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Julien Peyrton, Luc Avérous. Structure-properties relationships of cellular materials from biobased polyurethane foams. *Materials Science and Engineering: R: Reports*, 2021, 145, pp.100608. <10.1016/j.mser.2021.100608>. <hal-03478358>

HAL Id: hal-03478358

<https://hal.science/hal-03478358v1>

Submitted on 15 Mar 2023

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Structure-properties relationships of cellular materials from biobased polyurethane foams

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Abstract

The polyurethanes (PU) are a very versatile family of materials mainly obtained by combinations of polyols and polyisocyanates. Based on their annual worldwide production of around 20 million tons and a global market of \$50 billion (2016), PUs rank 6th among all polymers. Through their value chain, PUs involve different players: (i) the chemists producing most of PUs raw materials, (ii) the PUs producers from the raw materials, (iii) the compounders/assemblers who formulate PUs into their final products, and finally (iv) the end-users. Due to the multiplicity of their structures, PUs can be used in various forms and applications. Cellular materials are the largest part of this market (more than 60%) with segments including the furniture, automotive, bedding, insulation, building or construction markets. Two main types of foam can be fabricated: (i) flexible with open cells, stress and tensile properties, e.g., furniture or bedding, and (ii) rigid with closed cells, low thermal conductivity, low density and high dimensional stability mainly for thermal insulation, e.g., building industries. The formulation step significantly influences the microstructure or morphology of these cellular materials and impacts the final foam properties. Even if some partially biobased compounds (polyols) can be used, commercial PU cellular materials are till now mainly based on fossil resources. However, future materials will combine high performance with low environmental impact in order to

fulfill societal expectations. In this way, new biobased compounds combining different fields such as biotech, chemistry, science and materials engineering are more and more used in complex formulations for renewable foams, leading to specific renewable macromolecular architectures.

This review aims to highlight the main biobased components (polyols, polyisocyanates and additives) used in formulations for PU foams, in relation to the corresponding fabrications, morphologies and properties. The main renewable sources come from (mono and poly)sugars, oleo-chemistry, polyphenols (lignins, tannins ...), or different compounds from white biotech processes from agro-wastes ... The impact of these different components on material performances is discussed more particularly for rigid polyurethane foams. The structure-property relationships are analyzed with a scope on cellular morphology, mechanical, thermal properties, fire resistance, and insulation behavior. Finally, an analysis focus on future perspectives on biobased PU foams is conducted.

Keywords: Polyurethane, Foams, Biobased, Structure-properties, Sustainable.

1. Introduction

The depletion of some resources from fossil-based refineries, the degradation of the environment and its connection with the climate is at the core of every recent international forums. In 2015, the United Nations developed an agenda of action for people, planet, and prosperity regrouped in 17 establish goals. The “goal 12” entitled “Ensure sustainable consumption and production patterns” sets the sustainable management and efficient use of natural resources by 2030 [1]. In this hot context, the development of new and/or greener polymer materials with higher performances and lower environmental impacts from cradle to cradle than the traditional fossil-based equivalent is a priority [2]. This recent trend is also driven by the development of innovative molecular architectures with new properties, which can be extracted or bioproduced from various types of biomass combining different disciplines such as biotech, chemistry, science and materials engineering.

The global production of plastics reached around 360 million tons in 2018 [3]. The bioplastics, defined as biobased or biodegradable polymers, represent less than 1% of this worldwide plastics production [4,5]. Biobased polymers are defined as polymers obtained more or less directly from biomass, i.e., from all the living organisms, with a positive level of C¹⁴. The interest in biobased polymers knows an exponential growth in the last decades due to the desire to reduce the fossil-based products dependency [6] and the environmental impact. The production of biobased monomers for sustainable plastics was extensively developed to design common-like polymers such as polyamides [7], polyesters [8,9], polyethylenes [10] or polyurethanes (PUs) [11]. On the other hand, biodegradable plastics are defined as materials degraded into CO₂ or/and CH₄ and water mainly by the action of microorganisms [12] in normalized conditions (time, temperature, media). However, biodegradable polymers can also be produced from fossil-resource such as polycaprolactone. The development of biodegradable polymers is also linked to the vast and increasing problem of dispersion and accumulation of plastics in the environment. With the actual

growth of microplastics accumulation in the ocean [13] and global warming, the urge is to design sustainable polymeric materials.

Although PUs can be obtained without isocyanates (Non-Isocyanate Polyurethanes or NIPU) by, e.g., the reaction between polycyclocarbonates and polyamines [14], they are till now mostly obtained by polyaddition between polyisocyanates and polyols to obtain linear or crosslinked architectures. PU is the most versatile polymer family in terms of applications. This diversity originates from the myriad of chemical structures of the polyols and polyisocyanates and the particular property of the carbamate group. PUs rank 6th among all polymers with a production of around 22 million tons [15] and a global market of \$50 billion (2016). The PU market is usually segmented in 5 uneven parts with the foams (65% of the market), the coatings (13%), the elastomers (12%), the adhesives (7%) and the others, including the biomedical field (3%) [16,17]. Two main types of PU foams (PUFs) can be identified: the flexible foam (F-PUF) with an open cell structure and the rigid (R-PUF) one with a closed-cell structure. Of course, intermediate systems can also be developed, e.g., the spray foams are rigid with open-cell structures. PUFs structures and properties can be tailored by (i) the structure and quantity of the monomers, (ii) the catalysts, (iii) the surfactants and (iv) the blowing agents (BA). To this basic list, different other ingredients are also used, such as fillers, flame retardants (FR), pigments, or dyes.

F-PUFs representing the main part of the foams market (60%) are synthesized by molding or slabstock process [18]. As presented in Fig. 1, PUFs are classified into several categories depending on their properties. The high resilience foams provide resilience and buoyancy compared to viscoelastic foams, which respond slower to stress. Integral skin foams are composed of a high-density skin and low-density core foam sandwich structure [19] obtained, e.g., by reaction injection molding (RIM). The foams formulation and processing are key points to obtain the required properties. The walls are melted after the cellular material synthesis to obtain very high consistency and controlled porosity for filter applications [18]. F-PUFs are used in various everyday life applications, such as filters, automotive and furniture/bedding cushioning (Fig. 1).

The R-PUFs are classified into three categories (Fig. 1) such as (i) the sprayed foams which are produced on-site with a high-pressure gun, (ii) the boardstocks are flat sheet products made with flexible facings and (iii) the sandwich panels encased by rigid facings [18]. The major R-PUFs are designed to be used as thermal insulation in appliances, construction, transport or pipe insulation. Despite the emergence of new materials with low thermal conductivity [20–22], the R-PUF remains a major material used as thermal insulation due to their low thermal conductivity and density, compared to mineral wool, polystyrene or lignocellulose product [23]. Thermal insulation is nowadays a major strategic field, e.g. in 2018, one third of the worldwide energy consumption was used for the heating or cooling of buildings [24]. In this context, the development of new sustainable materials with better properties than their fossil-based counterparts is an actual fascinating challenge. The most significant variables to get the best environmental performances of PUF were linked to the low thermal conductivity and density of the biobased PUFs [2].

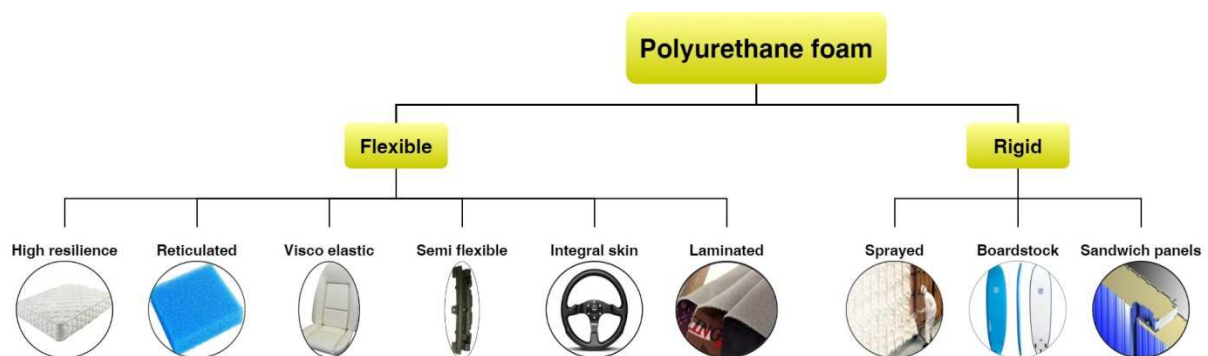


Fig. 1. Examples of F-PUF (Left) and R-PUF (right) applications.

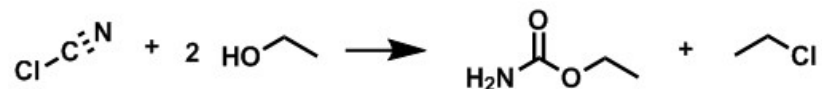
In the field of biobased PUs, different partial overviews can be found. Sustainable PUs were partially reviewed for adhesive applications [25] or foams [11,26,27]. The goal of this review is to complement, update and expand these previous states of the art. This work is also expected to provide a deep insight into the biobased PUFs field, especially in the study and analysis of the “structure-properties” relationships. The second section of this review gives an overview of basic information to know about PUFs, such as the isocyanate chemistry, the process of foam and the role of each component in the foam formation. The third section is focused on the renewable PUFs from

biomass such as triglycerides, carbohydrates, polyphenols (lignins and tannins), wastes, and different molecules obtained by bioproduction as biobased building blocks for PUFs elaboration. The fourth section carefully reviews the relationships between these new biobased PU architectures, the cell morphology and the related properties such as the mechanical, thermal, fire resistance and acoustic behaviors. In the last section, very recent perspectives on the elaboration of foams from, e.g., NIPU, are analyzed and discussed.

2. PUF engineering and fundamentals

2.1. Isocyanate chemistry

The synthesis of urethane groups was first investigated in 1846 by Charles Adolf Wurtz (1817-1884) with the study of the reaction between the cyanogen chloride and ethanol described in Scheme 1 [28]. Otto Bayer was a scientist in charge of finding a substitute for the Nylon 6.6 recently developed by Dupont when he discovered the PU by polyaddition between a diisocyanate and a polyester diol in 1937. The first thermoplastic PU (TPU) had elastic properties and was industrially developed during the Second World War as a rubber substitute from hevea in the USA. The development of isocyanate production and their fast reaction with hydrogen-labile groups helped the tremendous development of the urethane market [29].



Scheme 1. The first synthesis of carbamate by Charles Adolf Wurtz. Adapted from [28].

Nowadays, the PU synthesis is still and mainly based on the polyaddition between polyisocyanates and polyols due to the high reactivity of the isocyanate groups with hydrogen-labile compounds, explained by the carbon electron deficiency. The isocyanate addition is a reversible reaction, exploited, for instance, to produce vitrimers called vinylogous urethane [30]. However, the cyclization of the product or the generation of gas inhibits the reversibility. Fig. 2 shows that the products of the isocyanate reactions can be classed according to the number of isocyanate additions (first, second and third) to yield it. The main PU synthesis results from the addition of isocyanate with an alcohol (A) yielding urethane group. This reaction is exothermic and releases 100 kJ/mol of heat [31]. Water has a similar reactivity as alcohol and, by reaction with isocyanate (B), produces unstable carbamic acid, which is instantaneously decomposed into CO₂ and amine (C). The water-isocyanate reaction releases almost two times more heat (197 kJ/mol) than the alcohol-isocyanate system. The

gases released due to the isocyanate additions are exploited to rapidly expand the polymer matrix for PUFs elaboration, mainly for soft foams with open cells. Analogously to the amine formation, the formation of amide by isocyanate and carboxylic acid addition (D) is accompanied by gaseous CO₂ formation. For instance, when formic acid is used as carboxylic acid, the reaction produces an amine, CO₂ and CO (E). Compared to the water-isocyanate addition, this particular reaction releases two moles of gas per mole of isocyanate. Furthermore, the amine formed by water or formic acid addition also reacts with isocyanate to form a disubstituted urea group (F). The isocyanate can also react with compounds without labile-hydrogen, such as epoxides (G). In this case, the oxygen atom from the epoxide ring attacks the carbon of the isocyanate; therefore, the reaction is less favored and requires high temperatures and specific catalysts to yield oxazolidone.

The high reactivity of isocyanate enables the 2nd addition of isocyanate on the product resulting from a first addition. Both urethane and urea groups present labile hydrogens and can further react with isocyanate to synthesize allophanate (H) and biuret groups (I), respectively. Furthermore, isocyanate molecules can intermolecularly react and dimerize depending on the reaction conditions and catalysts into carbodiimide (J) or uretdione (K) [32]. Furthermore, the uretonimine group is irreversibly obtained after the third addition of isocyanate on carbodiimide (L). The combination of three isocyanate groups also leads to a stable and six-membered ring isocyanurate group. It was demonstrated that allophanate (M), biuret (N), oxazolidone (O) and uretdione (P) are intermediates in the synthetic pathway to isocyanurate [33–36]. The polymerization of isocyanates with an appropriate catalyst was used to produce rigid foam exclusively composed of polyisocyanurate (PIR) network.

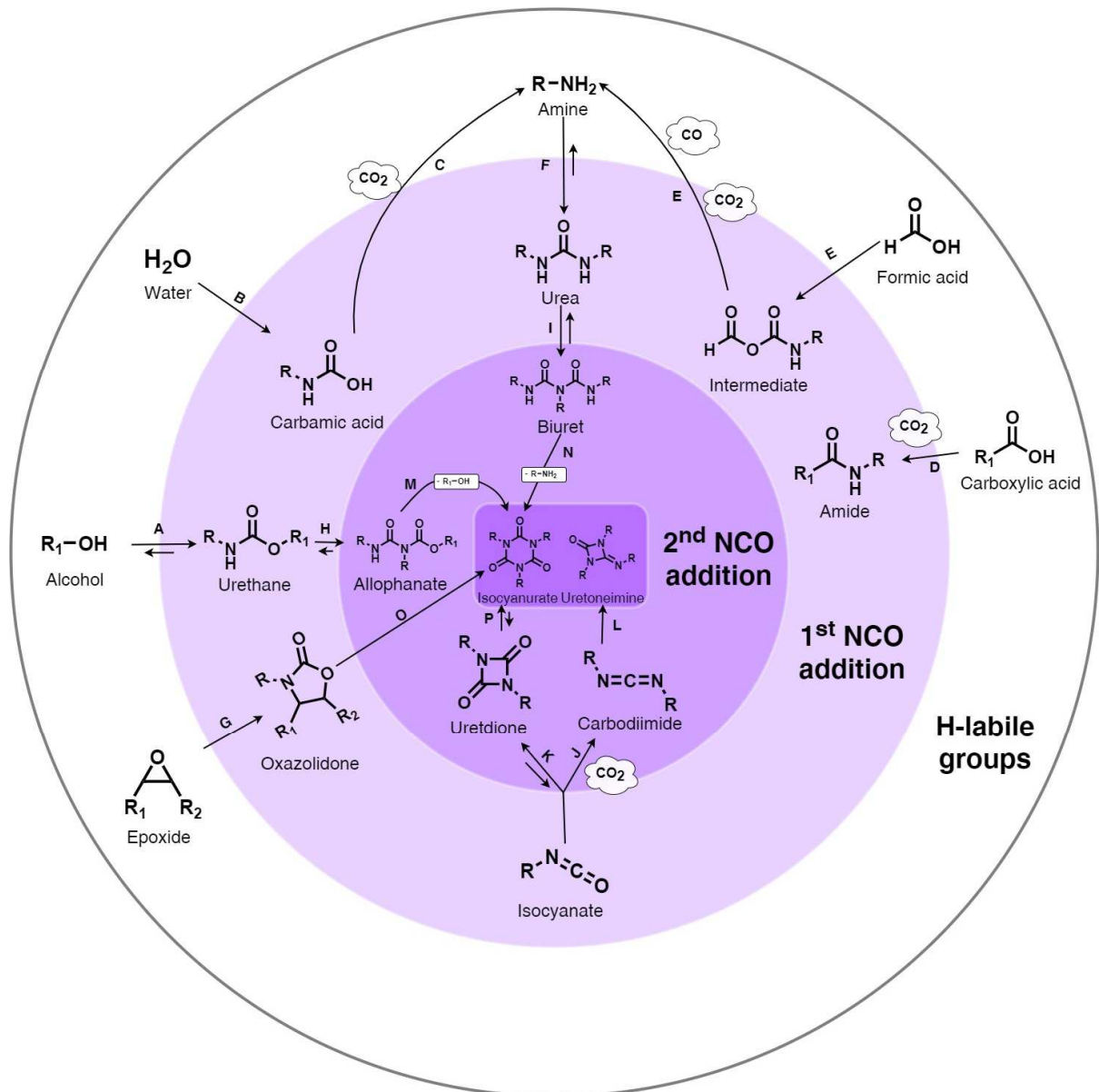


Fig. 2. Main isocyanate reactions with H-labile groups.

The diversity of the isocyanate reactions and the numerous different structures of polyols and polyisocyanates available make the PU a very versatile polymer family. PUs diversity of properties and the efficiency of the processing endorsed a growing market, which is mainly based on PUFs, from the soft to the rigid foams based on open or closed cells, respectively.

2.2. PUF Formulation

PUFs elaboration is a complex association of polyols, polyisocyanates, BAs, catalysts, surfactants and additives such as fillers or FRs. The general formulation quantities for PUFs in Table 1 are expressed in part by weight of polyol (pbw). The quantities of all components are calculated on a basis of 100 g of polyols to simplify the scale up or down. The BA quantity ranges from 3 to 30 pbw and depends on the targeted density and the BA structure. The dominant components in a PUF formulation are the polyisocyanate and polyol. Their contents, linked to the type of foam (R-PUF, F-PUF or PIR foam) and the targeted applications, are controlled by the NCO/OH index determined as the ratio between the isocyanate and the hydroxyl groups multiply by 100.

Table 1
General foam formulation with quantities expressed in part by weight of the polyol.

Foam component	Polyisocyanate	Polyol	BA	Surfactant	Catalyst	Additives
Quantity (pbw ¹)	100-300 ²	100	3-30 ³	1-3	1-3	1-10

¹ part by weight of polyol ² Quantity depending on the ratio NCO/OH ³ Molar mass-dependent

Fig. 3 presents the effect of the NCO/OH molar ratio on the chemical architectures of PUFs, hybrid PU-PIR foams and PIR foams. The PUFs are produced with a NCO/OH index between 80-120 to promote the urethane group formation. As presented in Fig. 3, the PIR foam elaborated mainly from isocyanate is highly crosslinked and, consequently, highly brittle or friable [37]. However, the PIR foam has excellent thermal stability properties due to the isocyanurate group. In order to take advantage of the thermal stability of the isocyanurate and avoid the formation of a highly crosslinked network, hybrid PU-PIR foams were developed. They are formulated with NCO/OH index higher than 120 to form an isocyanurate group and lower than 600 to avoid high friability [38].

The PU-PIR foam combined the thermal stability of the PIR network with the flexibility of the PUF [39]. They are classed among R-PUFs due to their similar mechanical properties and morphologies and consequently they are mainly used in thermal insulation. The PU-PIR foams are explicitly used when the fire hazard is high due to their higher thermal stability compared to R-PUFs.

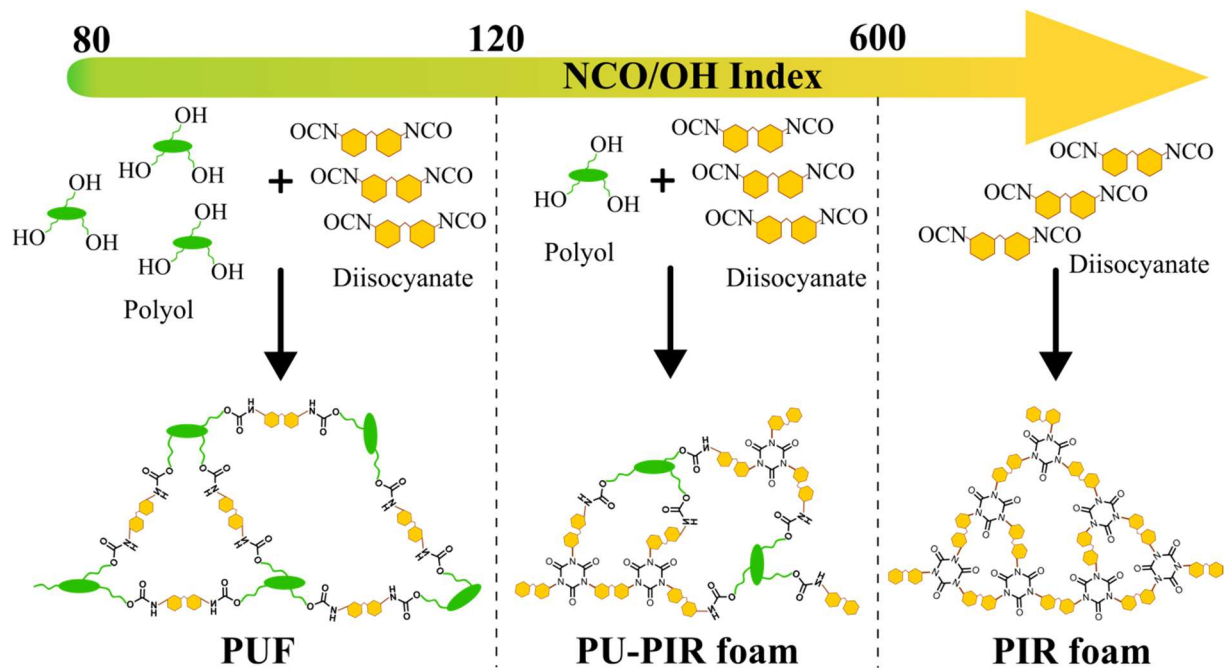


Fig. 3. Effect of the NCO/OH index on the chemical architectures of PUF, PU-PIR and PIR foam networks.

Several processes were developed industrially to produce PUFs, such as molding, slabstock, spaying, pour-in-place or frothing-in-place. In academic research, the two primary processes for the PUFs elaboration are the pour-in-place or molding method, described in Fig. 4. The foaming process is based on the one-shot method, where the polyol and polyisocyanate are intimately mixed. The components are usually separated into two parts with (i) the A-part containing the polyol, the BA, catalysts, surfactants and additives stirred vigorously to integrate air bubbles in the mixture and to obtain an emulsion (step 1 in Fig. 4) and (ii) the B-part composed of the polyisocyanate. Both parts are then mixed under stirring (steps 2 and 3 in Fig. 4). The reactive mixture is then poured into an open-cup for the pour-in-place process or in a closed mold with depending on the targeted application, an optional control of the temperature, for the molding process (step 4 in Fig. 4) where the polyaddition releases heat and forms the polymer network. The BA vaporizes and expands through the heat generated by the reaction, and the foam rises (step 5 in Fig. 4). In the end, a cellular material composed of gas-entrapping polymer cells is obtained (Step 6 in Fig. 4).

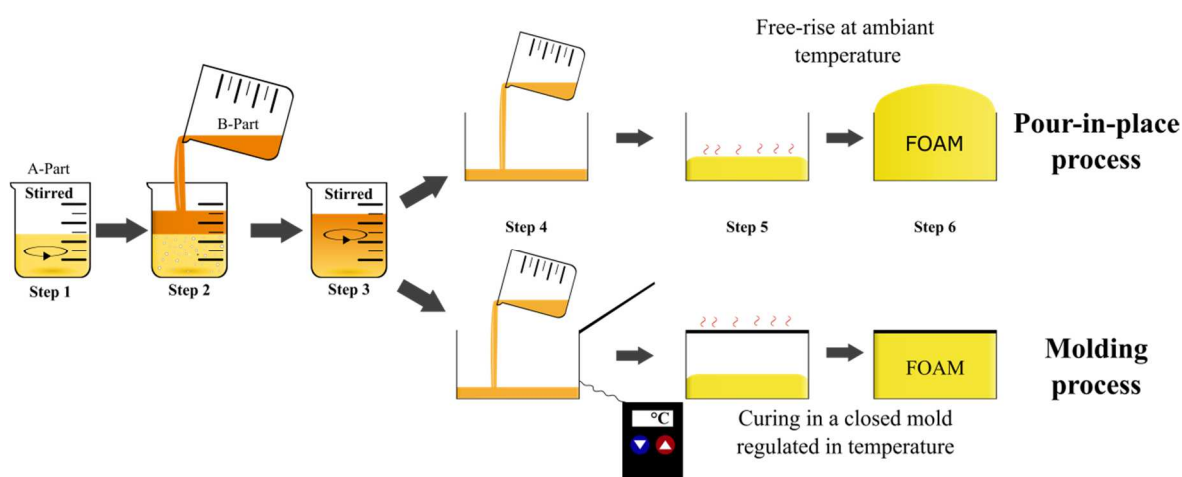


Fig. 4. Detailed usual processes at lab scale for PUF elaboration: pour-in-place or molding process.

2.2.1. Polyisocyanate

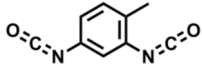
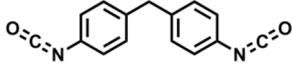
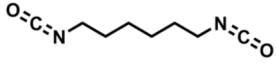
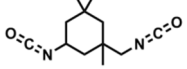
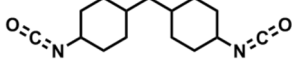
Several pathways can be used to synthesize isocyanate groups such as the Curtius, Hofmann or Lossen rearrangements but also the phosgenation of primary amine [29]. At the industrial scale, although toxic for human health, the phosgene is the preferred pathway for the production of isocyanate due to the difficulty of handling the unstable azide groups in the rearrangement reactions [40,41]. The main used isocyanates are the toluene diisocyanate (TDI), the methylene diphenyl 4,4'-diisocyanate (MDI) and its polymeric form (pMDI) [29], which is mostly used since it presents lower volatility and reduced toxicity compared to the monomer form. The pMDI superior functionality compared to the other polyisocyanates is also a key point for R-PUF elaboration, which require highly crosslink network. On the contrary to the aromatic monomer polyisocyanates, the pMDI is liquid at ambient temperature, facilitating the implementation at industrial scale. In addition to the aromatic polyisocyanates, some aliphatic polyisocyanates are used, such as the hexamethylenediisocyanate (HDI), the isophorone diisocyanate (IPDI), or the 4,4'-methylene bis cyclohexyl diisocyanate (H₁₂MDI). Their reactivities and structures are described in Table 2.

The stabilization of the mesomeric structures by the surroundings of the isocyanate group enhances the carbon electrophilic character and its reactivity. As shown in Table 2, the aromatic

isocyanates are more reactive than the aliphatic or cycloaliphatic counterparts due to the delocalization of the negative charge on the aromatic ring. The reactivity of the aromatic TDI and MDI is two orders of magnitude higher than the aliphatic HDI, H₁₂ MDI and IPDI.

Table 2 shows that the first addition of alcohol on a diisocyanate decreases the reactivity of the second addition. The foam elaboration requires high reactivity; therefore, aromatic polyisocyanates are used. Besides, the aromaticity brings several properties to the final products, such as, e.g., higher flame resistance and mechanical properties. In general, the MDI and TDI are used for F-PUFs and pMDI for R-PUFs. They are the primary polyisocyanates used in PUFs formulation.

Table 2
Relative reactivity of isocyanates with alcohol groups for the 1st and the 2nd additions. Adapted from [29].

Isocyanate	Structure	1 st addition	2 nd addition
TDI		702	58
MDI		561	193
HDI		1.8	0.9
IPDI		1.1	0.4
H ₁₂ MDI		1	0.7

2.2.2. Polyol

Since PUF are mainly crosslinked networks and since polyisocyanates are mainly bifunctional,

polyols must present, on average, a functionality (f) higher than 2. Polyol mixes are often used to obtain the suitable requirements. Polyols are usually viscous liquids containing at least two or more hydroxyl (OH) groups per molecule. They are characterized by their OHs density (I_{OH}) expressed in mg KOH/g. Both main types of polyols are oligomers of polyether and polyester with OH ending chains. First, polyethers are produced from the alkoxylation with ethylene (EO) or propylene oxide (PO) from a simple starter molecule containing several OH or amine groups, primary and secondary. The polyol-starters can be pentaerythritol (f=5), sorbitol (f=6) or glycerol (f=3) and the polyamine starters can be ethylenediamine (f=4) or diethylenetriamine (f=5). From the starter to the corresponding oligomer, the I_{OH} is decreased. Similarly, the polyester polyols are produced from controlled polycondensation or polyaddition between a dicarboxylic acid or an anhydride with a polyol-starter molecule. In general, polyether polyols generally present a lower viscosity and higher dispersity than polyester polyols, due to the flexible ether links. They also provide higher softness, hydrolytic and aging stabilities compared to polyester polyols [11].








Table 3
Main requirements on polyols properties for F-PUF and R-PUF. Adapted from [11,31].

PUF type	I_{OH} (mg KOH/g)	Functionality (f)	Molar mass (g/mol)	Viscosity (Pa.s)
Rigid	200-800	2-8	300-1000	2-50
Flexible	15-100	2-3	3000-6500	0.2-20

Polyols properties have a profound impact on the behaviors and structures of the final cellular materials. Polyols for R-PUF have I_{OH} ranging between 350 and 800 mg KOH/g, with between 3 and 8 OH groups per molecule (Table 3). On the contrary, the polyols used for F-PUFs have lower I_{OH} and functionality. The higher the functionality of the polyols is, the higher the crosslinking density and rigidity of the foam should be. As depicted in Table 4, the reactivity toward isocyanate is mainly related to the nature of the H-labile group. The primary and secondary aliphatic amines, generally toxic for human health [42], are 1000 times more reactive than their OH aliphatic counterparts. Water and primary aliphatic OHs have similar reactivities. Then, the reaction of water with

isocyanate formed a primary amine, which reacts immediately due to its high reactivity compared to OH. The urea formed by the addition of the amine and isocyanate is half as reactive as a secondary aliphatic hydroxyl. Therefore, the formation of biuret is generally considered as a source of crosslinking in foams. The aromatic OH, usually found in phenolic resources (e.g., lignin), is around 300 and 1000 times less reactive than secondary and primary aliphatic OHs, respectively. This explains the need to chemically modified polyphenol molecules before their introduction in PUF as shown in a next section.

Table 4
Relative reactivity of hydrogen active compounds without catalyst. Adapted from [31].

Hydrogen active compound	Structure	Uncatalyzed relative reactivity at 25 °C
Primary aliphatic amine	$R-NH_2$	3300
Secondary aliphatic amine	R_1-NH-R	650-1650
Primary aromatic amine		6.5-10
Primary aliphatic OH	$R-CH_2OH$	3.3
Water	$H-O-H$	3.3
Carboxylic acid		1.3
Secondary aliphatic OH		1
Urea		0.5
Tertiary aliphatic OH		0.0017
Phenolic OH		0.003-0.017
Urethane		0.0033

2.2.3. Blowing agent











The choice of the BA is crucial to determine essential properties and morphologies which are related to the applications. Two main types of BA are used: (i) Chemical, where BA reacts with a system component during the polymerization to generate the gas. As presented in Fig. 2, several H-

labile compounds release gas by an exothermic reaction with isocyanates and, e.g., water or formic acid. (ii) Physical BA presents a phase change from liquid to gas during the polymerization using the energy released by the exothermic polyol-polyisocyanate reaction, with a strong and fast volume increase of the mix.

The key parameters of physical BAs are the molar mass, the boiling point, the heat of vaporization and conductivity in the gas phase. They are detailed in Table 5. Firstly, the molar mass of BA is essential for economic reasons. The quantity of gas and, by extension, the foam produced is inversely proportional to the molar mass. Therefore, in a formulation with a fixed mass of BA, the BA with a lower molar mass will generate a higher gas volume [43]. To obtain foams with similar densities starting from the same formulation, a higher amount of, e.g., trichlorofluoromethane (137.4 g/mol) than n-pentane (72.2 g/mol) would be used. Secondly, the boiling point of BAs determines the temperature and then the time when the foam starts to rise. It is the main parameter for the fine-tuning of the foam expansion kinetic. In the case of one component-foam, the BA agent has a propellant role. It is common to use a BA with an ebullition temperature under 0 °C. Thirdly, the heat of vaporization represents the energy needed to phase change a liquid into gas. The quantity of heat released by the PU formation must be controlled to avoid attaining the critical degradation temperature of the PU. The endothermic vaporization of the BA consumes the heat released and decreases the temperature during the polymer formation, preventing degradation. Finally, some BA properties are related to particular applications such as R-PUF for thermal insulation, where the thermal conductivity must be the lowest. The total thermal conductivity is related to the conduction through the polymer matrix, through the gas phase and the radiation. In this case, the gas contribution accounts for 65% of the total thermal conductivity [44,45]. The lower the conductivity in the BA gas phase, the lower the overall conductivity of the foam should be. However, with the foam aging, the BA diffuses out of the cells and it is substituted by air.

Table 5
BA structures, name physical properties and global warming potential (GWP). Data from literature

[43,46–52].

Category	IUPAC name	Commercial name	Structure	Molar mass (g/mol)	Boiling point (°C)	Heat of vaporization (kJ/mol)	Conductivity (at 25 °C) (mW.K ⁻¹ .m ⁻¹)	GWP
Chemical BA	Carbon dioxide	CO ₂	O=C=O	44.0	-78.3	6.8	16.4	1
CFC ¹	Trichlorofluoromethane	CFC-11		137.4	23.8	24.8	7.9	4600
HCFC ²	1,1-dichloro-1-fluoroethane	HCFC-141b		116.9	32.9	25.8	10.0	700
HFC ³	1,1,1,3,3-pentafluoropropane	HFC-245fa		134.1	15.3	26.0	12.5	990
	1,1,1,3,3-pentafluorobutane	HFC-365mfc		148.1	40.2	26.2	11.6	910
HC ⁴	cyclopentane			70.1	49.3	27.3	12.8	11
	n-pentane			72.2	36.2	25.7	15.0	11
	iso-pentane			72.2	27.8	24.6	14.3	11
HFO ⁵	(Z)-1,1,1,4,4,4-hexafluorobut-2-ene	HFO-1336mzz (Z)		164.1	33.5	24.8	10.7	2
HCFO ⁶	(Z)-1-chloro-2,3,3,3-tetrafluoroprop-1-ene	HCFO-1224yd		148.5	14.6	21.6	9.1	1
	(E)-1-chloro-3,3,3-trifluoroprop-1-ene	HCFO-1233zd		130.5	18.3	22.3	10.2	7
Air							26.0	

¹ Chlorofluorocarbon, ² Hydrochlorofluorocarbon, ³ Hydrofluorocarbon, ⁴ Hydrocarbon, ⁵ Hydrofluoroolefin, ⁶ Hydrochlorofluoroolefin.

Historically, water was the only BA used until the 1950s and remains the primary chemical BA used today in F-PUFs. Foams developed only with water as BA faced several challenges: (i) high exothermic reaction causing scorching or fire, (ii) reduced flowability in mold due to higher viscosity, (iii) higher cost because water-blown foams consume more isocyanates. The water-blown R-PUF has high surface friability, high thermal conductivity, and poor dimensional stability. Furthermore, the higher amount of heat released by the urea induces a faster expansion of the foam. In consequence, some cell walls can be broken.

The development of the physical BA from 1970 to nowadays was conditioned by environmental concerns. The Montreal in 1987 and Kyoto in 1992 protocols banned chlorofluorocarbons, hydrofluorocarbons, and hydrochlorofluorocarbons due to their high ozone

depletion activities [53,54]. Indicators to measure the impact of a molecule on the environment, such as the ozone depletion potential, were implemented, i.e., the Global warming potential (GWP).

Despite the ongoing utilization of forbidden substances by international protocols, the research turns toward new BAs more environmentally friendly such as hydrocarbons, hydrofluoroolefins or hydrochlorofluoroolefins (Table 5) [49,55].

2.2.4. Surfactant

Fine and homogeneous cell structure cannot be obtained without surfactants. Fig. 5 details the principal surfactant structures used in PUFs formulation. The block and graft amphiphilic copolymers are based on hydrophobic siloxane groups and hydrophilic polyether grafted chains. The polyether/siloxane ratio, the EO unit content, the capping group (CAP in Fig. 5), the molar mass and the molecular architecture of the surfactant can be finely tuned to fit with the different polyols-BAs systems [56].

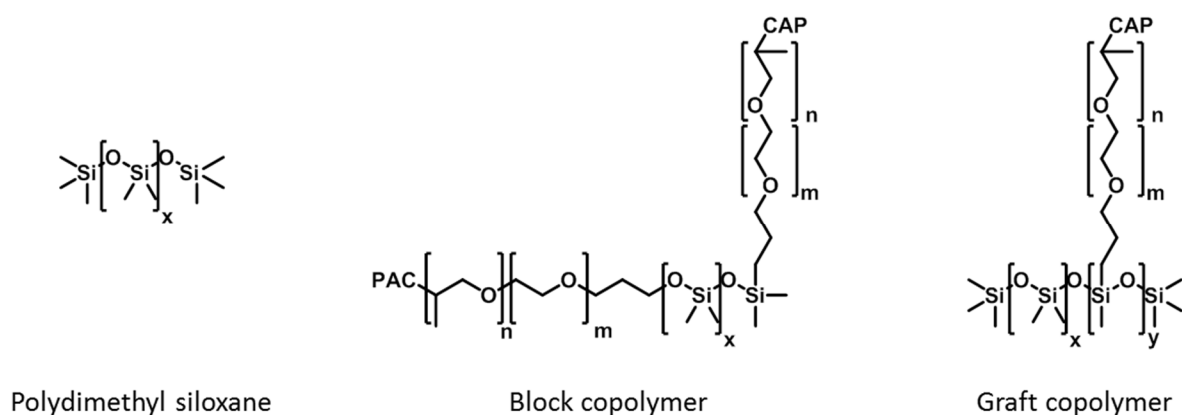


Fig. 5. Representation of silicone surfactant. Adapted from [57].

The surfactant has two main roles in the cell formation process: (i) the emulsification of the reagents and (ii) the stabilization of the formation of the bubbles [58]. Firstly, before the polyaddition starts, surfactants participate in the emulsification of the BA and the air in the monomers mixture, by

reduction of the surface tension [56]. Placed at the BA-polyol interfaces, the surfactant increases their miscibility and reduces the emulsion particle size. It was demonstrated that lower surface tension leads to higher bubble density in the A-part and, consequently, finer cell structure in the final foam [59].

The second role of the surfactant is the stabilization of the growing cells, along with the polymerization and foaming process. The cell growth is disrupted by two phenomena described in the left part of Fig. 6: (i) the Ostwald ripening and (ii) the cell drainage. The Ostwald ripening is controlled by the pressure difference between large and small bubbles. To equilibrate the pressure, the gas in small bubbles transfer into the larger ones (Fig. 6), and the exchange rate depends on the permeability of the cell walls [60]. As shown in Fig. 6, this phenomenon tends to decrease the bubble density and to form coarser cells if not controlled. Surfactant molecules aggregated at the surface between air and foaming liquid limit the Ostwald ripening (Fig. 6). The surfactant packing increases the permeability of the cell walls. Therefore, by limiting the gas transfer between two cells, a homogeneous cell structure is formed [56].

On the other side, cell drainage is governed by the pressure difference and the viscosity of the liquid phase [61]. Spherical bubbles collide when the gas volume fraction exceeds 70-75%, and distort into a multisided polyhedral [59]. The interface between two bubbles is described in the left bottom of Fig. 6. The liquid between two expanding bubbles is forced, due to capillary pressures, to flow toward the exterior forming the Plateau border and a thin film between bubbles. Once the polymerization is completed, the thin film between two cells is called cell wall, and the Plateau border is named cell strut (Fig. 6). Without surfactant, as shown in Fig. 6, the bubbles are open. The foam collapses if the cells are open too early in the foaming process.

The bubble expansion causes a gradient of surfactant concentration at the surface, as shown in Fig. 6. However, this surface tension gradient produces an antagonist effect on the film drainage, called the Marangoni effect. As shown in Fig. 6, surfactant molecules flow from the high to the low surfactant concentration to equally distribute the surfactant molecules at the interface. In this

motion, surfactant drags along foaming liquid and delays the cell opening [62]. The transport rate from the bulk phase to the interphase and the absorption-desorption kinetics of the surfactant affects the efficiency against drainage [63,64]. The cell drainage is fast without control, causing film ruptures, bubble coalescences, and very dense foams. In F-PUF formulations, cell rupture is wanted, and the surfactant controls the stage of cell opening. On the contrary, in R-PUF, the surfactant controls the film drainage to obtain closed cells.

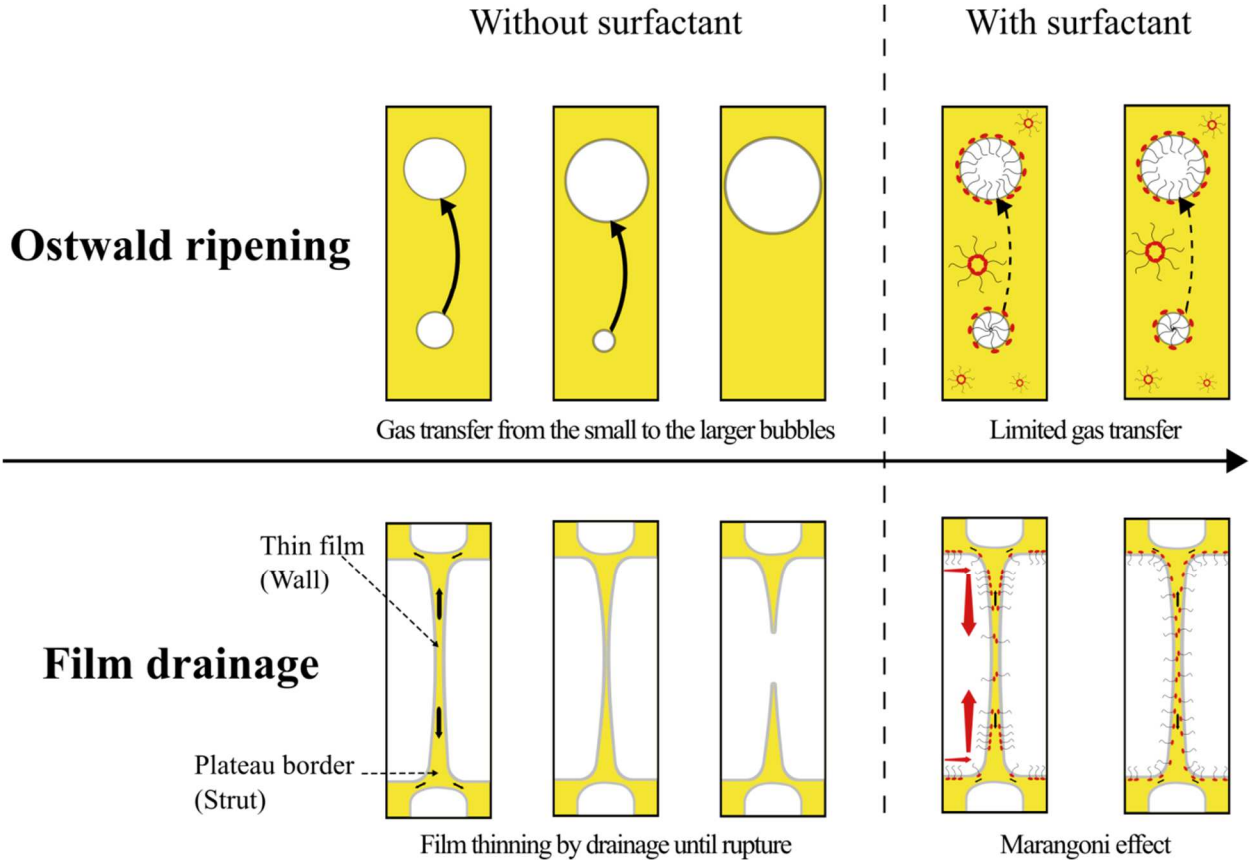


Fig. 6. Illustration of the significant perturbations in foam cell formation, with or without surfactant.

The surfactant has critical roles in the formation and expansion of bubbles and, by extension, the properties of the material. The surfactant quantity is optimized to obtain a good performance-price compromise. There were extensive researches to find the optimized quantity of surfactants to obtain the higher mechanical, thermal and morphological properties [65–67]. Between 1 and 1.5 pbw of the polyol are used in F-PUFs to control cell expansion and promote the cell opening.

However, too low quantity promotes collapsing, densification and splits of the foams [68]. On the contrary, higher quantities are used in R-PUFs to obtain closed-cell structures. The average amount of surfactant used is between 1 and 3 pbw of the polyol (Table 1).

2.2.5. Catalyst

The main catalytic mechanisms for the PU formation described in the literature follow mainly two potential pathways: (i) The increase of the carbon electrophile character of the isocyanate group or (ii) the increase of the nucleophile character of the H-labile compound [69]. In order to control the reaction kinetics, different catalysts presented in Fig. 7 can be used. Catalysts activities can favor the urethane network formation (gelling) or the generation of gas generally via the water-isocyanate reaction (blowing) [70]. The tin salts, i.e., stannous octoate and dibutyltin dilaurate, have higher gelling activity compared to hindered amine such as 1,4-diazabicyclo [2,2,2]octane (DABCO). The dibenzylamine, tetramethylethylenediamine and N,N-dimethylcyclohexanamine (Fig. 7), which are less hindered tertiary amines than DABCO, are classified as balanced catalyst because they promote both gelling and blowing reactions. Catalysts containing ether bonds close to the tertiary amine group such as 2,2' dimorpholinodiethylether or 2,2'-oxybis (N,N-dimethylethan-1-amine) promote the blowing reactions. The carboxylate-potassium salts for PIR foams favor the trimerization that actively participates in the molecular crosslinking. Therefore, they are ranked in the gelling activities of Fig. 7.

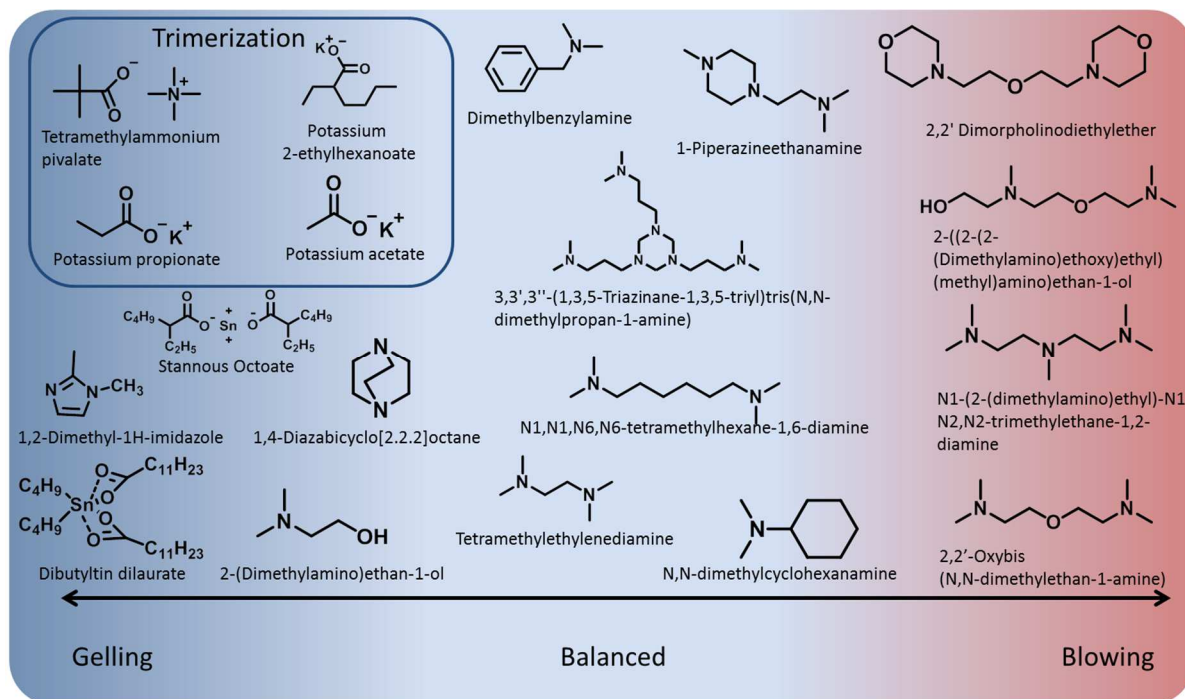


Fig. 7. Catalysts structures ranked according to their main activities in the foam formulation. Adapted from [70].

The PUF catalysts are trapped inside the polymer matrix and released over time. Therefore, a new generation of catalysts is designed with an H-labile group in their chemical structures to react with isocyanate and be part of the polymer network, to avoid a catalyst release. However, to obtain similar foaming kinetics, the catalyst loading tends to be higher due to the decreased catalytic activity linked to the loss of mobility.

In any case, the catalyst role is to equilibrate the blowing and gelling reaction to get the optimal foam. In the case of a fast gelling compared to the blowing reactions, the polymer gels faster and thus, the cells would not expand to the optimum volume [71]. Therefore, the density increase and all the properties related will be affected. On the contrary, a slow gelling produces a lower viscosity when the cells expand. In this case, the emulsion is destabilized. The gas blows the cell and the polymer gels later with big open cells [72].

2.2.6. Other additives

A large range of additives is used on PUF formulations. Additives such as FRs, dyes, pigments, or fillers can be, for instance, added. As inert additive or reactive systems, FRs are used in PUFs. Inert additives are directly added during the formulation. They are mainly composed of halogen or phosphorous compounds, although melamine, aluminum trihydrate and magnesium hydroxide may also be used [73]. Reactive systems are based on active groups that are chemically linked to the PUF network [73], which are based on bromine or phosphorous atoms. Besides, more thermally stable groups can be introduced in the polymer network, such as isocyanurate, uretdione or carbodiimide [74].

PU can also be formulated with macro or nano-fillers to improve the mechanical properties, the fire resistance or the nucleation during the foaming steps. This specific domain was recently reviewed [27,75] and will not be further detailed in this review.

2.2.7. Evolution of the cells morphology during the PUF processing

Foam expansions are monitored by three characteristic times taken along the foam elaboration process. First of all, the cream time is defined as the moment where the foam changes color and starts rising. Secondly, the gel time related to the formation of the polymer network (gelation of the polymer) is usually determined when the formation of a continuous film or a fine string between the foam and a wooden stick occurs. The foam will continue to cure and reach the tack-free time when the surface of the foam will no longer have tacking properties. For a standard PUF formulation, the characteristic times are, for instance, 2-20 sec, 10-100 sec and 15-300 sec for the cream, gel and tack-free time, respectively.

The foam development was followed by instrumented setups, which record the foam height, the temperature, the pressure inside the mold and the dielectric polarization constant over time. Equivalent characteristic times are determined from the corresponding-measured parameters. The cream time is characterized as when the foam reaches 15% of the maximum expansion rate.

Furthermore, 15% of the pressure derivative is defined as the gel time. Additional characteristic times are designated, such as the rise time when the 95-98% of the height is reached or the curing time when the dielectric polarization value is under 10% of the peak maximum. This curing time indicates the surface curing; the total curing time is proportional to the foam size. Generally, between 2 and 7 days at ambient temperature are sufficient.

Fig. 8 shows the different phases of the cell morphology evolution correlated with the temperature and viscosity evolution over time. Phase 1 is the mixing of the A-part before the start of the polymerization. Phase 2 is the cell nucleation where two theories are in competition, or can also be concomitant. First, the classical theory of nucleation is based on the generation of cells from BA droplets after dispersion. A microphases dispersion of BA in polyols is obtained due to the BA low miscibility into polyol. The high-speed stirring splits the dispersed bubbles until an equilibrium is reached. These small bubbles are expanded to form the final cells when the polyaddition can start [76]. A more recent theory is based on the effect of air pockets entrapped during the mixing stage (phase 1 in Fig. 8) [77]. In this case, the BA migrates through the matrix into the air bubbles during the expansion.

The phase 2 in Fig. 8 (expansion of the bubble) is controlled by the temperature and the viscosity of the mix. These two parameters are related to the kinetics of gelling and blowing steps and can be controlled by the catalyst. The temperature increase shown in Fig. 8 comes from the exothermic polyaddition of isocyanate with water and polyol. The temperature increase is caused by a small portion of water that rapidly reacts and releases twice more heat than the reaction with an hydroxyl. After the cream time, a slight increase in temperature is enough to make the gas bubbles to expand. The bubble expansion is followed by a viscosity increase shown in Fig. 8 since the bubbles act as thickener [78].

The immediate drop in viscosity after the expansion of the cell around 60 seconds in Fig. 8 is related to the thermal thinning of the reacting polymer. This drop in viscosity is beneficial for the cell expansion that starts to come into contact, forming the film, as shown in phase 4 of Fig. 8. The

temperature stabilizes after 70-80 seconds inside the foam because of the increased viscosity and thermal insulating material property of the foam (Fig. 8). The increased concentration of urea groups formed by the reaction between isocyanate and water is responsible for a second viscosity rise. Urea groups strongly H-bond together and form hard domains in the polymer matrix, acting as reticulation points [78]. The next drop-in viscosity shown in Fig. 8 around 100 seconds is explained by the delay between hard segments formation and gelation of the urethane network. As explained in a previous Section, the cell wall drained by pressure difference is held by the surfactant until the network gelation occurs (phase 5 in Fig. 8). The drop in viscosity is beneficial for the film breakage if the gelation of the network is too slow. Finally, the polyol reaction conversion with polyisocyanate reaches the gelation point, and the viscosity becomes infinite. The network gelation fixes the cell morphology of the foam.

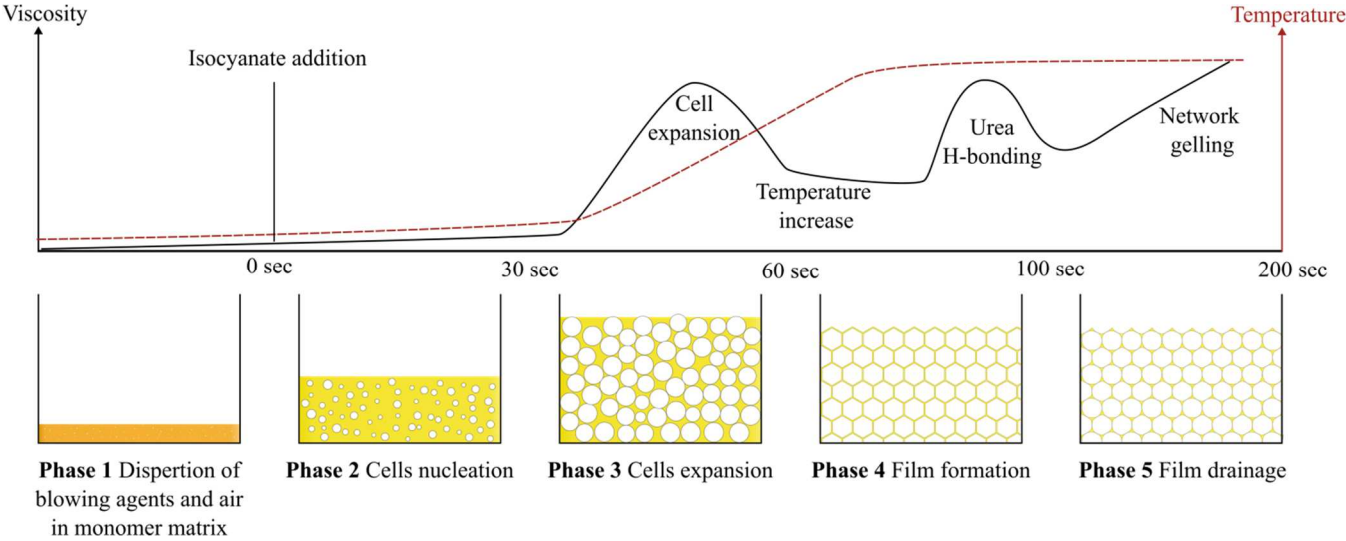


Fig. 8. Viscosity profile associated to the cell bubbles formation.

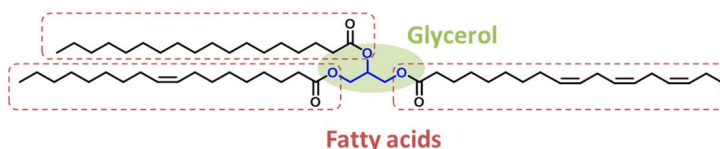
The profiles of temperature and viscosity in Fig. 8 present a general case. Nevertheless, it can differ. For example, in PIR foams, catalysts for the trimerization are thermally activated [79]. Therefore, the viscosity profile changes due to the additional reticulation points formed by the trimerization. Furthermore, in F-PUF, the drainage of the cell walls is controlled until the film rupture to produce open-cell.

3. From renewable sources to biobased components for PUF

This chapter describes the different strategies recently developed to obtain the different renewable components to produce biobased PUFs from a large range of biomass, mainly from lipids, carbohydrates, polyphenols (lignins and tannins), and different others molecules from biorefinery obtained by biochemistry process, for instance. To a lesser extent than the polyols, the amines are used as raw materials in PU chemistry, either in the synthesis of polyureas or, in the case of low molar mass polyamines, as polyether polyol starters. As the production of biobased amines was recently reviewed [80,81], the amines will not be incorporated in this review.

The biorefinery converts the biomass into different outputs such as fuels, energy, food, feed and/or chemicals through jointly applied conversion technology [82]. Biorefineries are classified according to different and successive generations depending on their feedstocks. The first generation consumes edible crops such as starch, for instance. The second generation uses industrial residues and non-edible crops such as lignocellulosic compounds from wood, without food competition. Finally, the third one is based on algae and microalgae without arable land uses [83]. The utilization of different biological systems, i.e., enzymes, cell extracts or whole microorganisms (biotechnology), is increasingly integrated into the biorefinery conversion processes. The development of white biotechnology, defined as the industrial production of chemicals, increases the availability of biobased building blocks, e.g., for PUFs synthesis [84]. The association between chemistry and biochemistry, also know as the chem-biotech approach, drives the evolution in the production of these renewable building blocks.

3.1. Lipids: Triglycerides and fatty acids



Name	Structure	Abbreviation
Caprylic		C8:0
Capric		C10:0
Lauric		C12:0
Myristic		C14:0
Palmitic		C16:0
Palmitoleic		C16:1
Stearic		C18:0
Oleic		C18:1
Linoleic		C18:2
Linolenic		C18:3
Ricinoleic		12-OH C18:1
Vernolic		12-epoxy C18:1
Docosapentaenoic		C22:5
Docosahexanoic		C22:6

Fig. 9. Triglyceride structure and the most abundant fatty acids in vegetables, seeds and microalgae oil.

Lipids are extracted from natural resources such as vegetables, seeds or micro-algae. They are composed of triglycerides, which can be decomposed in glycerol and three fatty acids per molecule, as shown in Fig. 9. On the contrary to plants oil, microalgae do not compete with food nor need arable land to grow [85,86]. They are an interesting source of lipids due to a higher average length and a higher number of double bonds per fatty acid.

The diversity in fatty acids presented in Fig. 9 relies on the chain length (mainly till 24 carbons), position, configuration and types of unsaturation and additional substituents such as epoxide or hydroxyl groups along the aliphatic chain [87]. The diversity of fatty acids distribution of lipids, which are species and growing conditions dependent, was used to develop various PU macromolecular architectures.

Taking into account the literature and the different previous reviews on this field [88–93], the main highlights of this state of the art are mainly based on recent publications on the transformation

of lipids into polyols, isocyanate or additives used in foam formulations. Esters and double bonds are the starting point of the oleochemistry described in Fig. 10 to access to different PUF components.

Fig. 10 shows the diversity of the oleochemistry with different pathways to obtain polyols. The particular case of castor oil, which contains an OH group, is described in the synthesis of an additive. The epoxidation and further ring-opening are the main transformations and were used to produce both polyols and additives.

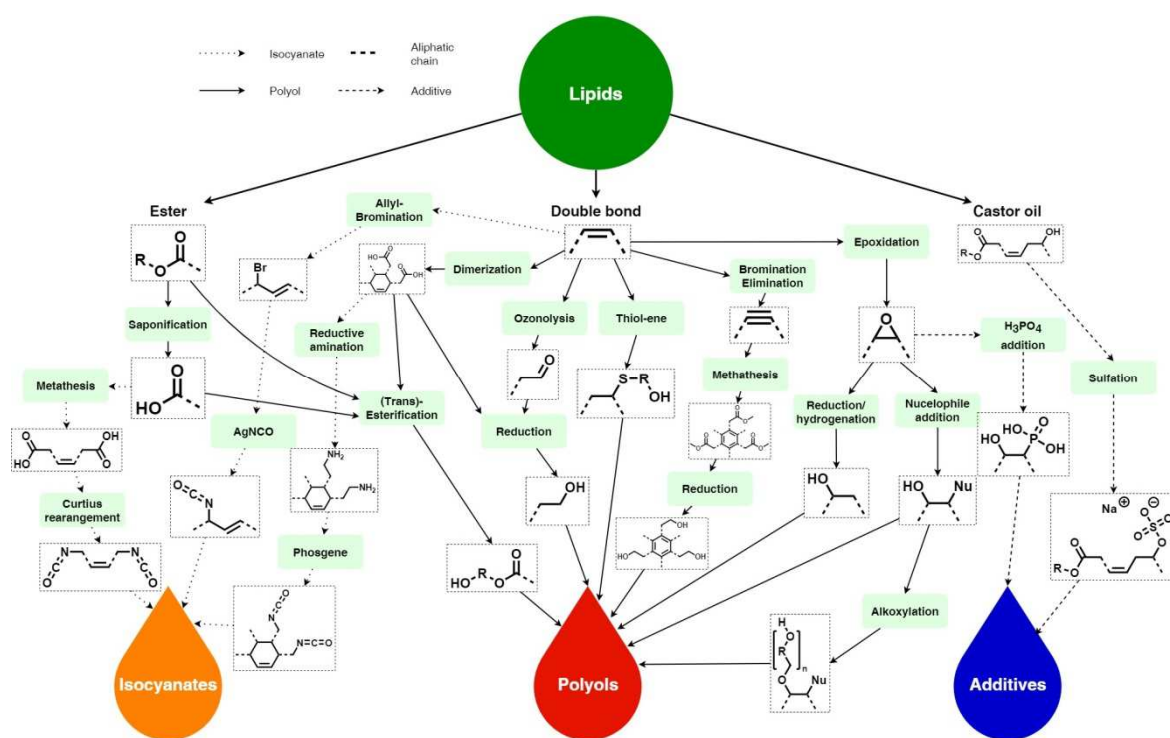


Fig. 10. Overview of the main oleochemistry pathways for the elaboration of different PUF components.

3.1.1. Polyols

Polyols are the main PUF components elaborated from fatty acid, even at an industrial scale.

In this way, different approaches have been recently developed.

3.1.1.1. Epoxidation and ring-opening

The formation of epoxide is one of the most investigated ways to obtain polyols via double

bonds modification. OH groups can be obtained in two steps from the double bonds with the epoxidation and the subsequent ring-opening synthesis. The electrophilic nature of the strained three-membered ring epoxide facilitates the nucleophilic attack to afford a beta-substituted OH group [94]. Among the large variety of nucleophile used for ring-opening reaction, mono-alcohols [95–99], diols [100–106], and carboxylic acids [98,101,103,107–109] were the most investigated. Weaker nucleophiles such as amines [110–112], water [99,113] or thiols [114] were also studied, but the ring-opening reaction was found to be slower. Nevertheless, polyols produced by ring-opening with secondary amines were demonstrated to have catalytic activity [98,115]. Efficient ring-opening nucleophiles rarely investigated are the hydrogen halides [98,116], even if they are used to quantitate epoxide groups on lipids since 1956 [117].

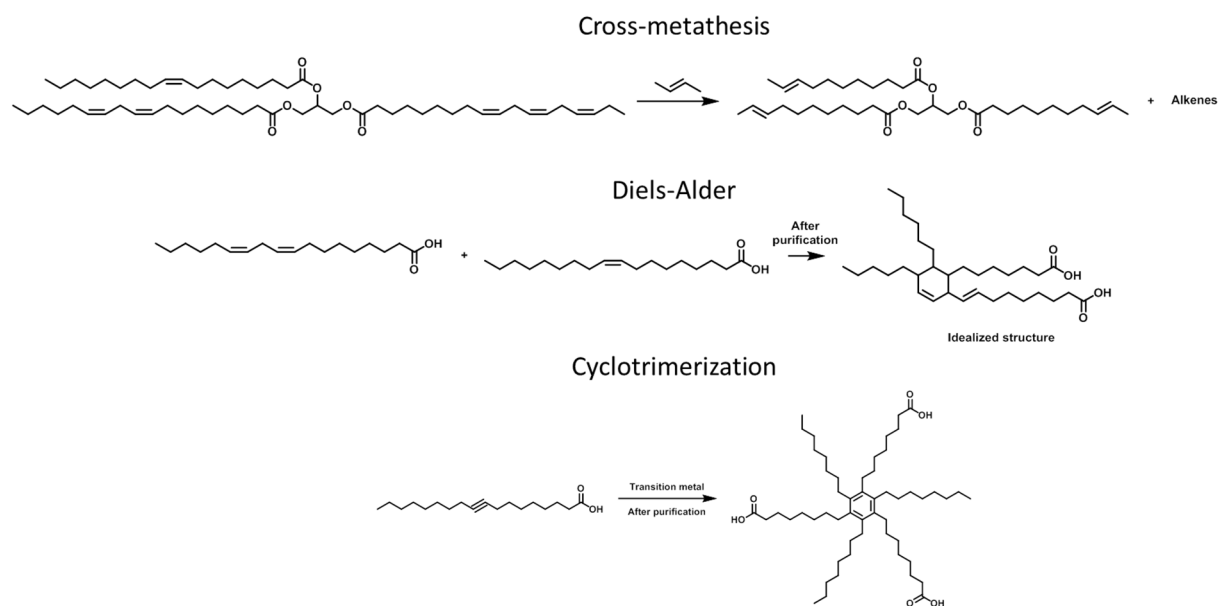
The secondary OH group was also formed by the reduction of the epoxide group with H₂ and Nickel of Raney [88,116,118]. Unfortunately, the method developed used an alkaline medium, which broke the ester, thus the triglyceride structure.

3.1.1.2. Miscellaneous double bond transformations

A recent trend in the modification of unsaturated triglyceride is the use of the “click” thiol-ene reaction where the double bond is transformed into thioether by radical addition of thiol under UV radiation. The mercaptoethanol was used to produced polyols for PUFs with castor, soybean or corn oil with high selectivity [119–121].

The cross-metathesis described in Scheme 2 is a reaction between the triglyceride double bond and an olefin yielding shorter monounsaturated fatty acid chains. The alkenes side products are hydrogenated to be suitable for diesel or jet propellant [122,123]. The previously developed double bond modification methods can be used to obtain polyols [124]. Another way to modify fatty acids is the 2+2 cycloaddition of oleic acid, and linoleic acid yields various six-membered cyclic diacids with long dangling chains, such as the theoretical structure shown in Scheme 2. OH groups can be introduced on this molecule by reduction or esterification of the carboxylic acid groups [125]. Oleon

and Croda developed diols based on the dimerization of fatty acids. As shown in Scheme 2, the cyclotrimerization of oleic acid was used to transform the flexible fatty acid chains into an aromatic core with dangling chains bearing carboxylic acids [126].



Scheme 2. Metathesis and cyclization reactions.

The ozonolysis of the double bonds of triglycerides was investigated on several substrates such as canola oil, soybean or trioline [127,128]. This reaction reduces the chain length of the fatty acid, sets the functionality at three and forms primary OH group.

3.1.1.3. Ester modifications

To obtain polyols, ester modification chemistry is largely less developed than the double bonds modification. There are only two possible pathways, such as (i) the transesterification of oil and (ii) the saponification of the ester, followed by esterification with a small polyol. The first method was extensively applied to castor oil due to the high content in ricinoleic fatty acid. The transesterification of castor oil was investigated with glycerol [129–132], ethylene glycol (EG) [133] or triethanolamine [131,133]. An acceleration was noted in the urethane formation kinetic with the

hydroxy ketone group due to the activation of the OH group via hydrogen bonding assistance [134]. The transesterification method was also applied to rapeseed [135], soybean [99], coconut [136] or andiroba oil [137].

The second method comprises one more step, but the polyols produced have higher molar masses compared to the transesterification method. As an example, the glycerol monostearate was oligomerized with glutaric acid and yield a polyol with an average molar mass superior to 3000 g/mol and thus a low I_{OH} [138]. The esterification consumes OH groups, which could be used in PU networks formation, to form ester bond; therefore, the ester formation reduces the I_{OH} . To avoid the reduction of I_{OH} , a polyol was produced by esterification of polymerized glycerol with castor oil fatty acid that contains an OH. In this particular case, the obtained polyols had an I_{OH} depending on the esterification time, around 550 mg KOH/g, suitable for PUFs synthesis [139,140].

3.1.2. Polyisocyanate

The most known diisocyanate produced from oleochemistry is the 2-Heptyl-3,4-bis(9-isocyanatononyl)-1-pentylcyclohexane, commercialized by Cognis-BASF under the name DDI1410. This biobased isocyanate was used in thermoplastic [141] or thermoset PU materials [142–144].

Other polyisocyanates were produced at a lower scale. Firstly, a dimer of oleic acid obtains by self-metathesis was transformed into diisocyanate by Curtius rearrangement [145]. Secondly, sebacic acid and undecylenic acid derived from castor oil by alkali fusion and pyrolysis, respectively, were also transformed in diisocyanate via Curtius rearrangement [146]. Thirdly, soybean oil was transformed by allylic bromination with N-bromosuccinimide, followed by substitution with silver isocyanate salt [147]. This is the only report of polyisocyanates ($f > 2$) derived from lipids resources.

3.1.3. Some additives

3.1.3.1. Surfactant

Similarly to surfactant, lipids are constituted of long aliphatic and hydrophobic chains and a polar core with the ester groups. Linseed oil has been recently used as a renewable modifier in PUFs. Mechanical and thermal properties improvement has been reported in PUFs containing linseed oil as a unique surfactant [148]. The sodium sulforicinate obtained by sulfation of castor oil dispersed in water was used in foam formulations, both as BA and surfactant [149].

3.1.3.2. FR

The modification of the lipids double bonds to enhance the thermal stability was achieved through the epoxidation and ring-opening process with phosphoric acid. The phosphorous compounds are known for their fire-retardant properties, especially in PUFs [150]. Another strategy based on fatty acid as a modifier for a well-known FR: the 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) can be applied. The synthesis procedure introduced the terminal fatty reactive epoxide group on the DOPO molecule [151]. With this modification, the labile FR molecule is then attached to the polymer network.

3.2. Carbohydrates

Initially, carbohydrates were defined as molecules exclusively composed of carbon, oxygen and hydrogen atoms following the formula $C_n(H_2O)_n$ [152]. However, the definition was enlarged to encounter the reduced, oxidized and heteroatoms (sulfur or nitrogen) containing molecules [153]. Carbohydrates are divided into two categories: (i) the monosaccharides composed of C5 or C6 molecules and numerous OH groups such as the sorbitol, sucrose and lactitol (Fig. 11). (ii) The polysaccharides obtained by condensation of monosaccharide building blocks, i.e., starch and chitosan (Fig. 11) [154]. The polysaccharides with a high molar mass such as starch, neat chitin or de-acetylated chitin (chitosan) are largely used for polymers synthesis [155–157].

The different pathways from carbohydrates (mono, di and long polysaccharides) to PUF components are described in Fig. 11. The esterification and the alkoxylation are the two main pathways for transforming mono, di and polysaccharides into polyols. The chitosan was slightly modified to be introduced as additives in PUFs. The isosorbide obtained from sorbitol was a platform for the biobased diisocyanates synthesis.

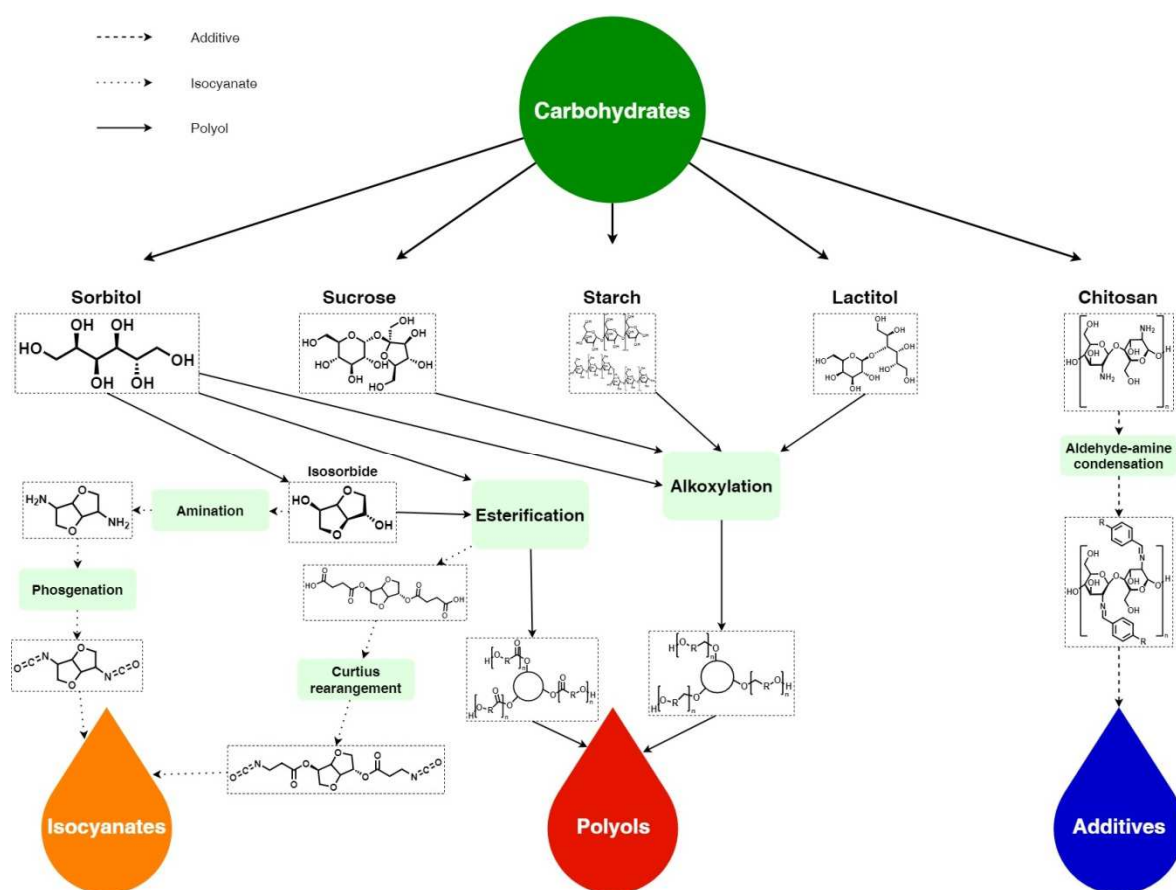


Fig. 11. Overview of the transformation of main carbohydrates into different PUF components.

3.2.1. Polyols

The carbohydrates are multi-OH compounds that are of great interest to produce polyols for PUFs formulation. Unfortunately, most of the carbohydrates are solids at ambient temperature, so impossible to use without modification. Several strategies were developed to modify the carbohydrates to produce adequate polyols for PUFs.

3.2.1.1. Alkoxylation

The first strategy, commonly called alkoxylation, is based on the anionic ring-opening polymerization (ROP) of epoxides. This reaction initiated by small polyols (starters) forms polyether chains ended by OHs. The reaction product has a higher molar mass and the same functionality in OH as the starter. It was early shown that the alkoxylation of monosaccharides produced polyols with suitable properties for PUFs. BASF was the first company to patent PUFs based on alkoxyated carbohydrates [158,159]. The alkoxylation was successfully applied to sucrose [160], lactitol [161], starch [162], sorbitol [163,164] and reduced lactose [165] to produce PUFs.

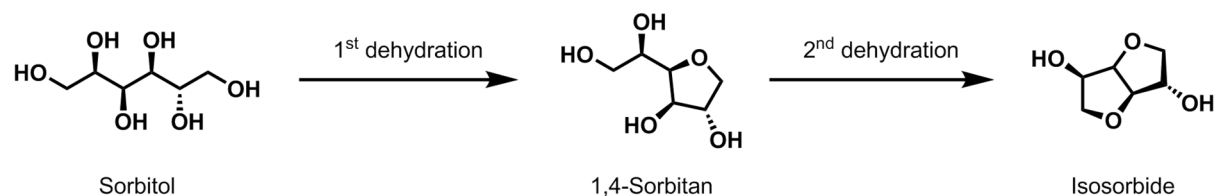
The major drawback of this reaction is the production of the epoxide reagents. 33 million tons of small epoxides such as EO, PO or, to a lesser extent, butylene oxide used for the alkoxylation are mainly fossil-based [166]. However, epoxides could be bio-derived from ethanol, butanol or glucose, in a greener way [167–169].

3.2.1.2. Esterification

Similarly to alkoxylation, the oligo-esterification increases the molar mass of monosaccharides with a reduction of the melting point and I_{OH} . For example, sorbitol esterification was realized in one step with adipic acid and dioctanol mediated by enzymatic catalysis [170]. Polyester polyols from sorbitol, adipic acid and diols with various chain lengths produced in two steps were also reported [171]. The resulting polyols based on two primary and four secondary OH groups were added in PUF and PU-PIR foams formulations [172,173].

The sorbitol was also transformed through dehydration, as described in Scheme 3, to form isosorbide. This product, commercialized by, e.g., Roquette (France), raised much interest due to the bicyclic rigid structure [174]. Suitable polyols for the PUFs industry were also obtained by esterification with fatty acid dimers [175]. The combinations between the rigidity of the isosorbide and the flexibility of fatty acids are an exciting way to obtain new properties. Neat Isosorbide was

also directly added in PUFs with reduced thermal reversibility of the urethane bond [176]. This reversibility at low temperatures was exploited to weaken the modulus of polymer located in the fragile thin wall. A decreased modulus combined with the heat increased the open-cell content.



Scheme 3. Isosorbide production pathway from sorbitol.

3.2.1.3. Miscellaneous transformations

Neat carbohydrates were used in the PU system in a pre-polymerization step with a default of diisocyanates [177,178] or as crosslinkers [179,180]. Furthermore, the integration of chitosans of different molar masses into a PUF formulation was tested with a higher reaction yield of chitosans with low molar masses [181].

3.2.2. Polyisocyanate

The too numerous OH groups of the carbohydrates limit the transformation into isocyanates. Therefore, the isosorbide was a molecule of choice due to its two OHs and their transformation into isocyanate groups was achieved through a traditional amination-phosgenation route [182]. Another strategy was applied with succinic anhydride to form acid pending groups on isosorbide. The isocyanate groups were then formed by Curtius rearrangement [183].

3.2.3. Additives

Chitosan was introduced in PU formulations with phosphate derivatives to improve the char layer formation and the FR properties [184,185]. Furthermore, with the same goal, carbohydrates were modified with an alkyl chain to improve the mixing with the PUF components [186]. The

synthesis of phosphorous-containing polyols with FR properties was achieved by the esterification of sorbitol and sucrose derivatives with dialkyl phosphonopropionate [187] or the treatment of propoxylated starch with polyphosphoric acid [188].

3.3. Polyphenols (Lignins and tannins)

Lignocellulosic resources presented in Fig. 12 are primarily composed of cellulose (40-60%), hemicellulose (25-35%) and lignins (15-30%). Terpenes, alkaloids, or tannins are also accumulated by plants. Polyphenols such as lignins and tannins are then abundant. They are the first and second most abundant sources of aromatic biomolecules on earth, with an estimated worldwide production of 50 and 0.16 million tons per year, respectively [189,190].

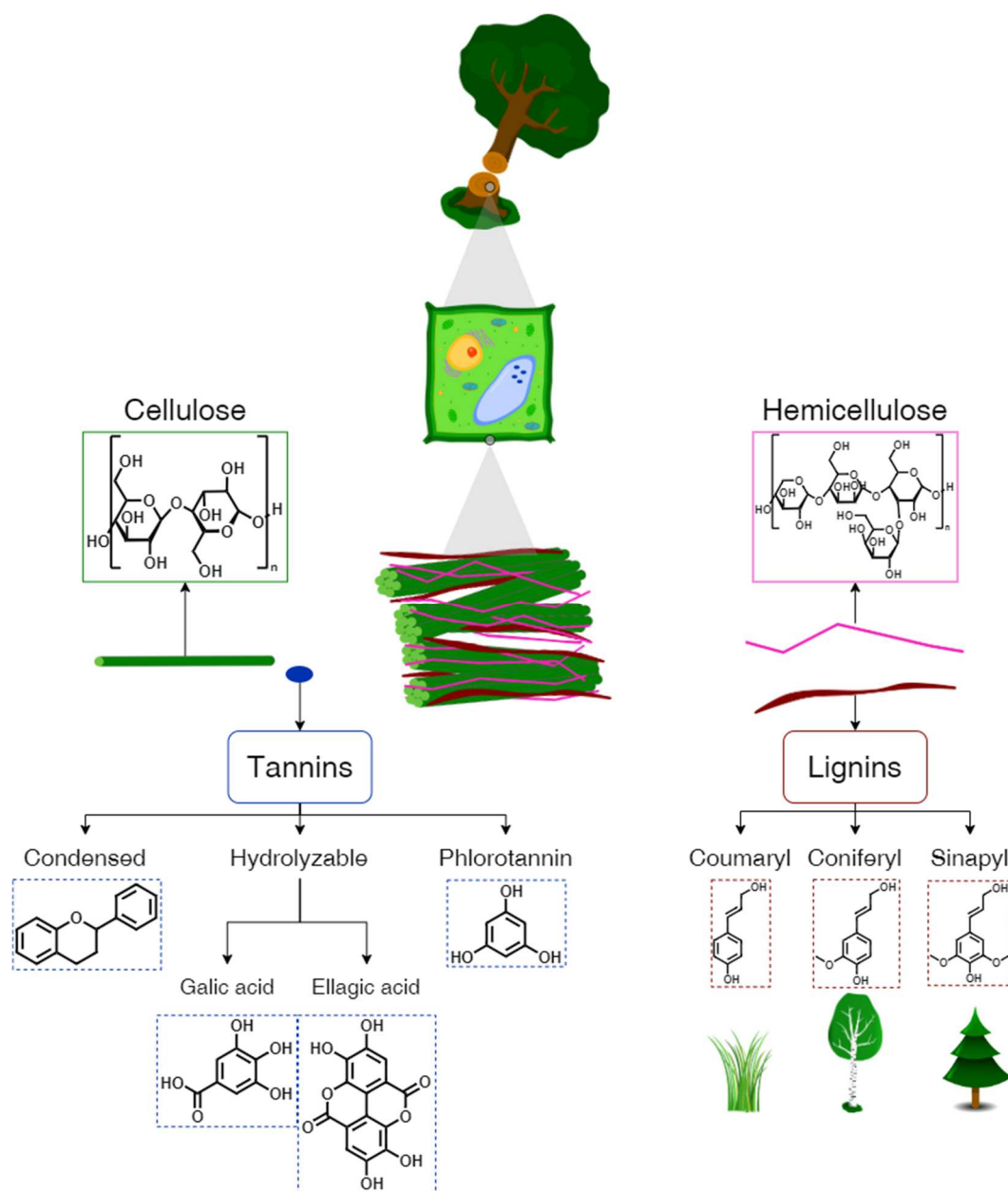


Fig. 12. Composition of lignocellulosic resources and classification of main polyphenols: tannins and lignins. Adapted from [191].

Lignins can be defined as amorphous polyphenolic materials arising from an enzyme-mediated dehydrogenative polymerization of three monolignols: coumaryl, coniferyl and sinapyl alcohols (Fig. 12) [192]. In softwood such as spruce, the lignin is primarily composed of coniferyl alcohol, while in hardwood (e.g., birch), the coniferyl and sinapyl monolignols are dominant. The coumaryl alcohol is mostly found in compression woods or grasses. It is mainly extracted from lignocellulosic resources through various processes (e.g., kraft, sulfite, solvent or soda pulping). Until

recently, the lignin was considered as a waste by-product of the paper and ethanol/fuel industries and burned for power and heat generation (black liquor) [189].

Tannins are polyphenols defined as soluble compounds with a molar mass between 500 and 3000 g/mol or by their ability to precipitate protein. They present particular chemical and biological activities [193]. On the contrary to lignin, tannins are found in soft tissues and play a vital role, such as the defense against mushrooms or insects [194]. The main categories of tannins presented in Fig. 12 are the condensed tannins based on flavonoids structure, the hydrolyzable tannins composed of gallic esters derivatives and the phlorotannins [195].

Lignins and tannins chemical structures depend mainly on the extraction methods, botanical sources, locations, and seasons. Nevertheless, for both resources, phenol, aliphatic OH and carboxylic acid are the primary chemical groups available for transformation. The chemical transformation of lignins and tannins has been extensively reviewed [190,196–199]. Main modifications are summarized in Fig. 13 with a focus on the modifications for PUFs fabrication. The polyphenols sources were mainly divided into lignin and tannin structures. The liquefaction is one of the main pathways to obtain polyols from lignins, tannins or natural polyphenols sources. As shown in Fig. 13, the aromatic structure of tannin was investigated to produce additives.

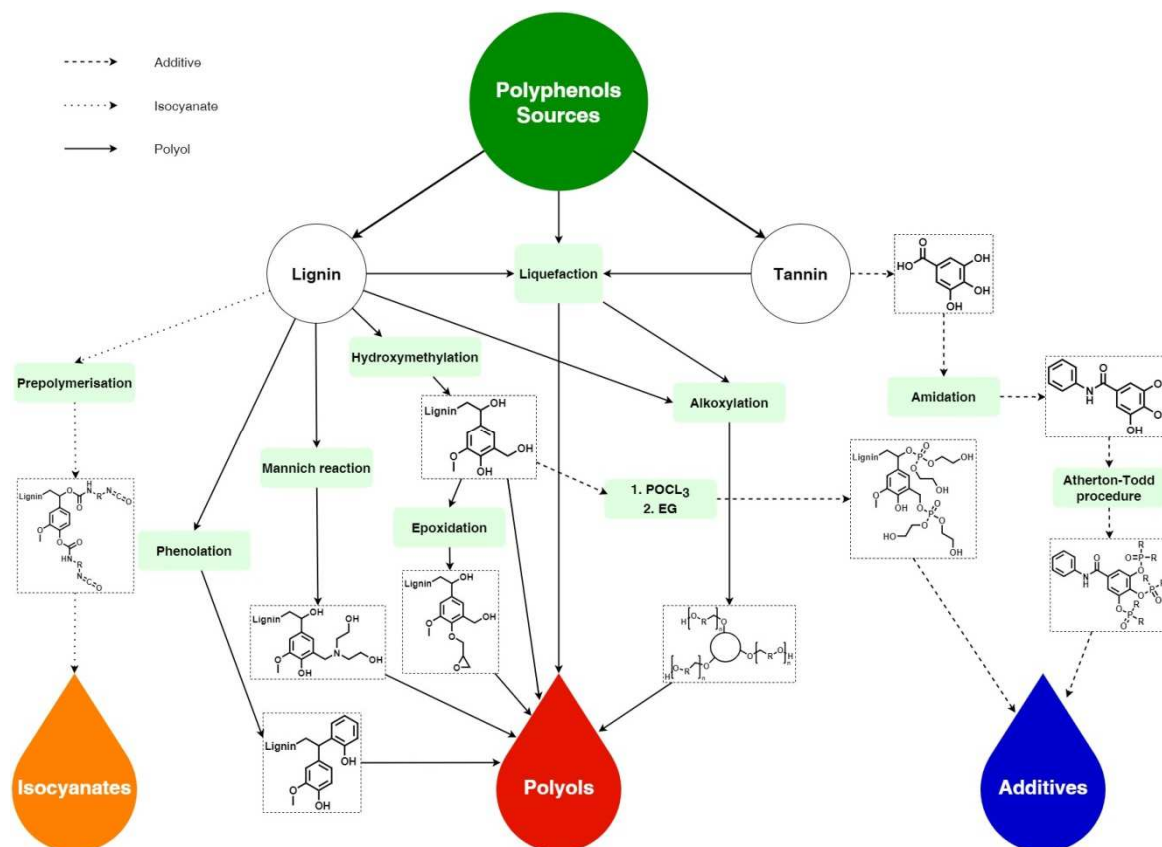


Fig. 13. Overview of the transformation of lignins and tannins into PUF components.

3.3.1. Development of aromatic polyols

3.3.1.1. Liquefaction

As described in Fig. 12, the plant cell walls are primarily composed of cellulose, hemicellulose and lignin. The solvolysis of this biomass in harsh conditions is called the liquefaction process and was recently reviewed [200–202]. This process was applied to produce polyols with lignins [203–208], woods [209–211], barks [212,213], celluloses [214] or wattle tannins [215]. Furthermore, the direct hydrolysis of lignin with water under strong alkali conditions was investigated and afforded suitable polyols for PUFA formulation [216–218]. The liquefaction process is a fast and efficient way to obtain a mixture of aliphatic and aromatic polyols for PUFA.

3.3.1.2. Alkoxylation

Similarly to carbohydrates, the different and more or less accessible OH groups can be transformed into more active OH groups at the end of polyether grafted chains via alkoxylation reactions. Organosolv [219–225], pyrolytic [226], Kraft [220–222,227–229], Soda [220,222] lignins and tannins [149,168] were transformed into suitable polyols by this way. Epoxide rings for the alkoxylation can be synthesized from double bonds presents in biomass products. Nevertheless, the propylene carbonate, a well-known and non-toxic O-alkylating agent of phenol was used to graft polyether chains originated from phenol groups. Similarly to the alkoxylation reaction, the average number of polyether units per chain increase with the excess of propylene carbonates [230]. The investigation with several carbonates demonstrated the potential of this solvent-free, fast and quantitative reaction to transform non-reactive phenol into reactive primary or secondary OHs toward isocyanate groups [231]. The utilization of a kraft lignin polyol derived by this technique for PUFs production was realized using polyethylene glycerol (PEG) as a solvent [232].

3.3.1.3. Neat Polyphenols

Contrary to polysaccharides, lignins with adapted extraction technics and also tannins can be used directly without modification, neat, in PUFs formulation. Nevertheless, the solid and powdery aspect of the extracted lignin is the major drawback for this utilization. The dissolution in different polyols such as di- (DEG), tri-ethylene glycol (TEG), PEG, alkoxyated sucrose or molasses circumvented this problem, and the mixture can be introduced in the formulations [26,233–236]. The properties of the corresponding PUFs can be adjusted depending on the lignin content. The utilization of biobased fatty acid and glycerol to disperse lignins was also investigated [237]. On the contrary to some works where the lignin is used as fillers [238], the utilization of neat organosolv and kraft lignins as a polyol in PUFs formulations resulted in the integration of the lignin into the network architecture with covalent bonds [239]. The dispersion of tannin in polyols was also applied with alkoxyated fatty amine to act as a reticulation agent [240]. Otherwise, the mildly-sulfided quebracho

wood tannin was mixed with furfuryl alcohol to form aromatic PUFs [241].

3.3.1.4. Miscellaneous transformations

The production of fully biobased polyol was achieved through the esterification of lignin with oleyl chloride and further epoxidation-ring opening of the oil double bonds [242]. Another strategy was the utilization of the Mannich reaction with lignin, diethanolamine and formaldehyde. The lignin-aminated was dissolved into PEG before the foaming process [243]. Otherwise, alkali lignins were modified by hydroxymethylation, epoxidation and phenolation and then introduced in polyols. Despite the low portion of added lignin (1 wt%), the effect on the foam properties was notable [244].

3.3.2. Polyisocyanates

The pre-polymerization of lignin with a diisocyanate excess is the only strategy used to form polyisocyanate from neat phenolic biomass. The functionalization of lignin with pMDI was, for instance, realized [245]. This surface-functionalized lignin was further introduced into PUFs [245,246].

3.3.3. Additives

Lignins and tannins were widely investigated to form polyol thanks to the well-known increase of mechanical properties brought by the aromatic structure. However, aromatic structures are also known to be used as FR systems. The modified lignin contains primary OH groups to covalently linked to the PUFs network and phosphorous and aromatic compound for the FR properties [247]. Another strategy was the transformation of a tannin monomer, the gallic acid [248].

3.4. Products from industrial wastes

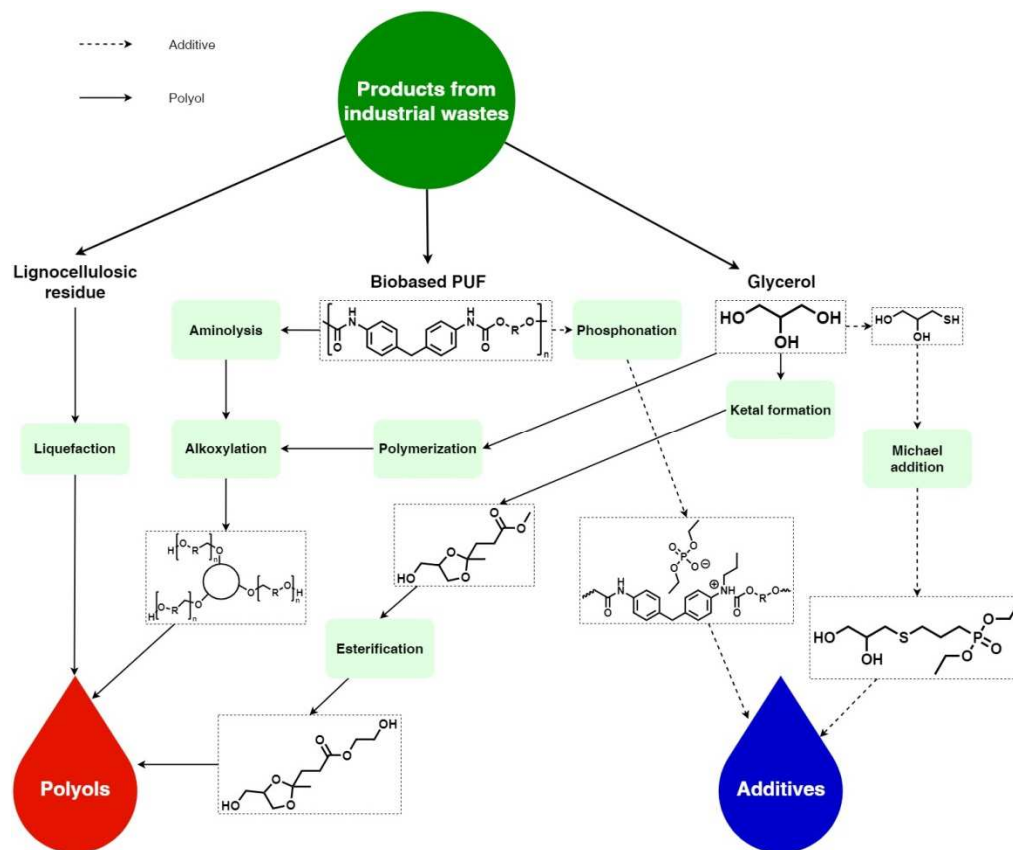


Fig. 14. Overview of the transformation of wastes from industrial processes into PUF components.

The production of industrial consumer goods inevitably generates wastes either from the production of non-compliant products or after the life of the product. This part is focused on the production of PUFs components based on three abundant wastes from industrial processes:

biobased PUs, crude glycerol, and lignocellulosic residues presented in Fig. 14.

Alkoxylation and liquefaction are the main pathways to develop polyols from lignocellulosic residues,

biobased PUs or glycerol, as shown with polyphenol resources. Actually, there are no developed

routes from industrial wastes toward isocyanates.

3.4.1. Polyols

3.4.1.1. Biobased PUF

One way to obtain biobased components for PUFs, such as polyols, is to use compounds obtained from recycling biobased PUs, such as chemical or biological recycling. Despite the recent and fast developments on the enzymatic degradation of PUs, there is still work to understand mechanisms and develop higher scale productions [249]. The chemical degradation of PUs is achieved through various processes such as hydrolysis, aminolysis, phosphatation or alcoholysis. The two first methods yield amine, which can be further used in the epoxy resin formulation [250,251], and the third, based on phosphate reaction, will be detailed later. Aminolysis has been used on F-PUFs, followed by an alkoxylation reaction to produce polyols [252]. However, the first process to obtain polyols from PUs wastes is the alcoholysis. The process was applied to numerous wastes such as RIM [253], foams [254,255] or scrapped PUs [256,257]. Green chemistry can be obtained, for instance, using transesterified coconut oil for the alcoholysis of PUs [136]. The major drawback of this strategy is the high-energy consumption, which is balanced by the valorization of “plastic” wastes.

3.4.1.2. Glycerol

The biodiesel produced from the transesterification of triglycerides generates a considerable amount of glycerol as side products. This crude glycerol contains sodium generally used as the catalyst for the transesterification, residue of oils and water, which can be removed to obtain high purity glycerol [258]. This triol with a high I_{OH} is introduced neat in a small portion as crosslinker with low I_{OH} co-polyol in PUFs formulations [128,138,171]. Glycerol can be polymerized to reduce the I_{OH} value and obtain long polyol chains [160,259]. Recently developed, the formation of a ketal between glycerol and the methyl levulinate derived from wheat straw was reported. The methyl ester was further transesterified with EG to form a diol introduced up to 100% in PUFs [260].

3.4.1.3. Liquefaction of waste from industrial process

Industrial processes such as sugar extraction from sugar cane generates biobased solid waste

composed mainly of the solid part of plant cell walls (Fig. 12). It can be valorized into polyols for PUFs by the liquefaction process as detailed in the lignins and tannins section. This reaction was used with food industry wastes [261–263,263–268], straws [269,270], digested sewage sludges [269] or microalgae biomass [140].

3.4.2. Additives

As previously presented, the PU can be degraded by phosphate. This strategy was employed to produce urethane oligomers with high phosphorous content [271]. Otherwise, a glycerol derivative was transformed in FR via a Michael addition. The thioglycerol was added to diethyl allyl phosphonate to produce a polyol with low viscosity and intrinsic FR properties due to the phosphorous compound [272].

3.5. Products from white biotechnology

This part is linked to Fig. 15. From different biobased molecules extracted from biomass mainly by biotechnology in biorefineries such as limonene, β -pinene, eugenol, malic and citric acid, furan, vanillic and syringic acid, oil cashew nut shell liquid (CNSL) or derived from amino acids, different PUFs components can be elaborated. One of the most common building blocks obtained by biotechnology for PU is the 1,4-butanediol. This diol is obtained industrially through hydrogenation of succinic acid obtained by biotechnology [84]. Genomatica developed another strategy by bioengineering an *Escherichia coli* strain to directly produce 1,4-butanediol from renewable carbohydrate feedstocks [273]. The 1,3-propanediol is another important diol bioproduced either from glycerol or glucose [84]. In PUFs, these biobased diols are used as chain extenders [225,274] or through the synthesis of polyols [171].

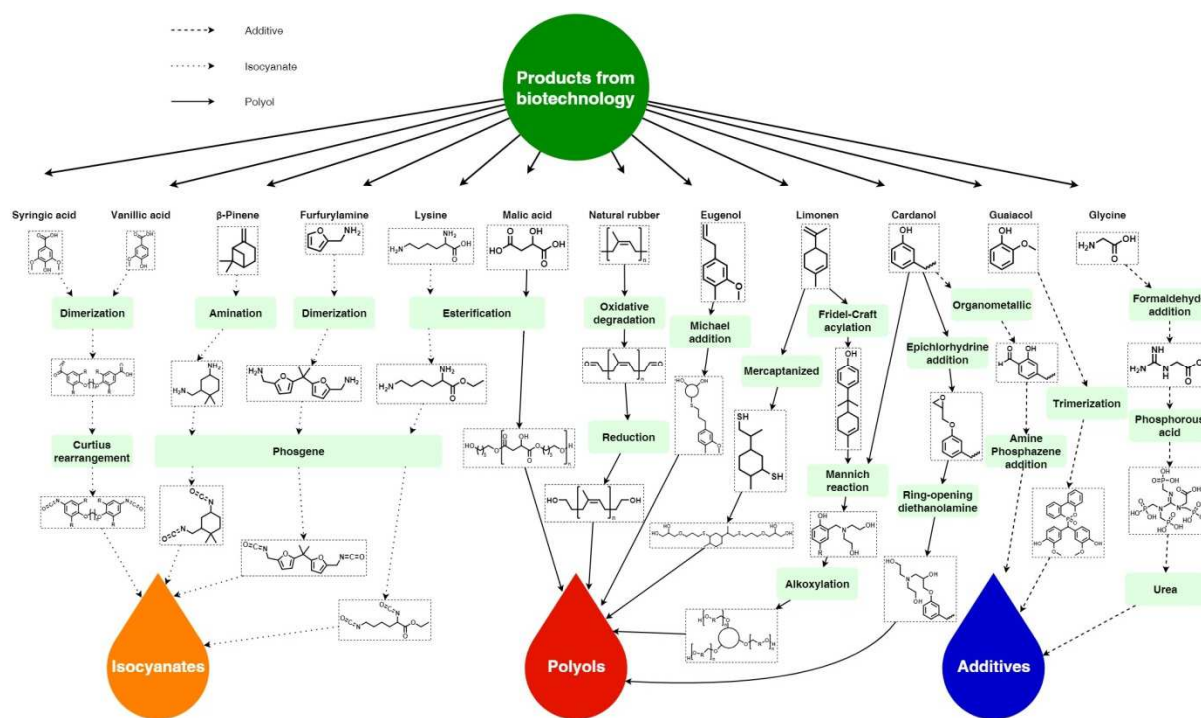


Fig. 15. Overview of the transformation of products from biotechnology into the PUF component.

3.5.1. Polyols

Different compounds can be more or less directly extracted from biomass to produce polyols. The processes are often integrated into biorefineries based on biotechnology and chemical steps.

For example, it is the case of the limonene, which is obtained, e.g., from orange peels or produced by microorganisms [275]. Based on a cyclic structure with two double bonds suitable for chemical transformation, it can be transformed into a Mannich polyol with 1,3-N-hydroxyethyl oxazolidine [276]. Otherwise, limonene was mercaptanized with hydrogen sulfide and then reacted with glycerol-1-allyl ether via Michael addition to form a polyol for PUFs [277]. In another study, the malic acid, a dicarboxylic acid potentially obtained by microbial fermentation [278], was oligomerized with 1,6 hexanediol to produce a polyol which is used in PUFs formulation. The presence of one OH group on malic acid increases the I_{OH} of the produced polyol [279].

As previously seen, carbohydrates are an important source for the elaboration of biobased molecules. The β -methyl- δ -valerolactone, a six-membered ester ring, was, for instance, synthesized

from glucose with mevalonate as an intermediate [280]. It was transformed into a polyol via acid-catalyzed ring-opening transesterification with trimethylolpropane ethoxylate [281].

Otherwise, alkoxyated [282] or not [283] eugenol extracted from cloves was transformed through thiol-ene chemistry to produce polyols. In another study, the natural rubber was transformed through controlled oxidative degradation, followed by a reduction to obtain a OH-terminated natural rubber [284].

Another source of recent innovation in terms of new molecules is the CNSL, which is composed at 90% of anacardic acid, a particular lipid formed by a phenol with a carboxylic acid in the ortho position and an unsaturated carbon chain in the para position. The decarboxylation of anacardic acid by heating yields cardanol [285]. It was transformed into polyols via alkoxylation [286] or Mannich [287–289] reaction. A hybrid polyol has recently been developed based on cardanol, composed of catalytic tertiary amine and polysiloxane chains similar to surfactants [290].

3.5.2. Additives

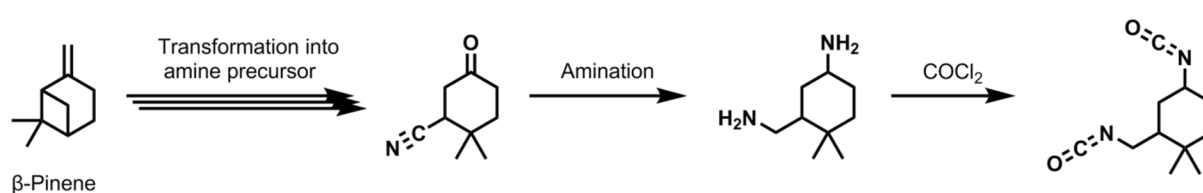
Cardanol was modified to obtain a FR molecule composed of 66% of cardanol and 3.4% of phosphorous [291]. The trimerization of vanillic acid, guaiacol and DOPO to form a FR containing phosphorous was developed for the epoxy resin, but it could be adapted to be used in PUFs formulation [292]. Another example, the guanidine acetic acid (glycocyanine), which is derived from the hydrolysis of proteins (i.e., glycine), was modified to form a FR compound [293].

3.5.3. Polyisocyanates

With lignin and tannins derivatives, aromatic isocyanates can be synthesized. Syringic and vanillic acid can be dimerized and further converted into isocyanate via Curtius rearrangement [294]. This method has the particularity to produce diisocyanate with a control chain length between the

two aromatic moieties.

The amino acid lysine was transformed into diisocyanate by esterification with ethanol and phosgenation of the amines. The ethyl ester (L) Lysine diisocyanate obtained is well known, especially in biomedical or coating applications [295–298]. Another synthetic route toward diisocyanate from β -pinene is described in Scheme 4. The β -pinene distilled from pine was transformed through several steps into a diamine and further in diisocyanate by phosgenation [299].



Scheme 4. Synthesis of diisocyanate from β -pinene. Adapted from [299].

The furan derivatives obtained by dehydration of monosaccharides could be good candidates for the replacement of aromatic structures. Extensive researches are conducted on the furan and a major component to produce PEF (equivalent to PET) the polyethylene 2,5-furan dicarboxylic acid [9]. The furfuryl amine obtained from the biotransformation of furfural [300] was dimerized with acetone under mild conditions; the obtained difurfurylamine was transformed via phosgenation into diisocyanate [301]. The reactivity of furan isocyanates was found to be similar to aromatic analogs (TDI) [302–304]. A novel strategy to develop foams from furan derivatives was based on the modification of two carboxylic groups of the bis(5-carboxyfurfuryl)ether into carboxylic-azide. This precursor was introduced with polyols and heated to induce the Curtius rearrangement to form isocyanate from azide. The nitrogen released by this reaction served as a BA for the foam network composed of the newly formed diisocyanate and the polyol [305].

4. Study of “structure-properties” relationships in the case of biobased R-PUF.

The goal of this chapter is to study the relationship between the structure or morphology of the foams and some specific properties. This chapter is mainly focused on biobased R-PUFs, which

are mainly used as insulation materials. The characterizations of these foams are then targeted and focussed on the application and largely less diverse than the F-PUFs. Besides, the processing and the additives differ from R-PUF to F-PUF, increasing the complexity to draw a general conclusion on the effect of the biobased components on all PUFs properties.

R-PUFs are at least mainly based on six components, such as the polyisocyanate, polyol, BA, surfactant, catalyst and additives (Table 1). The conventional polyisocyanates and surfactants are usually pMDI and polyether siloxane, respectively. The BAs and catalysts structures evolve in the formulation to reach the optimum properties in accordance with the targeted application. The comparison between the data of the literature is often difficult due to the multiplicity of foam formulations with different NCO/OH indexes, catalysts/surfactant loadings and structures, foaming environments or BAs.

4.1. Morphological and structural data

In R-PUFs, the cells are generally defined by a polyhedron shape close to an honeycomb structure. The faces of the polyhedron are called the walls, and the thicker edges the struts. In a partially open system such as a cup often use as a mold, the cells are elongated in the vertical direction. This phenomenon was explained by the constraint expansion by the cup walls inducing a faster growth in the vertical direction than the horizontal direction [306]. The cell morphology is defined by the density of the foam, the cells size and shape, and the closed-cell content. The related properties are affected by the foaming process and linked parameters (viscosity, surface tension, kinetics) and materials properties (phase separation).

4.1.1. Viscosity

Generally, the viscosity of polyols for R-PUFs is between 2 and 50 Pa.s (Table 3). Fig. 16

represents the dependence between cell size and viscosity. The data were compiled from the literature of foams made with a biobased sole polyol. As shown in Fig. 16, when the viscosity of the polyol is under 5 Pa.s, the produced foam presents dispersed cell sizes. On the contrary, the cells obtained with a moderately viscous polyol (5-25 Pa.s) are homogeneous and smalls, around 200 μm . Finally, few examples of cell size from foams realized with highly viscous (> 25 Pa.s) polyols are presented in Fig. 16. The size varies from 250 to 490 μm .

The high viscosity of biobased polyols can originate from triglycerides crystallization [138], branched structure of phenolic compounds [26,149,204,237], solid residues in the polyol [263] or high molar masses [172,257,307]. Moderate viscosity is requested to reduce the cell-size due to the limitation of bubble coalescence and expansion [106,149]. For example, the cell diameters of foam obtained from alkoxyated glycerol (0.2 Pa.s) and tannin (6.9 Pa.s) were 440 and 290 μm in the rise direction, respectively [149]. The authors attributed this decrease in cell size to the high viscosity and functionality of the alkoxyated tannin. Furthermore, the nucleation of cells is heavily affected by the viscosity of the foaming liquid. In more viscous polyols, the concentration of air bubbles is higher due to the limited diffusion and coalescence. The nucleation was enhanced by the branched and pendant chains of triglycerides polyols [105] or solid lignins dispersion in the polyol [26,203]. The incorporation of 10 wt% of the unmodified lignin particles in the polyol improved the nucleation and can decrease the average cell size from 510 to 430 μm [26]. The introduction of long aliphatic segments enhanced the flexibility and decreased the viscosity; therefore, coarser and more irregular cells were obtained [308]. However, too high polyol viscosity was also observed to cause coarser and less uniform cells. The polyols prepared with 40 wt% of lignin were highly viscous (16.7 Pa.s) and caused less uniform and coarser cells [239]. A similar trend was observed with soybean oil-based polyol. An increase in viscosity from 7 to 23 Pa.s of the soybean-polyols clearly produced PUFs with coarser cells affecting the nucleation process [109]. The high viscosity of polyols induces mixing drawbacks and therefore a higher dispersity in cell sizes, as shown in Fig. 16.

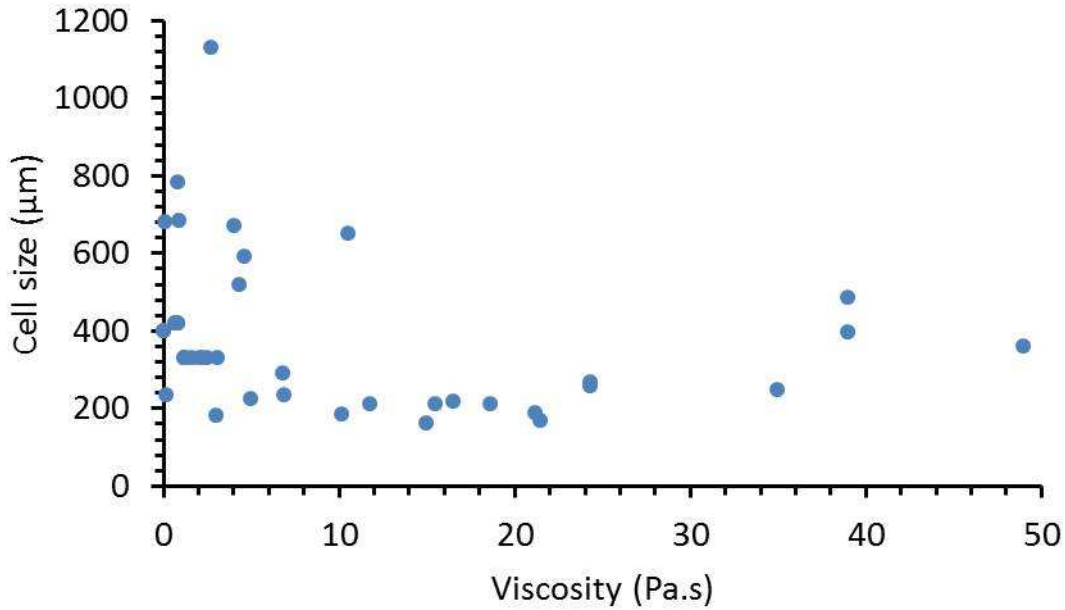


Fig. 16. Viscosity of polyol vs. the cell size for PUF. Compilation of data from literature [97,101,102,106,109,110,131,136,138,140,163,164,259,279,290,309].

4.1.2. Surface tension

The surface tension was shown to play a crucial role in the formation of small cells. The growth of bubbles is closely related to the surface tension of the foaming mixture by the Laplace equation [173]. The increase in surface tension induced by the sorbitol polyester polyol slows down the growth of the cell. Cell size can be partially controlled by formulation, cells were reduced from 410 to 270 μm in the longitudinal direction by the addition of polyester polyol from 10 to 35 wt% [173].

4.1.3. Reaction kinetics

In the same study [173], the faster gelling of the polymer network was shown to help the generation of small cells. As previously explained, the expansion of bubbles is closely related to the equilibrium between blowing and gelling reaction. Significant modification in the formulation, such

as the substitution of the polyol, alters the gelling/blowing balance. Fig. 17 represents the evolution of the temperature, viscosity and cell morphology over time in different cases: the balance is in favor of the blowing (Fig. 17A), equilibrium of the blowing/gelling balance (Fig. 17B) and the balance in favor of the gelling (Fig. 17C).

In the case of high blowing efficiency, the foam size increases rapidly due to a sudden temperature increase (Fig. 17A). Therefore, the cell size and elongation increase and the density decrease as represented in Fig. 17A in comparison with Fig. 17B. Moreover, fast cell expansion often induces breaks in the thin walls to form open cells (Fig. 17A). A decrease of density from 102 to 66 kg/m³ attributed to the increased blowing efficiency was observed when the polytrimethylene ether glycol content was increased in the foam formulation [163]. The hydrophilic character of the polyol and thus, its water content could explain this increased blowing activity, as it was observed with linseed oil used as a surfactant [148]. Higher water content promotes the rapid and sudden release of CO₂ producing larger cells with thinner walls [310]. Furthermore, the closed-cell content decreased under 10% with higher foaming rate polyols [172].

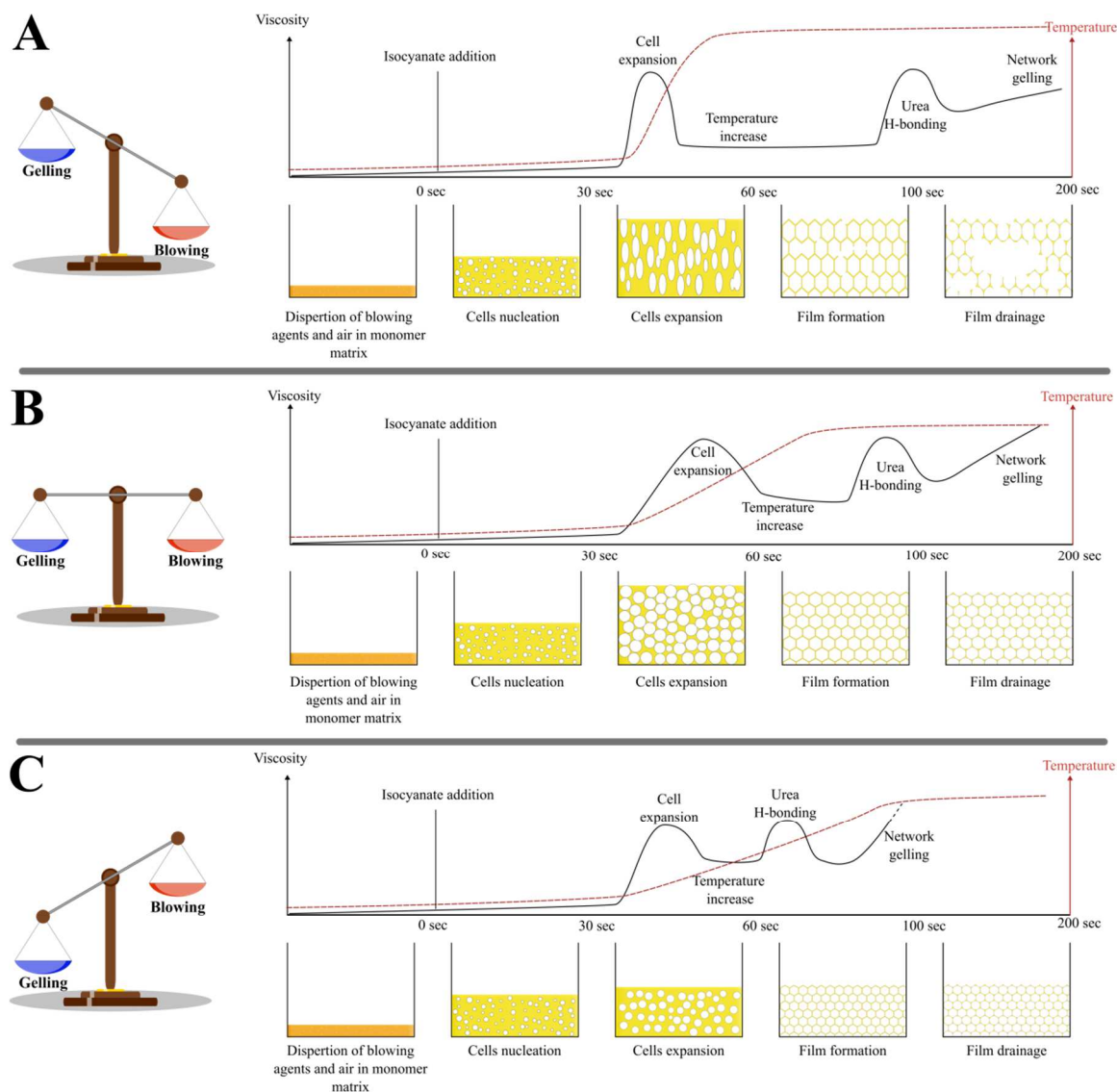


Fig. 17. Effect of the gelling/blowing balance vs. temperature, viscosity and foam cell morphology in three typical cases: (A) mainly blowing, (B) equilibrium and (C) mainly gelling.

Nevertheless, the primary effect observed, coupled with a higher blowing activity, is related to the decrease of the gelling activity. Fig.17A represents the evolution of the viscosity over time when the gelling is lower than the blowing activity. In this case, the longer gel time is characteristic of a slow network formation around the growing bubbles; thus, cell drainage and Ostwald ripening get a longer time to deteriorate the closed-cell morphology (Fig. 17A). Therefore, the cells are coarser, and the closed-cell content decrease [172,207,208,212,261]. For example, the introduction of less reactive liquefied lignin compared to conventional polyols was observed to produce a broader cell distribution [207]. In another study, the introduction of liquefied biomass formed large and widely

distributed cells. The coalescence of cells by Ostwald ripening explained the difference of the mean diameter between the reference foam made with PEG-glycerol (660 μm) and the biobased system (780 μm). The authors pointed out the low reactivity of phenols from the biobased aromatic polyols [261].

The lower reactivity of the polymer network formation was also explained by lower I_{OH} [163,211]. The OH density is related to the functionality of the polyol, and it is well known that the higher the functionality is, and the lower the conversion to reach the gel point will be [311,312]. Furthermore, with similar I_{OH} , the decrease in gelling rates can be explained by the lower reactivity of the secondary [98,105] or even phenolic OH groups [261], compared to primary OHs. Furthermore, a high acidity of the polyols resulting from the biomass transformation can reduce the amine catalysis activity and forms coarser cells [98,219]. The gel time was proved to increase from 200 to 510 s with the substitution of 50 wt% of the polyol by lignin. The authors explained that lignin contained free acetic/formic acid, which, once bonded with an amine catalyst, reduced its activity. This hypothesis was further supported by the decrease in density explained by the free carboxylic acid reaction with isocyanates forming amide and CO_2 [219]. If the gelling is very low compared to the blowing, the cells burst, and the foam falls back before the polymer solidifies [99,105,139].

On the contrary, when the gelling reaction is favored, the polymer solidifies faster than the gas expands. This is represented in Fig. 17C by a rapid increase in viscosity compared to Fig. 17B. Therefore, smaller cell size, higher closed cell content and an increase in density are generally observed (Fig. 17C). Polyols with high I_{OH} makes the polymer network gel faster because less conversion is required to form a crosslinked structure. For example, the transesterification of castor oil with crude glycerol produces polyols with lower I_{OH} (350 mg KOH/g) than neat glycerol (540 mg KOH/g). The crude glycerol polyol formed lighter foams (95 vs 245 kg/m^3) with bigger cells (600 vs 400 μm) [132]. Similar results were observed on biobased polyols with high I_{OH} produced with oils [313], carbohydrates [173] or liquefied lignins [225]. Furthermore, the shrinkage reduced from 4 to 0.4% and the collapsing from 2.3 to 0.1% within foam elaborated from 250 mg KOH/g polyol instead

of 100 mg KOH/g [313]. This is due to the thicker cell walls presented in Fig. 17C compared to Fig. 17B.

The higher content of more reactive primary OHs increased the gelling rate of foam [259,267]. As shown in Fig. 17C, a faster gelling form low cell size compared to Fig. 17B. A decrease in cell size of 150 μm was observed with the introduction of more reactive polyols obtained from liquefied spent coffee grounds. This phenomenon was explained by the reduction of the coalescence due to the faster polymerization [267]. Another way to increase the gelling activity of the polyol is the incorporation of catalytic sites inside the polyols structure. The introduction of a tertiary amine in model fatty ester alcohol was proved to increase the reaction rate between the OH group and isocyanate [115]. In PUFs, it was achieved with Mannich reaction on limonene based polyols [276], triglycerides epoxidation and ring-opening with amine [98] and modified cardanol [290]. However, this kind of polyol cannot substitute the standard polyol without a complete disequilibrium between the gelling and blowing balance. For example, the substitution of 25 wt% of conventional polyol by epoxidized microalgae oil ring-opened with diethylamine was proved to increase the kinetics of the foam and deteriorate the cell morphology [98]. However, in the same study, the epoxidized soybean oil ring-opened by diethylamine was successfully used as a unique catalyst to form low-density foams (36 kg/m^3). Another strategy can balance blowing and gelling with a cardanol based "autocatalytic" polyol [290].

In some rare cases, the substitution of biobased polyols did not affect the foaming process (Fig. 17B). For example, the introduction of alkoxyated lignin produces foam with similar reactivity compared to fossil-based polyol. It was assumed that a similar structure composed of PO units plays a key role in similar kinetics [208]. Despite the lower reactivity observed with an oil-based polyol, the foaming process and the cell morphology were not affected [100,107].

4.1.4. Microphase segregation

A particularity of the PU networks is the capacity to segregate into (i) strongly H-bonded hard segments and (ii) long flexible chains called soft segments. The microphase separation in PUFs generally explains a defect in the foam, such as irregular pores [95,138] or wrinkles [164]. The activity of the soft segments formed by the long and flexible chain on the microphase separation is not yet fully understood. Some theories claimed that the higher flexibility of this soft segment allows a better migration of the surfactant with the formation of coarser cells and lower densities [100,108]. It was also noticed that the small molar mass molecules in liquefied bark polyols had a plasticizing effect increasing the drainage and open-cell content. Otherwise, the decline in the free volume of polymer with the gradual substitution of glycerol by lignin extended the density from 60 kg/m³ to 115 kg/m³ with 10 wt% and 40 wt% of lignin, respectively [237]. Nevertheless, these effects need to be further investigated with more in-depth analysis.

To summarize, the cell morphology is highly influenced by the structure of the biobased component via its reactivity, viscosity, nucleation capacity, surface tension or resulting microphase separation. In most cases, the foams are formulated by substitution of a weight portion of the fossil-based polyol by the biobased one, with every other parameters being constant. The advantage of this method is to show the influence of the biobased compound on the foaming process by the characterization of the density, cell size and closed-cell content. Formulation optimization should always complete this approach because the biobased polyol, by its structure difference, have certainly different interaction compared to the fossil-based. Furthermore, the morphology of the cell profoundly affects other properties such as mechanical, thermal or fire resistance. Consequently, the biobased compound impact on these properties is never really isolated and then determined.

4.2. Mechanical properties

Cellular materials are a combination of excellent mechanical properties on lightweight

materials [314]. In PUFs, the compression strength is the most common measurement to evaluate the mechanical properties of the material. The compression behavior of foams can be decomposed into several stages: First, the linear region is governed by the compression and bending of the cells struts, then the stretching of the cell walls and finally, the compression of the trapped gases [315]. The effects of the cell morphology, the crosslink density and the structure of the biobased component on the compression strength properties of PUFs are given below.

4.2.1. Morphological structure of cells

The compression strength highly depends on the density of the material. The lower the density is, the lower the compression strength will be [110,307]. Fig. 18A shows the evolution of the density and the compressive strength of foams with a gradual introduction of lignin-based polyol [207]. Fig. 18A shows that the increase in compressive strength follows directly the increase in density. Furthermore, the compression strength (σ) was correlated with the foam density (ρ) with a power-law model expressed in Equation 1.

$$\log(\sigma) = \log A + B * \log(\rho) \quad (1)$$

Fig. 18B represents the compressive strength evolution over the density in logarithmic scales, modeled by Equation 1. The linear regression slope value was 1.5 in Fig. 18B for a series of water-blown foams realized with varying amounts of water. This value was in agreement with the literature value ranging between 1 and 2 [316]. The compressive strength can be normalized according to Gibson-Ashby [317] equation, expressed in Equation 2 to compare foams with different densities.

$$\sigma_n = \sigma_m * \left(\frac{X}{\rho_f}\right)^2 \left(\frac{1 + \sqrt{\frac{X}{\rho_s}}}{1 + \sqrt{\frac{\rho_f}{\rho_s}}}\right)^2 \quad (2)$$

Where σ_n is the normalized compressive strength, σ_m the measured, ρ_f the measured density of the PUF, ρ_s the density of solid PU (1200 kg/m³) and X the density of normalization [257]. The

compressive strength of the flexible cell foams relies on bending and cell wall axial deformation. On the contrary, in closed-cell foams, the air inside the cell and the walls contribute to the compressive strength [149,212,317]. It is worth mentioning that open-cell foams have higher compressive strength than closed-cell material with cell walls ruptured. The broken walls are unable to contribute to stress reinforcement and will initiate rupture when the cells are under load [128]. The homogeneity and cell size also affect the mechanical properties such as compression. R-PUFs with small and organized cells have higher compression strength due to homogeneous repartition of the load [109,130,138,212,220,232,239,261].

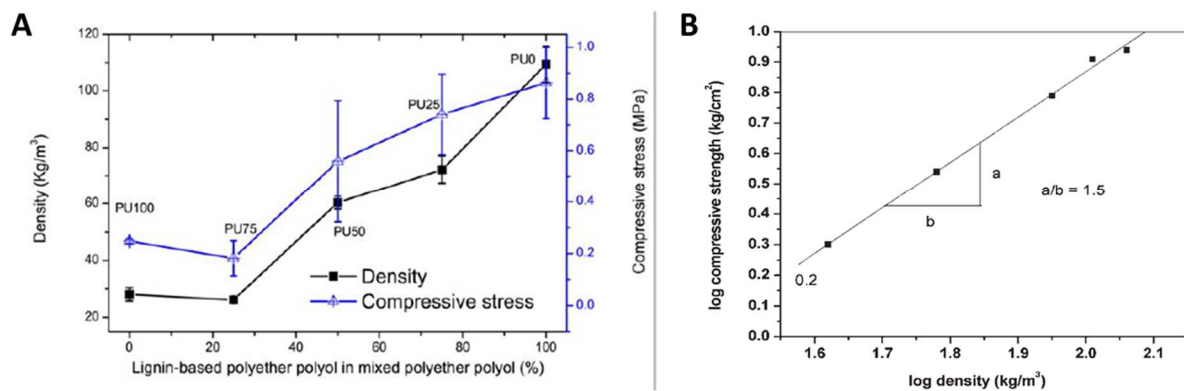


Fig. 18. (A) Effect of the introduction of lignin-based polyol on the density and compressive strength of PUF. (B) Dependence of the compressive strength on density. Reproduced with permission from [207] and [316].

4.2.2. Crosslink density

I_{OH} represents the OH groups density of a given system. In the final material, OHs are transformed into urethane groups; therefore, the higher the I_{OH} of the polyol is, the higher the density of urethane and crosslinking will be. This property indicates the strength of the polymer network and profoundly affects the mechanical properties. A high I_{OH} gives high compressive strength [26,138,140,149,208,211,224,263,313,318] and vice-versa [121,163,164,239,261]. For example, an increase in compressive strength from 26 to 81 kPa has been obtained with an increase of I_{OH} from 100 to 250 mg KOH/g [313]. Furthermore, the gradual substitution from 0 to 70 wt% of

fossil-based by crude glycerol-based polyol demonstrated a constant increase in compressive strength in parallel and perpendicular directions [140]. Finally, the compressive strength of foams realized with an increasing portion of liquefied biomass was shown to increase due to the larger crosslink density of the sample. The authors confirmed this hypothesis with the decrease of the soluble fraction in the foam elaborated with the highest I_{OH} [214]. However, the introduction of biobased polyol with lower I_{OH} can be detrimental to the mechanical properties as Eceiza and coworkers showed with the introduction of 30 wt% of polytrimethylene ether glycol. The specific compressive properties decreased from 9.9 to 6.0 kPa.kg⁻¹.m³ with the substitution of the fossil-based (444 mg KOH/g) by the biobased (80 mg KOH/g) polyol.

4.2.3. Molecular structure

The different biomass sources, previously described, present a large range of chemical structures. This variety of biobased components induces a multitude of new macromolecular architectures. The compression strength of the PUFs depends on the molecular level interactions in the studied system. The next part aims to detail the impact of the different biobased structures on the mechanical properties.

The triglycerides are composed of different long aliphatic chains. The corresponding increase of flexibility in the polyols gives higher elastic properties to the polymer network and then impacts the compression strength. The foam realized with 50 wt% of polyol synthesized from mercaptoethanol thiol-ene addition with corn oil had a compressive strength of 120 kPa [121]. This value was lower than foam with similar density realized by epoxidation and ring-opening with ethanol of microalgae oil (270 kPa) [98]. This difference can be explained by the higher I_{OH} due to the higher double bonds quantity of the microalgae compared to corn oil, for instance. Furthermore, the concentration of unfunctionalized long fatty chains called dangling chains higher in corn oil caused higher flexibility.

The increasing portion of dangling chains is said to plasticize the network, reducing the compression strength [102,124,128,138]. Narine and coworkers studied the effect of the dangling ends in PUFs. They used different polyols with similar I_{OH} synthesized by various methods. The authors found that the compressive strength of soybean polyol realized by epoxidation and ring-opening was the lowest with the plasticizing effect of the dangling ends [128]. The PUF realized with rapeseed oil-based polyol had compression strength 15% lower than the fossil-based reference due to the plasticizing effect of dangling chains-ends [102].

As previously explained, the epoxidation followed by ring-opening is one of the most popular ways to obtain polyols from vegetable oil. The ring-opening reaction is often accompanied by side reactions such as epoxide polymerization, which can modify the final properties. Then, an unexpected increase of compressive strength was obtained for foams with 30 to 50 wt% of epoxidized soybean oil ring-opened by EG. The authors hypothesized that the polyether network formed by this polymerization supported the network [105].

Lignins produced with different extraction methods are often a powder. Unfortunately, the foam processing is not adapted for the integration of solid polyols at high content. This is shown in Fig. 19, by the compressive strength evolution over the lignin/polyol ratio. The introduction of a small portion (25 wt%) of raw lignin instead of the polyol made the compressive strength drop from 500 to 250 kPa without significant change in density [239]. In Fig. 19, the gradual introduction of lignins into PUFs showed a plateau in compressive strength from 25 to 60 wt%. However, after 60%, the poor dispersion of lignin into the matrix results in a ruin of mechanical properties (Fig. 19).

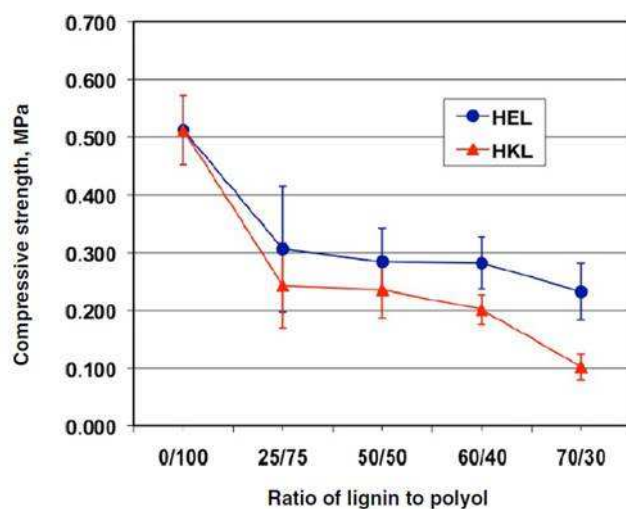


Fig. 19. Effect of lignin addition on the compressive strength of R-PUF. The ratio of lignin to polyol, the molar ratio of the OH groups from lignin. Hardwood ethanol organosolv lignin (HEL) and hardwood kraft lignin (HKL). Reproduced with permission from [239].

As previously detailed, the liquefaction or alkoxylation of lignin was explored to introduce a higher lignin content into PUF. The liquefaction and alkoxylation products are a mixture of lignin with flexible chains bearing OH groups with unreacted low molar mass glycols. It is well-known that the alkoxylation generates free homopolymer chains of polyethers as by-products. This homopolymer can be removed by solvent extraction. However, to avoid extra steps, this by-product is often let in the mix [319]. These small polyols increase the flexibility of the polymer network and thus decrease the compression strength [207,220,229]. The introduction of 25 wt% of liquefied lignin polyol in PUFs decreased the compressive strength despite similar I_{OH} and density. The authors explained this trend by the flexibility of PEG 400 used for the liquefaction of the lignin [207].

The addition of alkoxyated lignin as a unique polyol increased the compression strength of the network from 100 to 140 kPa due to the rigid aromatic and 3D structures of the lignocellulosic resources [229]. Furthermore, polyols made from rapeseed oil or lignin with similar I_{OH} were gradually introduced up to 30 wt% in PUFs. The compressive strength of the lignin-based foams was always superior to the one realized with triglycerides. The authors explained this behavior by the presence of aromatic rings, which increase the rigidity [224]. Another example, the increase in mechanical properties in PUFs made with alkoxyated lignin could be related to the PPO chains,

which enhance the miscibility of modified lignin in the network [226].

Another possibility to produce biobased polyols with an aromatic structure is the alcoholysis of biobased PUs with small diols or triols. The capacity of the aromatic to stack added with a high crosslink density generates a highly rigid and brittle structure detrimental to the compressive strength. A polyol was obtained from liquefied aromatic wastes by transesterified coconut oil. The long and flexible chain of coconut oil avoided the excessive rigidity and brittleness of the PUFs. Furthermore, the authors claimed that the combination of rigid aromatic and aliphatic flexible structure provided optimal block segregation [136]. CNSL combined rigid aromatic structures like lignins and flexible aliphatic chains as triglycerides. The introduction of a higher portion into PUFs was found to increase the compression strength thanks to the rigid aromatic structure [287].

4.3. Thermal properties

R-PUFs are widely used as thermal insulation material in the building industry or for transportation where the thermal conductivity is a primary property [320]. The thermal insulation is related to the cell morphology, e.g., cell size, closed-cell content and density, the material properties, e.g., conductivity and complex index of refraction of the polymer and the conductivity of the gas entrapped in the cells [45]. From a physical point of view, the thermal conductivity (λ) of the foams is related to the total heat transfer (q_t) passing through a thickness of foam (L) induced by a delta of temperature ΔT , as described by Equation 3.

$$\lambda = q_t * \frac{L}{\Delta T} \quad (3)$$

Where q_t is a sum of three components which are described in Equation 4 with the conduction through the polymer matrix (q_{PUR}), through the gas phase (q_{gas}) and the radiation (q_{rad}). The convection transfer is negligible for closed-cell porous materials with a cell size inferior to 3 mm [317].

$$q_t = q_{PUR} + q_{gas} + q_{rad} \quad (4)$$

The different contributions were physically examined and detailed in Equation 5, 6 and 7 [321].

$$q_g = -\delta \sum_{i=1}^N \frac{y_i * k_{g_i}}{\sum_{j=1}^N y_j A_{ij}} \frac{dT}{dX} \quad (5)$$

$$\text{With } \delta \approx 1 - \frac{\rho_f}{\rho_s}$$

Where δ is called the void fraction, ρ_f the foam density and ρ_s the solid polymer density, y_i is the mole fraction of the i^{th} gas in the foam, N the number of gases in the foam, k_{g_i} the thermal conductivity of the pur i^{th} gas and A_{ij} a complex coefficient depending on the viscosity, molar mass and temperature of gases.

$$q_s = -\frac{1-\delta}{3} * k_p \left[f_s \sqrt{a/b} + 2(1-f_s) * \left(\frac{a}{b} \right)^{0.25} \right] \frac{dT}{dX} \quad (6)$$

Where k_p is the conductivity of the polymer and a/b the cell aspect ratio.

$$q_r = -\frac{16\sigma T^3}{3K} \frac{dT}{dX} \quad (7)$$

$$\text{With } K = \frac{4.10}{d} * \sqrt{\frac{f_s \rho_f}{\rho_s}} + \left[\frac{(1-f_s)\rho_f}{\rho_s} \right] K_w$$

Where d is the cell diameter, f_s the solid fraction, σ is the Boltzmann constant and k_w the extinction coefficient of the solid polymer. Equation 7 is known as the Rossland equation.

This equation shows the multitude of factors that affect the total thermal conductivity. Fig. 20A shows the evolution of the modeled thermal conductivity of R-PUFs over the closed-cell content. The conductivity through the gas phase accounts for 70% of the total thermal conductivity. The conduction through the polymer matrix is 20%, and the radiation is 10% [45]. Fig. 20A demonstrates that the reduction of the total thermal conductivity with the porosity depends on the reduction of the conduction through the solid part of the foam.

The major contribution depends on the gas mixture enclosed in cells, which tends to flow out and be substituted by air over time. The thermal conductivity was measured on PUFs samples over 900 days to study the diffusion of the BA gases out of cells, and the results are shown in Fig. 20. Within 100 days, the substitution of low conductivity BA gases (16.4 $\text{mW}\cdot\text{K}^{-1}\cdot\text{m}^{-1}$ for CO_2 and 12.8 $\text{mW}\cdot\text{K}^{-1}\cdot\text{m}^{-1}$ for cyclopentane) by atmospheric air (25.6 $\text{mW}\cdot\text{K}^{-1}\cdot\text{m}^{-1}$ at 20 °C) raise the initial 21 $\text{mW}\cdot\text{K}^{-1}\cdot\text{m}^{-1}$ thermal conductivity to almost 27 $\text{mW}\cdot\text{K}^{-1}\cdot\text{m}^{-1}$ [322]. Fig. 20B shows the thermal conductivity value plateau around 29 $\text{mW}\cdot\text{K}^{-1}\cdot\text{m}^{-1}$ after one year of aging. Therefore, the thermal conductivity must be analyzed in the utilization conditions and not considered as a constant property [323].

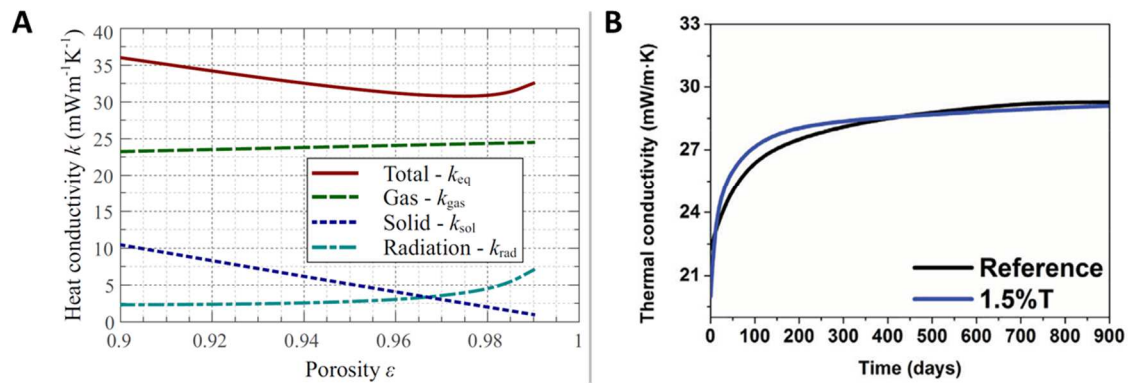


Fig. 20. (A) Dependence of the heat conductivity on porosity modeled with cell size of 300 μm and filled with air (B) Thermal conductivity evolution over 900 days of PUF and PUF modified with 1.5% of talc. Reproduced with permission from [45] and [322].

4.3.1. Effect of closed cell-content

Low closed cell content enhances the diffusion phenomenon and the substitution of BA gases by air; thus, decreasing the overall thermal conductivity of foams. As previously described, the utilization of biobased components directly impacts cell morphology. As a result, the decrease of the closed-cell content reduced the thermal conductivity [26,100,139,149,259]. For example, the decline of closed-cell content from 95 to 85% implied an increase in thermal conductivity of 5 $\text{mW}\cdot\text{K}^{-1}\cdot\text{m}^{-1}$ [139]. The thermal conductivity decreased linearly with the closed-cell content [259].

Furthermore, it has been proved that the increase in average cell diameters from 250 to 600

μm caused an increase in the thermal conductivity coefficient by almost 50% [18]. This variation is explained by the Rossland equation (7), where the lower cell size (d) contributes to the reduction of the radiative transfers [149,163,173]. Besides, in denser materials, the heat transport passed through more quantity of solid; therefore, the contribution to the foam overall conductivity with the conduction through the polymer matrix (q_{PUR}) is more important in denser materials [139]. The thermal conductivity increases with the density of the material due to the increased quantity of solid material by which the heat must be transported [163].

4.3.2. Effect of the chemical structure

To some extent, the thermal conductivity was directly correlated to the chemical structure of the biobased components. The addition of long dangling chain-end in the polymer network with triglycerides polyol seems to enhance the diffusion of heat in the material [100]. An increase in thermal conductivity from 20 to 25 $\text{mW}\cdot\text{K}^{-1}\cdot\text{m}^{-1}$ with the increased substitution of fossil-based polyol by modified mustard oil was shown. Otherwise, the utilization of 2.5 to 5 wt% of kraft lignin as polyol was beneficial for the thermal conductivity, which was observed to decrease from 25.6 to 24.7 $\text{mW}\cdot\text{K}^{-1}\cdot\text{m}^{-1}$ due to the increased aromaticity, which reduces the gas transfer outward of the foam and therefore increases the thermal conductivity [26].

4.4. Fire resistance

The test of the FR-based materials depends on the application and, thus, the corresponding fire risk scenario. In PUFs, the assessment of the enhancement or degradation of the fire resistance properties by a biobased material is performed with thermogravimetric analysis (TGA) measurement, burning test or determining the limiting oxygen index (LOI).

TGA is a dynamic measurement of material degradation. The weight of a material is followed

over a determined temperature cycle, generally a rise at 10 or 20 °C/min. The degradation of PUFs samples takes place in two steps: (i) the urethane and urea bonds dissociation in the hard domain (200-300 °C) and (ii) the decomposition of the fragments and the isocyanurate structures (400-500 °C) [106,173]. The burning test is the application of a flame, for 15 or 30 s depending on the test condition, on a foam specimen, and the flaming time is recorded (EN ISO 11925-2). The LOI is an international normalized test (ISO 4589-2). A candle-like flame is applied to the top of a specific PUFs specimen under a controlled atmosphere. The objective is to find the minimum oxygen concentration in nitrogen that will induce a combustion of at least 3 min [73].

Thermal decomposition and degradation must be dissociated. The first one is the degradation of material properties due to exposure to heat, and the latter is related to the free-radical bond cleavage and subsequent pyrolysis of smaller molar mass fragments of a polymer upon exposure to heat [73]. The relations between the enhancement or degradation of the FR properties of PUFs and the structure of the biobased polyol defined by the I_{OH} , the rigidity, the molecular composition, the low molar mass compounds added through chemical transformation and the insoluble content are given below.

4.4.1. OH Index

In TGA analysis, characteristic temperatures are recorded at 5, 10 and 50% of weight loss to measure the FR of the related materials. Furthermore, the quantity of samples at the end of the measurement called char residue is also an indicator of the fire resistance of the foam. The evolution of the char residue, weight loss at 5, 10 and 50% over the average polyol I_{OH} is represented in Fig. 21. The data were compiled from the literature of foams made without FR additive. The general trend observed in Fig. 21 is an increase of the characteristic temperature with I_{OH} augmentation. The char residue presented in Fig. 21A is close to 0% when the I_{OH} is inferior to 200 mg KOH/g. Such polyols are often used in F-PUFs (Table 3), producing open-cells morphology. As discussed previously, low

closed cell content decreases the thermal insulation properties. Therefore, the heat transfer is facilitated, and the material burns completely. In the case of higher closed-cell content, the heat transfer toward the center is hindered by the numerous cells wall. Fig. 21A shows an increase in char residue after 200 mg KOH/g. This is linked to the foam structure formed by a higher crosslink density, which limits heat transfers [313]. Besides, a crosslinked network requires higher activation energy to initiate chain movement and decomposition compared to less branched polymers [163,209].

Fig. 21B, Fig. 21C and Fig. 21D present a high distribution of value directly linked to the difference in foam formulations. However, the general trend observed is the increase in the temperature at 5, 10 or 50% weight loss with the average I_{OH} of polyol increase. The thermal decomposition of PUFs starts with the urethane bond dissociation around 250 °C. The high density of OH groups will be transformed into urethane groups in the final materials. Therefore, a polyol with high I_{OH} will produce a material that will take an extended time to dissociate [173,290]. Finally, the increase of FR properties with the I_{OH} presented in Fig. 21 is low, and other factors such as the molecular energy, the molar mass and the structure of the polyol affect the fire resistance of the foam.

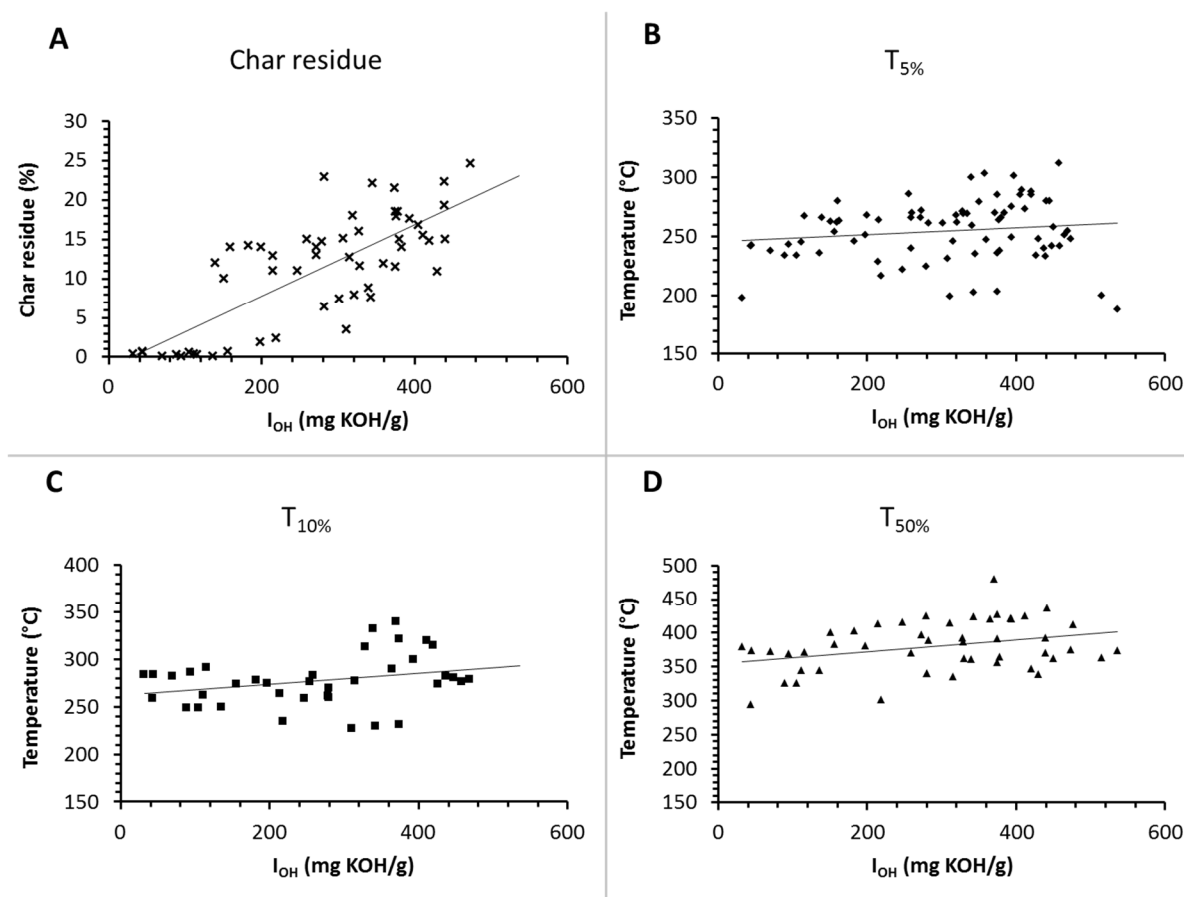


Fig. 21. Dependence of the char residue (A), weight loss at 5% (B), 10% (C) and 50% (D) on the I_{OH} of the polyol. The straight line represents the general trend of the data compiled from the literature.

Compilation of data from literature [97,102,103,106,108–110,131,136,138,140,163,164,259,260,279,290,309].

4.4.2. Activation energy

The activation energy of materials decomposition is directly related to the mobility of the chains. A very stable alkane structure forms the dangling chains in lipids-based polyols. Therefore, PUF realized with similar I_{OH} , but different dangling chain quantities had different thermal stability. The polyol prepared via ozonolysis, which reduced by 60%, the end chains had the fastest first loss at 335 °C compared to castor oil or epoxidized and ring-opened soybean oil-polyol (380 °C) [128]. On the contrary, the rigid structure formed by isosorbide polyol needs higher energy to initiate

decomposition [164]. The 3D structure of lignin, liquefied or alkoxyated, is stiffer than fossil-based polyol and degraded at higher temperatures [207,226].

4.4.3. Low molar mass compounds

Low molar mass polyols such as PEG or glycerol are introduced into foams via biobased polyols synthesis (e.g., alcoholysis of wastes, lignin liquefaction or dispersion) or as an additional polyol. Their thermal stability was also investigated; for example, PEG is known to enhance the thermal stability of foams due to the thermally stable ether bonds and the increase in crosslink density [130,138,209]. For example, the temperature of 50% weight loss shifted from 379 to 370 °C, with the integration of 0 to 100% of palm oil polyester polyol. The authors explained this trend by the decrease in PEG added as co-polyol [138]. In another study, foam realized with 40 wt% of EG had a higher LOI value (25%), than without (20%) [130]. Furthermore, the addition of crude glycerol increased the onset temperature in TGA measurements from 210 to 223 °C with 0 and 70 wt% of crude glycerol, respectively [140].

4.4.4. Molecular architecture

As introduced in the last section, the polyol structure plays a key role in the degradation of cellular materials. For instance, the presence of sulfur in the chemical structure of the mustard oil polyol increases the LOI value from 23 to 26% and thus, the thermal stability of the PUFs. Sulfur has several oxidation levels and is transformed into SO_2 and SO_3 acids in the decomposition process. This oxygen consumption, combined with the catalytic activity of these acids for the decomposition of a fire intermediate (ionic peroxide), inhibited the chain reaction of oxidation [100].

The epoxidation and further ring-opening reactions produced numerous lipids based polyols was previously detailed. To reduce the synthesis steps, 25 wt% of epoxidized oil were directly

introduced in PUFs formulations and compared to polyols formed one step further. The weight loss for the first degradation peak was improved from 45 to 40% with a polyol and with epoxidized oil, respectively. Some authors hypothesized the enhancement to originate from the formation of thermally stable oxazolidone groups [95]. However, the oxazolidone formation was not evidenced in PUFs with epoxidized oils.

Otherwise, polyester polyol based on sorbitol had a low onset temperature (170 °C) compared to conventional PUFs (200-250 °C). The authors explained that the ester scissions happen at lower temperatures than ether groups. Therefore, the decomposition of the soft segment is detected at a lower temperature in TGA [172].

Aromatic structures are well known to improve the thermal degradation with smoke production, which expands the char layer. This expanded layer is denoted as intumescent and protects the material from flame exposition and limits the transfer of oxygen toward the flame [324]. The improvement of thermal stability by an increased aromatic content was observed with tannins [149], lignins [212,225], PUFs wastes [136,257] and CNSL [287], for instance. Foam realized with oxypropylated tannin had a lower peak of heat released and propagation of the flame rates than oxypropylated glycerol. The authors explained that the aromatic structure of the tannin is coke forming. This hypothesis was supported by the measurement of the total smoke release, which was higher with tannin than glycerol-based polyol [149]. With 15 and 30 wt% of fractionated and alkoxyated lignin, the maximum loss rate was lower than without. Furthermore, the temperature at half mass loss and the residual mass at 800 °C was also higher than the reference foam. This degradation profile seems to be linked to the higher density of the aromatic structure.

It is well-known that the presence of thermally stable fillers increases the overall thermal stability of the foams by increasing the residue amounts [325]. The evolution of the foam flammability over the content of insoluble residue in the liquefaction mixture of the polyol is represented in Fig. 22. The trend was clear; the flammability decreased with the increase of insoluble residue (Fig. 22). The recalcitrant liquefaction residue of lignin improved the FR properties of the

PUFs made thereof. This improvement is explained by the inorganic components present in liquefied bark polyol [213].

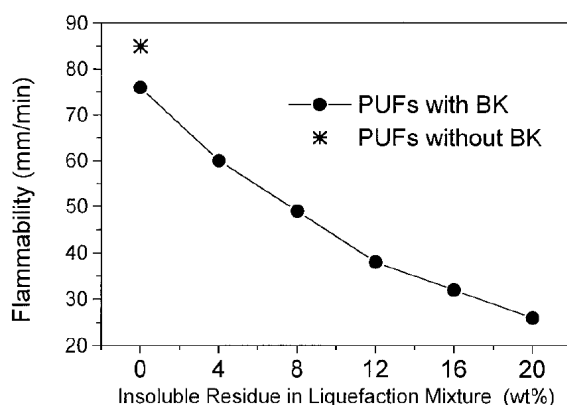


Fig. 22. Effect of the amount of insoluble bark residue on the flammability of PUF. Reproduced with permission from [213][211]

4.5. Some advanced properties

4.5.1. Glass transition temperature

The glass transition temperature (T_g) of a polymer is critical information to know the network better. In thermosets like PUFs, the α -transition temperature determined by temperature-dependent dynamic mechanical analysis in temperature is linked to the T_g determined by differential scanning calorimetry. Transition temperatures depend on the isocyanate index, cross-link density, aromaticity, plasticizer and PIR content in PUFs [326]. When phase separation occurred, two T_g are identified, the first one for the soft segment around $-50\text{ }^\circ\text{C}$ and the second for the hard segment found between 50 and $80\text{ }^\circ\text{C}$ in R-PUFs. The substitution of fossil-based polyol by a biobased one induces a change in the network structure, which can be seen by a T_g shift. The dangling chains and the long flexible structure of lipids based polyols are responsible for a plasticizing effect and a decrease in T_g [97,102]. The small reactants present for the polyglycerol formation are also plasticizers of the PUFs network [259]. Furthermore, the T_g heavily depends on the PEG length used to plasticize lignins [233]. The other

effect observed with biobased polyols is the correlation between the T_g increase and the augmentation in crosslink density explained by the reduced chain motions [26,103,128,318].

4.5.2. Acoustic property

R-PUFs are principally used in thermal insulation, and their acoustic properties are often overlooked because open cell structures are considered good sound absorbers. It was proved that lower closed cell content resulted in higher sound absorption [327]. However, foams based on palm oil with closed cell structure has been elaborated for such applications. High sound absorption coefficients (< 90%) defined as the ratio of the acoustic energy absorbed by the foam to the incident acoustic energy, were obtained. They explained that the damping effect from the increased urethane group content and network density dissipated sound energy into heat [313].

The R-PUFs properties can be affected by numerous factors represented in Fig. 23, and the structure of the components and the cell morphology are the dominant effects.

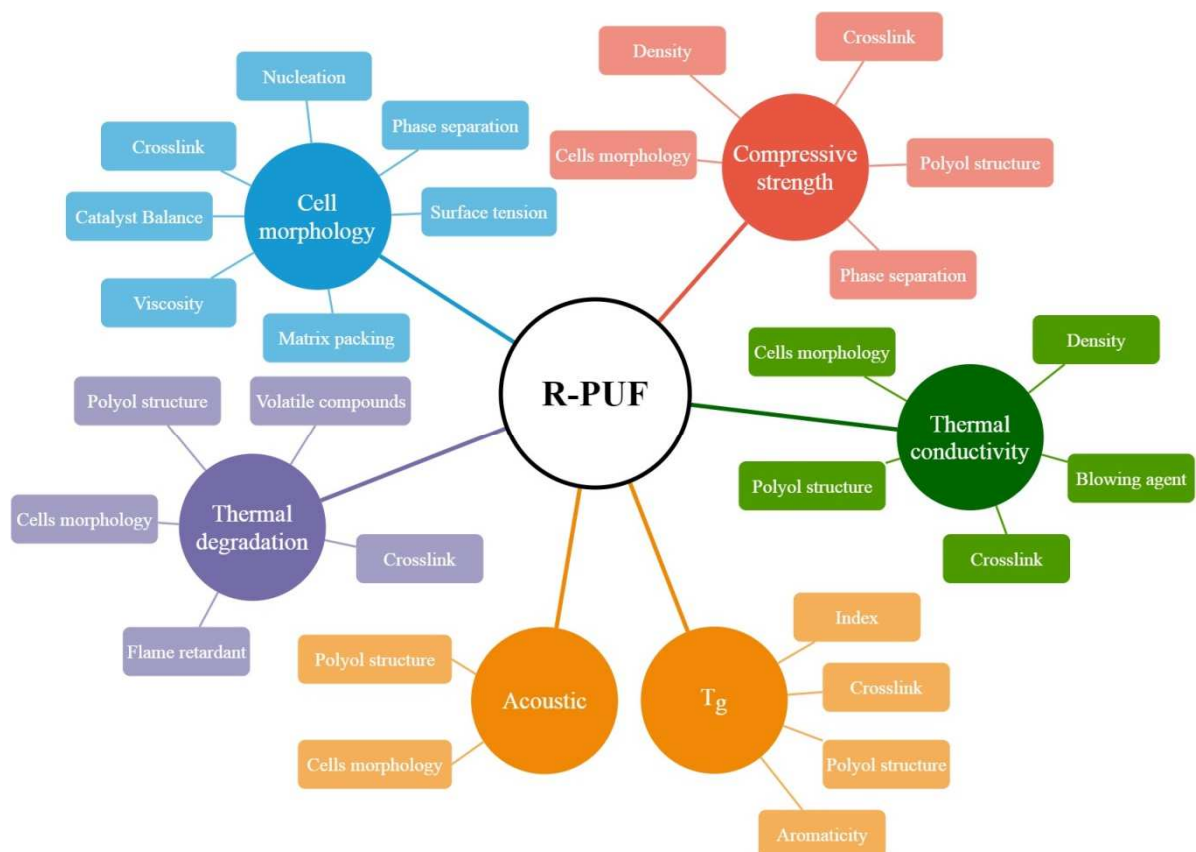


Fig. 23. Overview of the different factors affecting several properties (cell morphology, mechanical, thermal and fire resistance behaviors).

5. Perspectives on Biobased PUF

Polyols are one of the main biobased compounds used in PUFs formulations. However, it represents often less than 50 wt% of the PUF (Table 1). Another major component are the polyisocyanates, which are more rarely biobased. Besides, the toxicity for human health [328,329] of the isocyanate group is highly problematic. Moreover, their industrial synthesis is based on hazardous compounds (e.g., phosgene). The isocyanate reduction and elimination in the foam elaboration join the sustainability approach discussed in this review. In the next part, NIPU and other chemistries are outlined to produce greener biobased foams without isocyanate for a more sustainable and safe future.

5.1. Non-isocyanate polyurethane

Urethane groups are usually formed by addition of isocyanate and hydroxyl groups. However, several alternative pathways presented in Fig. 24 to form NIPU can be developed [330–334]. Carbamoyl chloride, ring-opening polymerization, chloroformate, aziridine and alkyl-carbonate routes presented in Fig. 24 involve precursors synthesized via toxic phosgene derivatives, or the precursor itself (e.g., aziridine) is hazardous [335]. Furthermore, all these routes require elevated temperatures. The polyaddition between cyclocarbonates and amines forming polyhydroxyurethane (PHU) networks can be carried out at ambient temperature, and no toxic phosgene is involved. Moreover, PHU precursors have manageable toxicity and can be conveniently obtained from a wide range of renewable and sustainable resources [14,330,335]. In the green chemistry frame, the cyclic carbonate route is the most sustainable pathway to obtain NIPU.

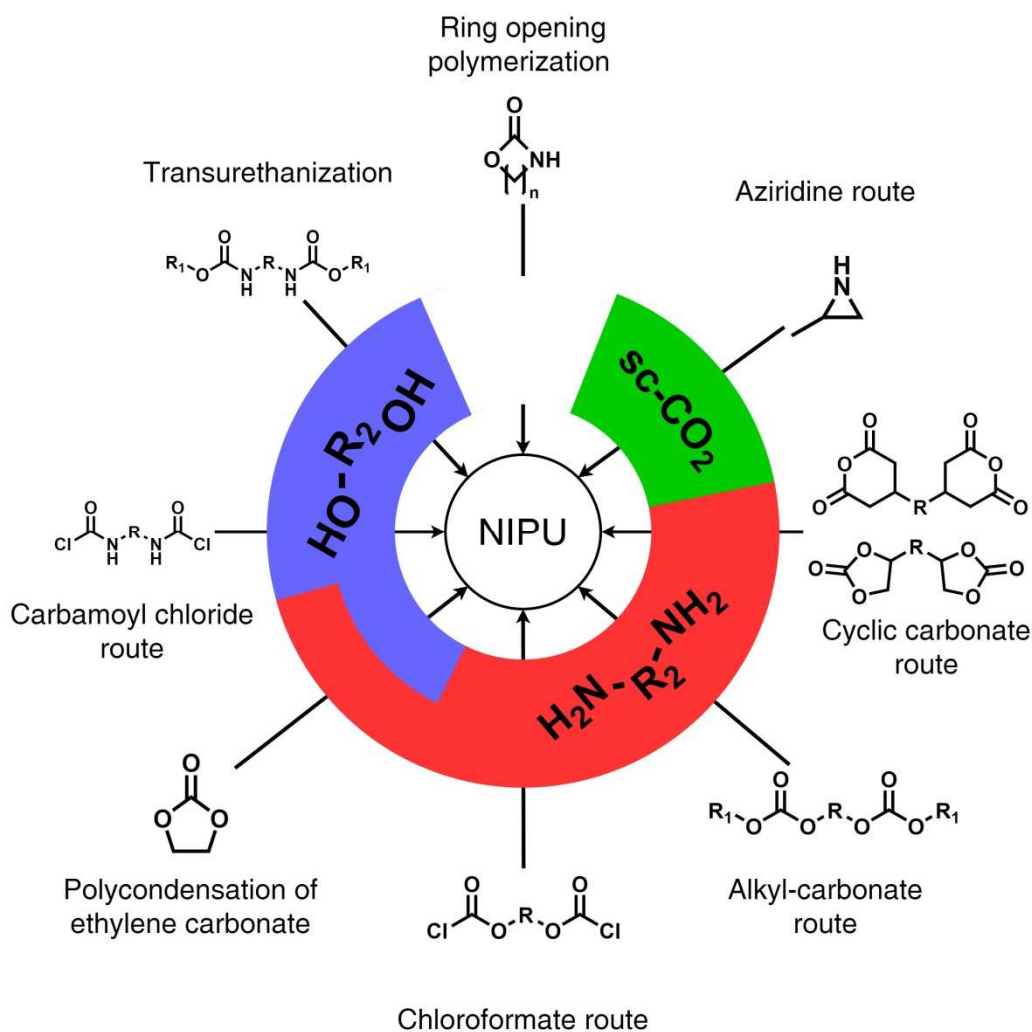


Fig. 24. Overview of the main synthetic routes to NIPU.

Fig. 24 shows that polyamines and 5 or 6-membered cyclic carbonates are the main building blocks toward a biobased PHU network. Although very few natural amines are available (i.e., chitosan and lysine), sustainable amines can be produced through various chemical processes from carbohydrate, lignins or oleochemical sources [80,81]. One promising route toward sustainable diamines was recently highlighted as dianiline was recovered from the enzymatic recycling of PUs [336].

Cyclocarbonates were initially synthesized from the reaction between diol and phosgene [337]. However, the current and industrial common pathway transforms epoxide into cyclocarbonates with high pressure of sustainable and naturally occurring CO₂ [14], for instance from

fermentation process. The production of fully biobased carbonates was achieved through the carboxylation of epoxidized oil [338,339].

In PHU synthesis, no difference in reaction conditions, kinetics, products, nor side reactions was observed between structurally similar biobased and fossil-based monomers [14]. Similarly to conventional PUs, the nature of the renewable source directly impacts the properties of the PHU. Therefore, the development of innovative molecular architectures extracted or bioproduced from various biomass types can bring new properties for the PHU networks. Very recently, the synthesis of the PHU network from carbonated biobased triglycerides and glycine was patented. The authors claimed similar mechanical properties as conventional PUs [340].

Figvosky patented the first NIPU solution to substitute conventional PUFs in 2004. In this study, acrylic NIPU was foamed by radical polymerization of acrylate with pentane as BA [341]. The first foam realized with the reaction between cyclic carbonate and diamine to obtain PHU networks was recently developed by Caillol and coworkers. The reagents were mixed with polymethylhydrogenosiloxane, which H₂ release after reaction with diamine and heated at 80 °C [342]. The corresponding foams were dense (200-300 kg/m³) compared to conventional PUFs. The method was improved by adding thiourea as a catalyst; therefore, the curing temperature was reduced until ambient [343]. The resulting foams were still dense (270-300 kg/m³). Furthermore, the open cells of the NIPU foams were coarser (300-1300 μm) compared to conventional PUFs (350-850 μm). Due to the bigger open-cells, the thermal conductivity was higher (100 vs. 67 mW.K⁻¹.m⁻¹), and the thermal stability was slightly inferior compared to the conventional PUFs.

The synthesis of closed and small cells NIPU foams was achieved with supercritical CO₂ at high temperature or high pressure. The samples were foamed by fast depressurization of the cell leading to a density of 110 kg/m³ with small pores (10 μm) and high thermal conductivity (50 mW.K⁻¹.m⁻¹) [344]. Mulhaupt and coworkers used a liquid hydrofluorocarbon to produce NIPU foams at 80 °C [345]. The authors produced dense foams (142 kg/m³) with cell size similar to R-PUFs (171 μm). Pizzi and coworkers developed self-blowing NIPU foams. The reaction was performed between a

synthesized glucose-NIPU with maleic acid and glutaraldehyde as a crosslinker. The soft foam was formed within 5 hours at ambient temperature [346]. Recently, self-blowing NIPU foams were elaborated by amine and thiol reaction with cyclo-carbonates catalyzed by 1,8-diazabicyclo[5.4.0]undec-7-ene [347]. As the reaction thiol-cyclocarbonate reaction forms hydroxythioether and carbon dioxide, thiol is used as chemical blowing agent. Unfortunately, as most of the other, these NIPU foams are slow to form, mainly open cells and flexible. In order to improve the mechanical properties of NIPU foams by aminolysis, rigid cyclocarbonate such as lignin could be used [348]. Another development axis toward green foams, could be the adaptation of new chemical BAs, a subject recently reviewed [349], to new polymers or formulations. However, the route toward a large substitution of R-PUF and F-PUF by NIPU foams or equivalents is still long.

5.2 Other potential approaches

The question linked to the future of the foams could be not only related to PU macromolecular architectures. As previously described, the formation of reactive foams needs an exothermic and fast reaction associated with a BA. The development of the well-known epoxide chemistry with epoxidized oil was widely investigated to produce foams [350–353]. Furthermore, some recent investigations raised some exciting new pathways toward biobased foams. The modification of soybean oil was achieved to introduce alkoxy silane groups. They were subsequently used in a Piers-Rubinsztajn reaction, which released methane to expand the polymer and produce foams. PDMS added as chain extender controls the density and Young's modulus of the produced foams [354]. Carbon-Michael chemistry has been investigated as a new way of foam elaboration. First, they quickly transformed polyols used in PUFs into poly-acetoacetate, a Michael donor, via transesterification. These new molecules were added into a mix of polyacrylates (Michael acceptor), surfactants, catalysts and physical BAs. The foams had entirely raised in less than 5 minutes, with more than 80% of closed cells and a low density of around 35 kg/m³ comparable to conventional

PUFs [355]. Another approach has been recently developed. A fully biobased foam with closed-cell was developed by Pelletier and coworkers, based on fungal mycelium. It was found to be promising fully biobased alternatives for acoustic shielding to the traditional fossil-based polymer based on synthetic fibers [356].

Acknowledgment

This study was funded by the Programme d'investissements d'avenir (PIA) of Bpifrance (Trans'alg Project).

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Curriculum Vitae

Julien Peyrton

Julien Peyrton obtained his Master's degree in chemistry with a specialization in polymer engineering in 2017 in the European Engineering School of Polymers, Chemistry and Materials in Strasbourg, France. He earned his Ph. D. in polymer science in 2020 at the Institute of Chemistry and Processes for Energy, Environment and Health – University of Strasbourg/CNRS in Strasbourg, France, under the supervision of Prof. L. Avérous. His interests cover several aspects of biobased chemicals and renewable polymer materials. During his doctoral studies, his research focuses on the synthesis of new biobased building blocks coming from micro-algal resources in order to develop cellular materials with new macromolecular architectures. Collaboration with the national institute for research and development in chemistry and petrochemistry in Romania led to the development of new olive oil based flexible polyurethane foams. He co-authored a publication in *Molecules* investigating the kinetics of the oil modifications toward the utilization in polyurethane synthesis and a publication in *ACS Sustainable* studying the impact of modified microalgae oil on rigid polyurethane foam.

Luc Avérous

Prof. Luc Avérous is a Group Leader (BioTeam), Head of the Polymer Research Department and former Lab Director at the ICPEES (UMR CNRS 7515) - Univ. of Strasbourg (France). In 2003, he became a full Professor at the ECPM (Strasbourg-France), where he teaches biopolymer science, biomaterials, composites, plastic processing & polymer characterization. Over the past two decades, his major research projects have dealt with biobased and/or biodegradable polymers. As a leading international expert in these fields, he has developed strong collaborations with several foreign labs (Australia, Brazil, Canada, Spain) and major companies. He serves as a member of research advisory boards for several different companies. In France and overseas, he is regularly invited to co-organize conferences, to chair symposia, and to give plenary/keynote lectures. He has co-edited 4 books (2 Wiley, 1 Elsevier & 1 Springer). He is a member of the editorial board and/or guest Editor for several scientific journals. He is also a referee for many scientific journals, books and international projects. He has published hundreds of scientific communications such as 16 review articles, with more than 11,000 citations (H-Index = 48 – Scopus data).

Figures captions

Fig. 1. Examples of F-PUF (Left) and R-PUF (right) applications.

Fig. 2. Main isocyanate reactions with H-labile groups.

Fig. 3. Effect of the NCO/OH index on the chemical architectures of PUF, PU-PIR and PIR foam networks.

Fig. 4. Detailed usual processes at lab scale for PUF elaboration: pour-in-place or molding process.

Fig. 5. Representation of silicone surfactant. Adapted from [57].

Fig. 6. Illustration of the significant perturbations in foam cell formation, with or without surfactant.

Fig. 7. Catalysts structures ranked according to their main activities in the foam formulation. Adapted from [70].

Fig. 8. Viscosity profile associated to the cell bubbles formation.

Fig. 9. Triglyceride structure and the most abundant fatty acids in vegetables, seeds and microalgae oil.

Fig. 10. Overview of the main oleochemistry pathways for the elaboration of different PUF components.

Fig. 11. Overview of the transformation of main carbohydrates into different PUF components.

Fig. 12. Composition of lignocellulosic resources and classification of main polyphenols: tannins and lignins. Adapted from [189].

Fig. 13. Overview of the transformation of lignins and tannins into PUF components.

Fig. 14. Overview of the transformation of wastes from industrial processes into PUF components.

Fig. 15. Overview of the transformation of products from biotechnology into the PUF component.

Fig. 16. Viscosity of polyol vs. the cell size for PUF. Compilation of data from literature [95,99,100,104,107,108,129,134,136,138,161,162,257,277,288,307].

Fig. 17. Effect of the gelling/blowing balance vs. temperature, viscosity and foam cell morphology in three typical cases: (A) mainly blowing, (B) equilibrium and (C) mainly gelling.

Fig. 18. (A) Effect of the introduction of lignin-based polyol on the density and compressive strength of PUF. (B) Dependence of the compressive strength on density. Reproduced with permission from [205] and [314].

Fig. 19. Effect of lignin addition on the compressive strength of R-PUF. The ratio of lignin to polyol, the molar ratio of the OH groups from lignin. Hardwood ethanol organosolv lignin (HEL) and hardwood kraft lignin (HKL). Reproduced with permission from [237].

Fig. 20. (A) Dependence of the heat conductivity on porosity modeled with cell size of 300 μm and filled with air (B) Thermal conductivity evolution over 900 days of PUF and PUF modified with 1.5% of talc. Reproduced with permission from [45] and [320].

Fig. 21. Dependence of the char residue (A), weight loss at 5% (B), 10% (C) and 50% (D) on the I_{OH} of the polyol. The straight line represents the general trend of the data compiled from the literature.

Compilation of data from literature [95,100,101,104,106–108,129,134,136,138,161,162,257,258,277,288,307].

Fig. 22. Effect of the amount of insoluble bark residue on the flammability of PUF. Reproduced with permission from [211].

Fig. 23. Overview of the different factors affecting several properties (cell morphology, mechanical, thermal and fire resistance behaviors).

Fig. 24. Overview of the main synthetic routes to NIPU.

Table captions

Table 1. General foam formulation with quantities expressed in part by weight of the polyol.

Table 2. Relative reactivity of isocyanates with alcohol groups for the 1st and the 2nd additions.

Adapted from [29].

Table 3. Main requirements on polyols properties for F-PUF and R-PUF. Adapted from [11,31].

Table 4. Relative reactivity of hydrogen active compounds without catalyst. Adapted from [31].

Table 5. BA structures, name physical properties and global warming potential (GWP). Data from literature [43,46–52].

Scheme captions

Scheme 1. The first synthesis of carbamate by Charles Adolf Wurtz. Adapted from [28].

Scheme 2. Metathesis and cyclization reactions.

Scheme 3. Isosorbide production pathway from sorbitol.

Scheme 4. Synthesis of diisocyanate from β -pinene. Adapted from [297].