® A-360, Soybean phosphate ester polyol	0	105	62	NR	0.39	NR	NR	NR	173	Luo et al. [20]
			5		65		0.4				177	
			10		76		0.46				181	

			15		86		0.32				182	
Direct incorporation	BIOLIGNIN ™	Lupranol ® 3330, Lupranol ® 3422	0	120	53	NR	0.26	NR	NR	NR	NR	Arshanitsa et al. [21]
			5		48		0.22					
			10		47		0.21					
			20		45		0.21					
			30		42		0.19					
			40		42		0.17					
			50		40		0.15		NR			
Direct incorporation	Softwood lignin	Soy based polyol	0	110	303	NR	NR	NR	NR	NR	NR	Luo et al. [22]
			5		264							
			10		257							
			15		223							
			20		220							
			25		196							
Direct incorporation	LS	DEG	0	120	NR	NR	NR	NR	NR	NR	~130	Asano et al. [23]
		TEG	0								~95	

		PEG-200	0								~75	
		DEG	19.8								~120	
		TEG	19.8								~100	
		PEG-200	19.8								~90	
Direct incorporation	BIOLIGNIN ™	Tall oil polyol,	0	155	50	35.2	0.31	0.28	NR	NR	NR	Paberza et al. [24]
		Lupranol ® 3422,	1.88		51	NR	0.33	0.3				
		glycerol	3.75		52	NR	0.35	0.31				
			7.5		51	32.4	0.33	0.26				
			15		59	NR	0.34	0.17				
			22.5		63	29.8	0.28	0.21				
Direct incorporation	KL	DEG/PEG	0	110	62	NR	0.33	NR	8.15	NR	NR	Luo et al. [25]
			5		100		0.73		10			
			10		108		0.69		10.4			
			15		111		0.66		10.5			
			20		115		0.64		14.7			
Direct incorporation	LS	PPG/ glycerol (100:0)	0	107	17	NR	1.62	NR	NR	NR	100	Wysocka et al. [26]

		0/0	100		20		4.42				29	
		70/0	30		18		3.81				23	
		60/10	30		36		1.11				48	
		60/20	20		22		0.95				21	
		70/10	20		20		3.11				62	
Direct incorporation	KL	Castor oil/glycerol	17.5	110	54.9	NR	0.04	NR	0.01	NR	NR	Carrico et al [27]
Water					54.9		0.04		0.01			
n-pentane					71.1		0.03		0.03			
Cyclopentane					81.3		0.02		0.04			
Water/ cyclopentane					71.4		0.02		0.03			
Direct incorporation		PEG-2000	0	110	207	NR	NR	NR	0.02	NR	NR	Wang et al. [28]
	Alkali lignin		20	108	344				0.02			
Direct incorporation	SL	polyether polyol 330	0	1.73	75	NR	0	NR	0.01	NR	NR	Zhu et al. [29]
			2.5	1.25	60		0.001		0.02			

			5	0.98	66		0.002		0.04			
			7.5	0.81	75		0.003		0.04			
			10	0.69	85		0.003		0.05			
			15	0.53	115		0.06		0.09			
Lignin-polyol grafting	Alkali lignin/PEG 2000	PEG-2000	20	104	120				0.09			Wang et al. [30]
			33.3	98	130				0.27			
			50	95	201				0.09			
Modification of existing functional groups	KL	Voranol ™ 360	0	110	38.2	25.2	0.14	0.15	3.9	3.99	135	Hayati et al. [16]b
		glycerol	2.5		38.7	25	0.16	0.16	4.5	3.95	133	
			5		39.3	24.6	0.2	0.17	5.4	4.05	149	
			10		36.9	26.7	0.09	0.07	2.7	1.8	171	
Modification of existing functional groups		PEG/ glycerol (9:1)	0	105	NR	NR	NR	NR	NR	NR	NR	Muller et al. [31]
	KL	Glycerol/KL (9:1)	10	105	79	39	0.35					
	LS	Glycerol/LS (9:1)	10		154	48	0.25					

	OL	Glycerol/OL (9:1)	10		70	42	0.05					
Oxypropylation	Alcell	Lupranol® 3323, (lignin/propylene oxide/ KOH catalyst;	100	110	22.3	25.7	NR	NR	3.1	NR	NR	Cateto et al. [32]
	Alcell	30/70/2)	50		25.1	26.9			3			
	Indulin AT		100		23.1	27.4			4			
	Indulin AT		50		23.7	29.1			3.6			
Oxypropylation	Alcell	Lupranol® 3323) (lignin/propylene oxide/ KOH catalyst;	100	110	20.9	26.7	NR	NR	2.5	NR	NR	Cateto et al. [32]
	Alcell	20/80/5)	50		23.9	30.5			3.3			
	Indulin AT		100		19.2	26.8			2.6			
	Indulin AT		50		22.4	32.9			2.4			
	Curan 27		100		18.4	28.5			2.3			
	Curan 27		50		19.4	31.3			2.7			
	Reference polyol		0		31.1	30.3			4.6			
Oxyropylation	OSL	lignin/propylene oxide/ KOH	20/80/		35	24			1.2		-63	Abid et al. [33]

		catalyst;	4									
			20/80/5		37	26.5			1.6		-61	
		Reference			30	19			0.1			
Oxypropylation	KL	20/80/5)	0	120	NR	NR	0.1	NR	1.45	NR	NR	Li and Ragauskas [34]
			10				0.1		1.56			
			30				0.11		1.58			
			60				0.1		1.13			
			100				0.09		1.11			
		Oxypropylated KL	100				0.14		3.41			
Oxypropylation	Alcell Lignin polyol	Rokopol ® RF551	0	110	45.4	22.9	0.38	0.19	NR	NR	NR	Kuranska et al. [35]
			10		43.8	22.8	0.38	0.18				
			20		43	22.8	0.35	0.18				
			30		41.4	22.9	0.34	0.16				
Oxypropylation	KL	Rokopol ® RF551	0	200	83	NR	0.63	NR	NR	NR	NR	Gosz et al. [36]
			25		99		0.7					

			50		150		0.86					
Oxypropylation	LignoPolyol	Lupranol ® 3330,	0	120	53		0.26	NR	NR	NR	NR	Arshanitsa et al. [21]
		Lupranol ® 3422	1.9		NR	NR	0.23					
			3.8				0.26					
			5.7				0.27					
			7.5				0.31					
Glycolysis	KL	Recycled aromatic PET polyol	0	260	29.3	23.9	0.19	NR	NR	NR	NR	Rogers et al. [37]
			2.5		29.8	24.3	0.21					
			5		29.3	24.1	0.24					
			10		30.3	24.3	0.23					
			15		30.3	24.5	0.24					
Fractionation and oxypropylation	OSL	Polyether polyol (polyether 4110)	0	105	130	46.5	0.7	NR	NR	NR	NR	Li et al. [38]
	8.87% (yield%)		50		73	37	0.75					
			100		85	37.1	0.83					
	20.12%		50		85	38.4	0.75					
			100		95	38.6	0.78					

	8.37%		50		102	36	0.25					
			100		105	45.1	0.5					
	1.63%		50		91	33.5	0.21					
			100		70	49.1	0.16					
Depolymerisation, oxypropylation	KL	Sucrose polyol	0	110	54	33	0.327	NR	NR	NR	NR	Mahmood et al. [39]
		Depolymerised KL	50		104	32	0.374					
		Oxypropylated-Depolymerised KL	100		55	29	0.515					
Liquefaction, oxyproproylation	HL	JEFFOL SD-361,	50/50	110	44.7	29	0.39	NR	9.2	NR	NR	Mahmood et al. [40]
		Liquefied/ Oxypropylated lignin	60/40		61	30	1.09		19.8			
			70/30		64.5	30	1.06		21.2			
Liquefaction	Phenolated lignin	PEG	0	NR	NR	NR	NR	NR	NR	NR	NR	Yang et al. [41]
			0.5				0.07					
			1				0.11					
			1.5				0.13					

			2			0.12	
			2.5			0.09	
			3			0.09	
Fractionation	KL		0	100	155		Mardiyati et al. [42]
			5		412		
			10		610		
			20		764		
			30		804		
			40		886		
Liquefaction	KL	PPG	0		35		Jeong et al. [43]
			1		39		
			1.5		39		
			3		40		
			6		41		
Liquefaction	acetone-soluble lignin	Glycerol	0	100	35	0.08	Tran et al. [44]
			1		32	0.21	

			2		36		0.22					
			3		39		0.055					
Liquefaction	Empty fruit bunch (EFB) lignin	PEG300, glycerol	110		25		0.09					Lee at al. [45]
		reference			24.8		0.09					
Liquefaction	KL	PEG400, glycerol	12.6	100	187				0.67		66	Mohammadpour et al. [46]
			12.6	200	220				2.89		65	
Introduction of New Functional Groups	Epoxidated lignin	PEG	0	NR	NR	NR	NR	NR	NR	NR	NR	Yang et al. [41]
			0.5				0.05					
			1				0.06					
			1.5				0.08					
			2				0.08					
			2.5				0.09					
			3				0.09					
Introduction of New Functional	DES treated regenerated	PEG, glycerol	0	23		0.45						Xue et al. [47]

Groups	lignin											
			10	32		0.53						
			20	48		0.54						
			30	65		0.68						
			40	29		0.3						
			50	32		0.2						
Hydrolyis	LS	PPG /glycerol	100	107	NR	NR	NR	NR	NR	NR	NR	Wysocka et al. [26]
		70/0	30		13		0.46				100	
		60/10	30		11		0.9				41	
		60/20	20		19		0.86				36	
		70/10	20		18		0.84				56	
Liquefaction	HL	PPG400 and glycerol	0	120	58	45	0.52	NR	9.2	NR	NR	Mahmood et al. [48]a
			30		55.6	38	0.16		0.18		138	
			50		99	39	0.09		0.11		146	
		JEFFOL SD-361	0	120	30.1	44	0.09	NR	1.03	NR	N	Mahmood et al. [48]b
			30		35.4	35	0.19		3.34		178	

			50		65.1	37	0.25		3.29		189	
Modification of existing functional groups		PEG-400	0	NR	149	14	0.94	NR	NR	NR	311	Liu et al. [49]
	Refined KL		15		79.5	12	0.41				281	
	Modified KL		15		110	10	0.5				320	
Oxyalkylation with ethylene carbonate and polyethylene glycol	KL	PEG-400/EC	0	120	NR	NR	NR	NR	NR	NR	NR	Zhang et al. [50]
			20		120		0.18					
			25		110		0.18					
			30		123		0.17					
			35		125		0.16					
			40		122		0.14					
			45		120		0.14					
			50		128		0.14					

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