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Origin and Industrial Applications of Lignosulfonates with a Focus on their Use as Superplasticizers in Concrete

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Abstract

In concrete technology, superplasticizers (SPs) are commonly used to reduce water content in concrete admixtures. Although most of them are fossil fuel-based, some derive from lignosulfonates (LS), that are sustainable and environmentally-friendly polyphenolic crosslinked polymers. Indeed, LS are an inexpensive and abundant raw material that contains a variety of functional groups including hydroxyls which can be involved in a wide range of chemical modifications to finely tune the physico-chemical properties of the material. This review presents: (1) the current SPs and their mechanism of adsorption and dispersion as admixtures to improve the properties of fresh concrete (e.g., workability, fluidity,

setting time and water reducing ability) and that of hardened concrete (e.g., compressive and flexural strength), (2) LS origin and structure, (3) the various LS functionalization methods reported in the literature since 2000, and (4) their corresponding applications in the different fields such as water depollution, dispersant, superadsorbant, antioxidant, material replacement, and more specifically as water reducers for concrete. A special focus is made on the cement-SPs interactions and the impact of the modified-LS structures on the efficiency of concrete. This review aims at demonstrating that, in the context of green chemistry, biorefinery and bioeconomy, sustainable chemical modification of low cost and abundant LS is a worthwhile approach to design materials that find applications in critical industries such as the concrete sector.

Introduction

High-range water reducers, better known as superplasticizers (SPs), are concrete admixtures used in construction industries as dispersants for aqueous mineral suspensions in order to alter the properties of fresh and hardened materials. SPs affect the physical properties of these materials such as rheology, workability, compressive and flexural strength. Moreover, their chemical structures impact the adsorption, conductivity and zeta potential of the fresh concrete. A number of reviews have described the research carried out in the development of concrete admixtures and the structure-properties relationships.[1-3] For instance, Khudhair et al.[1] described the various chemical admixtures used as formulations for building materials. Houst et al.[2] discussed the several parameters considered in the calculation of interparticle forces in cementitious suspensions. Furthermore, Mollah et al.[3] covered the interfacial structure, properties and effects of SPs structure on the cement-SPs interactions. All these reviews explained the action of SPs admixtures during the hydration of cement particles, i.e., the setting phase of cement where the concrete turns from fluid to hard.

However, due to the rise of environmental awareness caused by the continuous use of fossil fuel resources, the demand of renewable and natural products is greatly increasing. Indeed, the vast majority of SPs used as concrete admixture are fossil fuel-derived (e.g., polycarboxylate ether). Thus, the transition from current non-renewable SPs to new sustainable materials is highly needed. In this context, lignosulfonate (LS), a renewable byproduct of wood pulp production, holds tremendous potential for the synthesis of biobased SPs.

The scope of this review is mainly focused on the reported modifications of LS since 2000 with a special attention to the applications of these modifications in the field of concrete industry. For a better understanding of the structure-properties relationships, the action of SPs is described while explaining the interaction between concrete and SPs molecular structures. Furthermore, a state-of-the-art is given on the most common SPs employed for building applications.

Action mechanisms of SPs and interaction with concrete

The main role of SPs is to reduce the amount of mixing water, known as water reduction, while improving or maintaining the workability of concrete by retarding agglomeration. Having an excess amount of water during the concrete hardening leads to the creation of porosity after partial water consumption/evaporation. This can limit the strength and durability of the concrete. Concisely, SPs adsorb on the surface of the cement particles due to the presence of calcium ions at the interface between the cement particles and the interstitial solution (Figure 1a). Firstly, thanks to their negative charges, the attractive forces between the aggregates are reduced, and flocculation is limited (electrostatic hindrance). Moreover, the newly formed layer of SP hinders the diffusion of calcium ions into the matrix by complexation - an important

step of cement hydration - thus retarding the entire process and changing the setting time. Secondly, with the most recent generations of SPs, hydrosoluble side chains such as polyethylene oxide (PEO) are grafted on the polymers in order to achieve a better dispersion. Indeed, the added side chains can be deployed in water due to their affinity and interpenetrate each other. Such interpenetration increases the repulsive force of the “hairy”-like chains which improves the dispersion of cement-SPs aggregates in the system while avoiding flocculation. This is called the steric (or entropic) effect (Figure 1b). All these changes brought by efficient SPs improve the rheological behavior of the fresh concrete and allow good workability without the need for an excess amount of water.

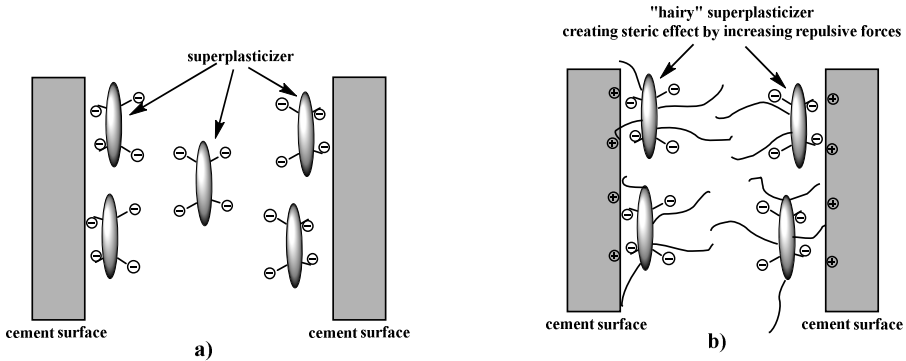


Figure 1: a) Classical adsorption of SPs on the cement surface, b) entropic effect

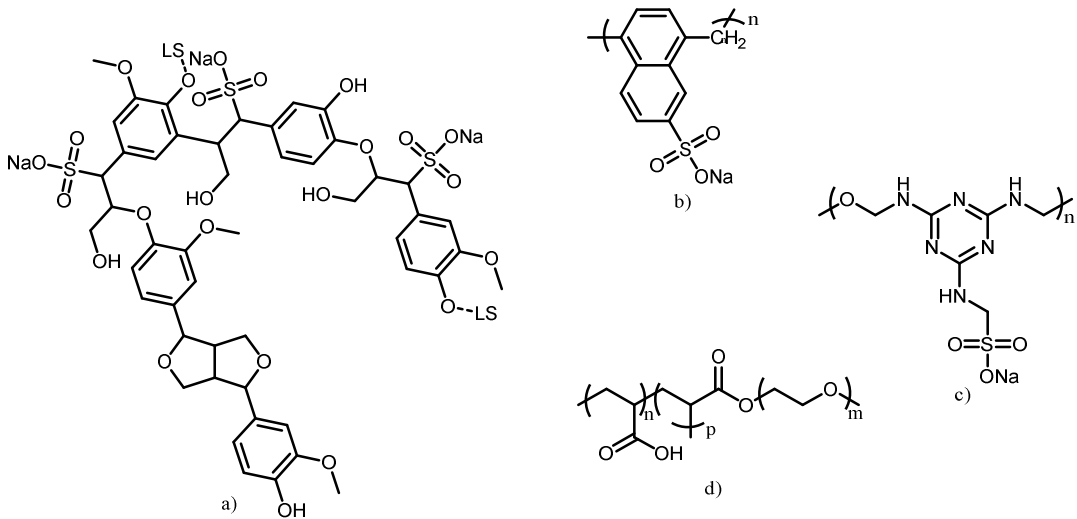


Figure 2: Structural representation of a) LS, b) PNS, c) PMS, d) PCE

Evolution of Superplasticizers

SPs and simple plasticizers are hydrosoluble polymers that can be natural, such as LS, or synthetic such as polynaphtalene sulfonate (PNS), polymelamine sulfonate (PMS) and polycarboxylate ether (PCE), the most common polymers used for this purpose (Figure 2). According to the NF EN 934 French regulation, SPs - such as PCE - reduce water by more than 12%, whereas the range of water reduction for simple plasticizers such as LS is 5-12%.

LS was the first tested polymer exhibiting good adsorption, i.e., an electrostatic repulsion effect. This natural polymer was used without any modification in the 1930s owing to its high availability and low cost.[4],[5],[6] However, LS showed a limited water reduction capability of 8-10%.[4] Although LS is among the cheapest admixtures present in the market, such low water reduction prevented its usage to design high-performance concrete. Consequently, constant investigations showed that increasing the molecular weight (M_w) of LS to 80 kDa leads to an increase in the water reduction to reach 20% and improves the workability retention.[4]

In the same period, PNS was developed for textile chemicals and synthetic rubbers. PNS was later found suitable for their use as a water reducer in the 1960s[6] due to their dispersing effect.[7] Aside from improving the workability and water reduction, PNS brings a certain resistance to freeze-thaw cycle for concrete.[8]

Later, PMS was discovered in the 1970s. Although the plasticizing ability and water reduction of PMS are comparable to that of PNS, PMS provides higher slump loss, i.e., a decrease in fluidity, while bringing less retardation during cement hydration.[9] Nevertheless, because of the negative impact on the environment due to the residual formaldehyde (Volatile Organic Chemical, VOC) liberated during the hardening[10] and the lack of diversity in the number and types of the monomers used, these synthetic polymers were replaced.

In the late 1980s, polyacrylate-based polymers appeared as interesting candidates due to the large variety of the constituting monomers,[6],[11],[12] and led to the development of polycarboxylate ether (PCE). PCE is composed of: (1) a backbone chain assembled through the radical polymerization of vinylic acid such as acrylic acid, maleic acid or methacrylic acid, and (2) side-chains such as polyethylene oxide (PEO) or polypropylene oxide (PPO). The dispersing abilities of these polymers principally come from the non-adsorbing side chains that create an entropic effect and lead, in the case of PCE, to a water reduction of around 40%. Moreover, PCE improves the slump life, in addition to the retardation of the hydration process. In fact, the performance of PCE depends on many parameters including the length, chemical nature, distribution, anionic charge density of both backbone and side-chains.[13],[14] Several reviews on PCE have been published in the last few years and show how rapidly this field has been evolving.[15],[16] Nevertheless, PCEs, as well as PNS and PMS, are mainly obtained from non-renewable fossil fuel feedstocks which necessitate their replacement by new biomass-derived substitutes. Indeed, in the context of the revolution of circular economy, special considerations are being directed to make products from biomass by-products such as LS. Nonetheless, in most cases, such renewable materials suffer from the poor properties that need to be improved to comply with the applications sought in the industrial sectors such as

concrete. For instance, although LS was used previously for the presence of sulfonate groups that enhance its solubility in aqueous solution, unmodified LS does not provide concrete with efficient properties due to the lack of entropic effect.[2] For this reason, various research groups have dedicated great efforts to modify the LS through the functionalization of the reactive groups present in their structure (e.g., phenolic groups, alcohols). [32],[33],[70],[79],[88],[89][92],[93] Such an approach can improve the properties of LS and widen its range of applications as a cheap and abundant biobased product.

Structure, characterization and production of lignin derivatives

Lignocellulosic biomass is the most abundant natural resource on Earth. It contains lignin that can be extracted by the wood-pulp industries for industrial and academic use.[17] Lignin, and all its technical derivatives such as LS, have very complex and heterogeneous structures that are not only based on three constituting phenolic monomers (monolignols: coniferyl alcohol, coumaryl alcohol, and sinapyl alcohol; Figure 3), but also strongly depends on the plants/tree species and environment. As represented in Figure 4, monolignols can connect to each other through various covalent linkages, namely α -O-4, β -5, β -O-4, 5-5, 4-O-5, β -1 and β - β bonds. The proportions of the monomers and that of the different strong C-C and labile C-O-C linkages greatly depend on the origin of lignin (e.g., softwood or hardwood).[18] The characterization of lignin was thus a great challenge to tackle due to the complexity of the crosslinked structure of lignin and the diverse occurrence of monomers and linkages. Continuous investigations showed how lignin main structure can be more precisely determined through spectroscopy (UV, FTIR, ^{31}P -NMR, ^1H -NMR, ^{13}C -NMR and 2D-HSQC-NMR) and size exclusion chromatography (SEC) that provide crucial insights on the structure and M_w , respectively [19],[20],[21],[22].

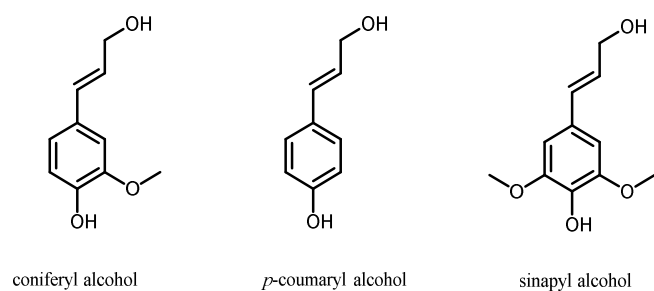


Figure 3: The three constituting monolignols in lignins

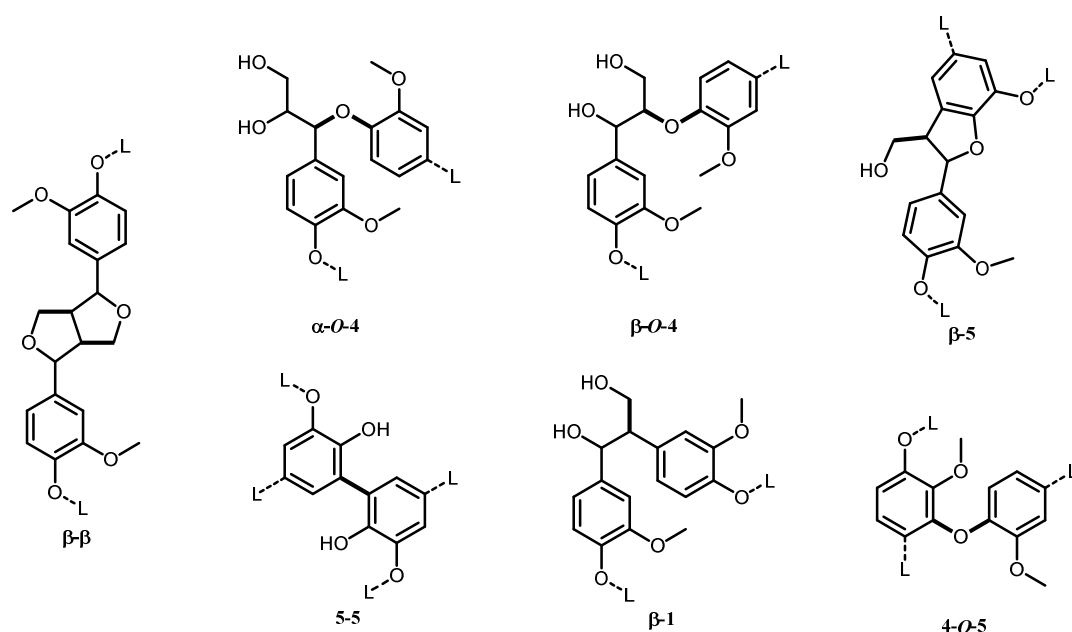
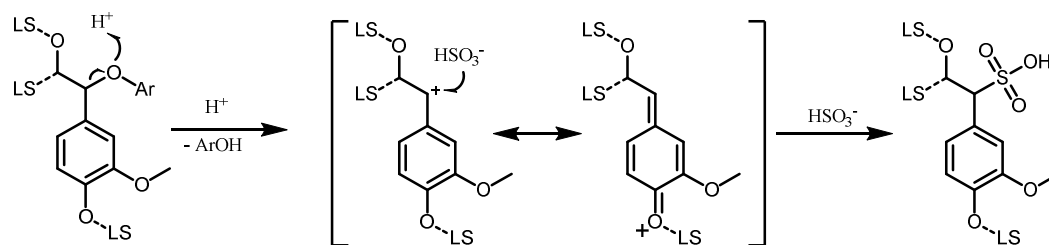


Figure 4: Possible linkages of lignin

LS are obtained through the sulfite pulping process (Scheme 1),^[23] that was integrated into a biorefinery for the first time in the 1990s.^[24] The degradation mechanism of lignin into LS starts with the acid-catalyzed cleavage of the β -*O*-4 linkage that creates a benzylic carbocation intermediate while reducing native lignin M_w . The transient carbocation then undergoes a nucleophilic attack by a sulfite to provide LS. The spent sulfite liquor obtained through this

process contains lignosulfonate as well as mono/oligosaccharides and acetic acid. Finally, the process ends with extraction to provide pure LS.

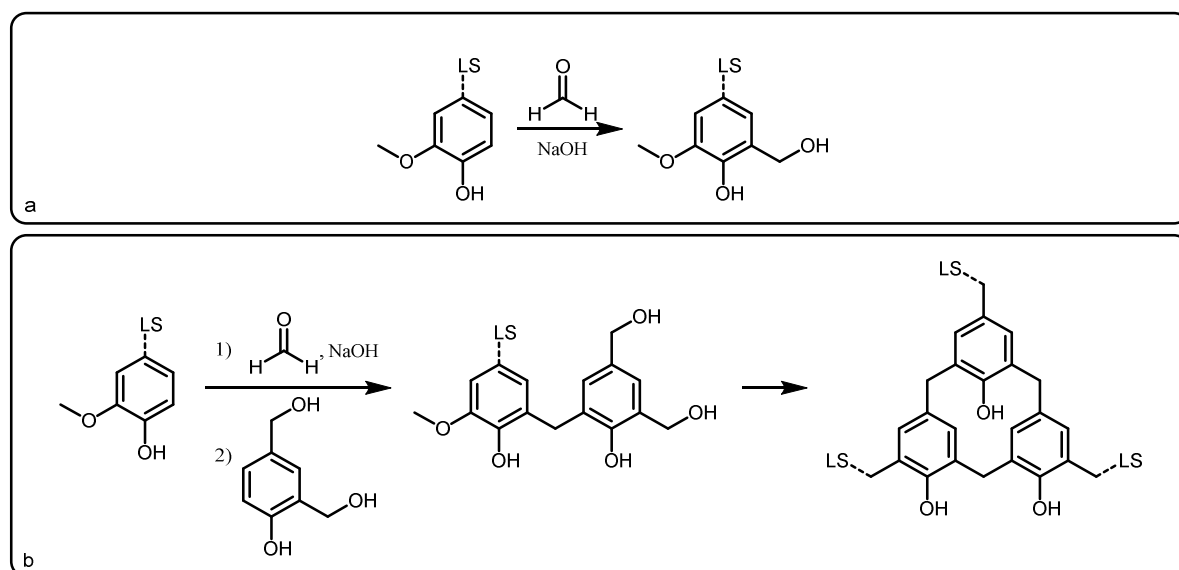


Scheme 1: Mechanism of the sulfite process

Methylation

Methylation, also known as hydroxymethylation, is an old and classical way to functionalize LS. The Lederer Manasse reaction is used to add new aliphatic hydroxyl groups on the phenolic structures in presence of formaldehyde under basic conditions (Scheme 2a). Alonso et al.[25] reported that softwood LS is preferable for an efficient methylation reaction to occur due to the higher number of aromatic protons and phenolic hydroxyl groups compared to hardwood LS. This reaction was employed by different research groups to access a wide variety of products. For instance, Yamini et al.[26] used it to prepare epoxy resins, Bai et al.[27] for urea-formaldehyde polymer, Wang et al.[28] for phenolic resin, and Yanhua et al.[29] for grafting aliphatic polyamine by a one-pot reaction on LS in the presence of sodium hydroxide and formaldehyde. Other researchers such as Wang et al.,[30] used a dialdehyde (*e.g.*, glutaraldehyde) instead of formaldehyde to crosslink triethylenetetramine and LS in order to create an adsorbent for dye molecule.

This formaldehyde-mediated reaction can be useful to create nanosphere by crosslinking LS with other molecules. Pandey et al.[31] synthesized a nanosphere for biomedical and environmental use by crosslinking LS and chitosan in presence of formaldehyde and sulfuric acid. Wang et al.[28] reported the crosslinking of phenol with LS to prepare core-shell microspheres for highly efficient removal of cationic dyes from aqueous solution (Scheme 2b).



Scheme 2: (a) methylation of LS, (b) synthesis of resin phenol-LS

Sulfonation

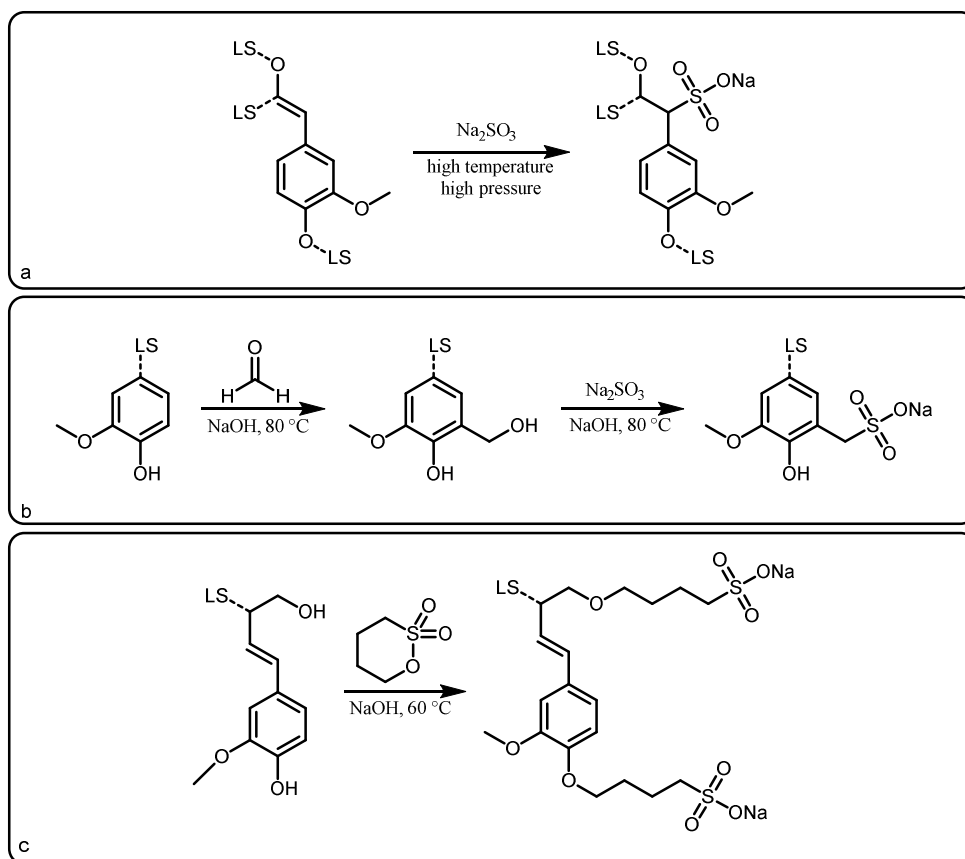
The sulfonate content is an important parameter to consider if one wants to improve some properties related to the adsorption phenomenon. This parameter can be improved according to three main approaches.

The first one was developed to turn classical lignin into sodium LS in the presence of Na₂SO₃ at high temperature and high pressure (Scheme 3a). This approach is similar to the sulfite process previously described in Scheme 1, except that the M_w is not affected because

the sulfonate groups are grafted on the benzylic double bond in the presence of Na_2SO_3 rather than breaking it.

The second sulfonation approach relies on the new hydroxyl groups formed by methylation. These groups can be employed to access LS having higher sulfonate content compared to the synthesis reported in the first strategy thanks to the increased number of hydroxyl groups (Scheme 3b). For example, Yu et al.[32] and Wu et al.[33] performed such modification of LS to produce LS-based SP. Furthermore, Yanhua et al.[29] and Li et al.[34] studied the effect of sulfonate content on the surface activity, and showed that the latter increases when LS was used instead of kraft lignin.

Recently, Qiu et al.[35],[36] developed a third approach to significantly improve the sulfonate content and studied the dispersion properties of the resulting material. In this reaction, cyclic 1,4-butanedisulfone is opened by the phenolic and aliphatic hydroxyl groups of the LS in the presence of sodium hydroxide (Scheme 3c). It is noteworthy to mention that no formaldehyde, which is a highly toxic and volatile, is required in this approach.



Scheme 3: (a) classical way for modification of lignin into sodium liginosulfonate, (b) sulfomethylation, (c) sulfobutylation

Lee et al.[37] found a method to obtain a sulfonated material from LS by treating it with a large excess of sulfuric acid at high temperature (<200 °C). The resulting product is represented in Figure 5. It was tested as a catalyst for classical esterification reactions.[37]

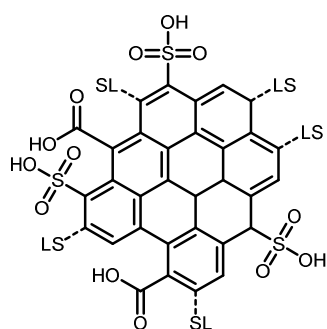


Figure 5: The resulting product from LS under concentrated sulfuric acid (<200 °C)

Esterification

One of the best methods to improve LS properties is to perform the esterification of the aliphatic and phenolic hydroxyl groups, as well as the carboxylic acids.

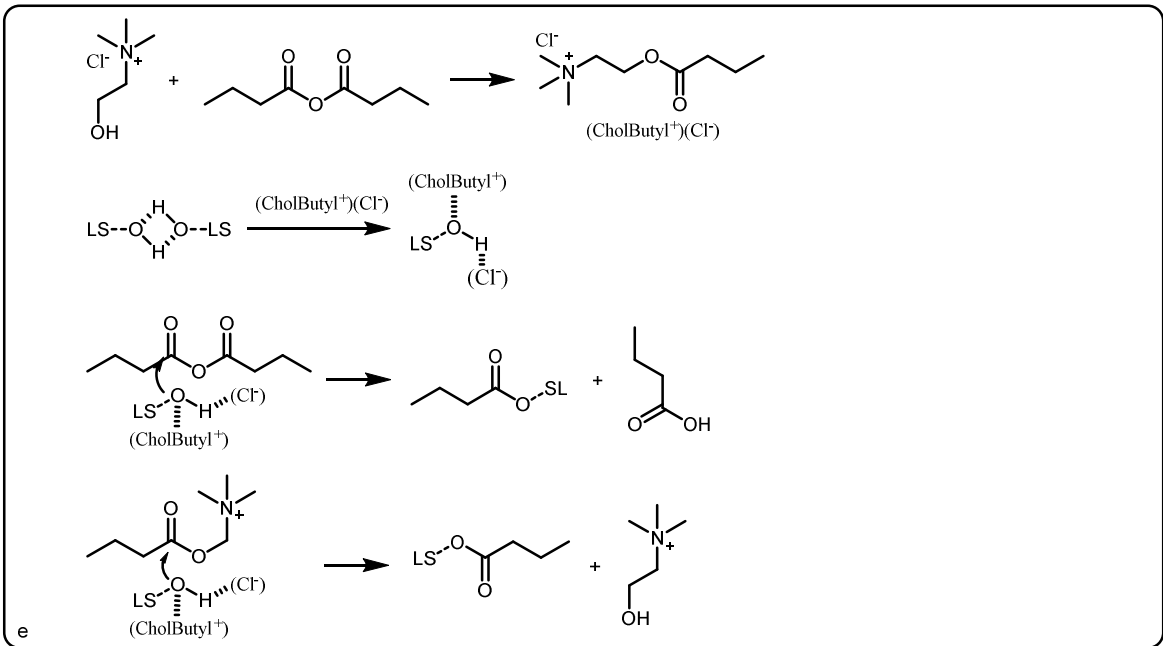
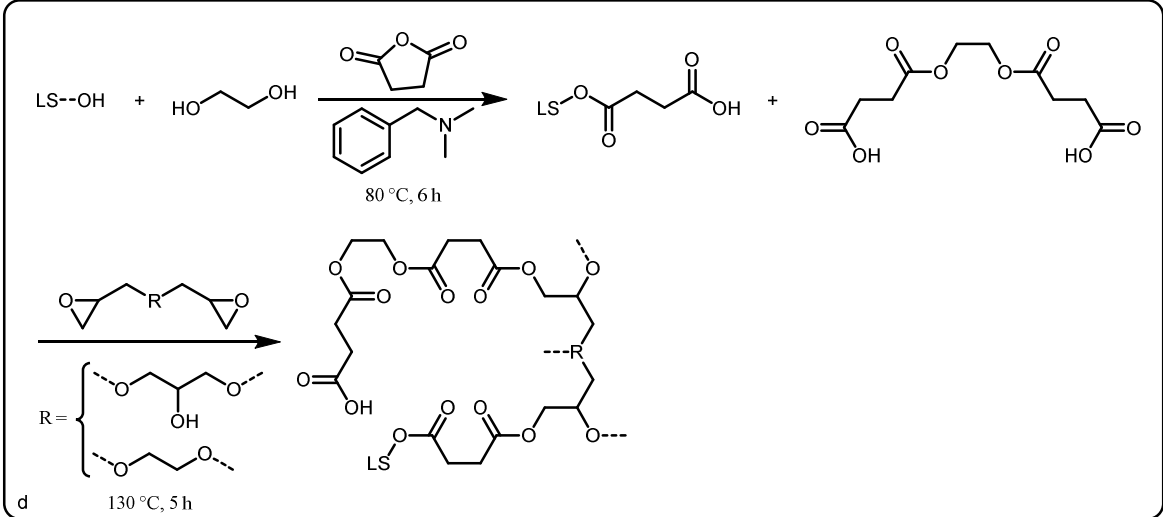
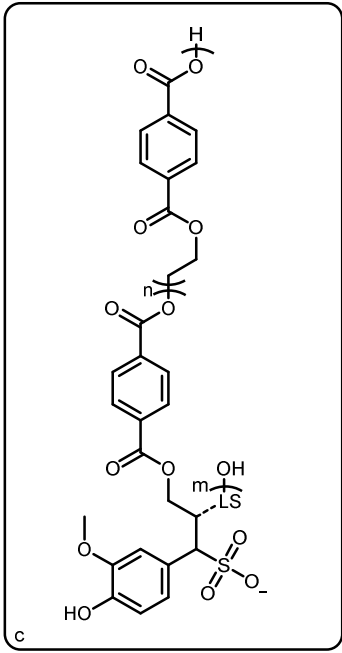
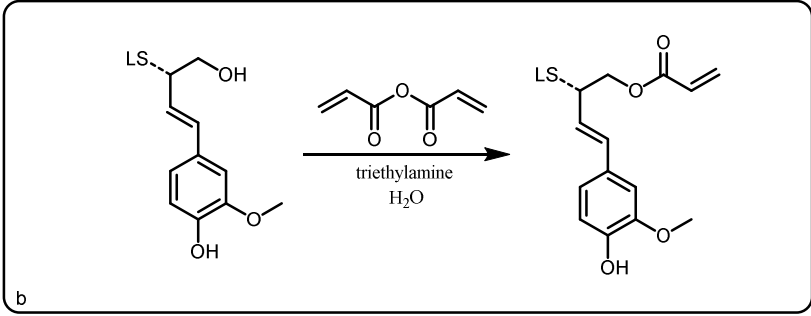
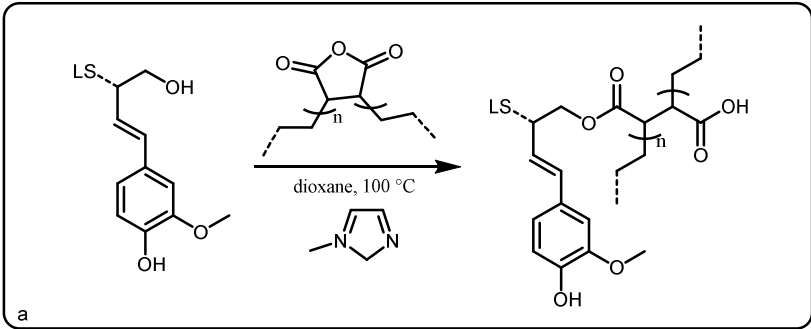
LS can be used as a biomass-derived building block to prepare renewable materials, such as hydrogels, by grafting prepolymers on it. Wang et al.[38],[39] used maleic anhydride under basic conditions to improve mechanical and thermal properties of LS in LS/poly(ϵ -caprolactone) blends. Similarly, Panzarasa et al.[40] used a copolymer - poly(ethylene-*alt*-maleic anhydride) - allowing to graft different functions in a one-pot reaction (Scheme 4a).

Another way to obtain hydrogels through the esterification of LS was explored by Jin et al.[41] who used esterification to graft chemical groups bearing a double bond such as methacrylic anhydride. This newly formed acrylate was then subjected to radical polymerization (Scheme 4b).

Polyethylene terephthalate (PET), which is produced from the esterification of ethylene glycol (EG) and terephthalic acid (TA) using Sb_2O_3 as a catalyst, is one of the most used commodity polymers. Ma et al.[42] reported a novel family of PET/LS copolymers containing 0.5%w/w to reinforce the mechanical and dielectric properties of PET. Nevertheless, they showed that the amount of LS must be kept as low as 0.5%w/w otherwise an excessive amount of LS would have a detrimental effect on the mechanical properties of PET. The molecule is represented in Scheme 4c.

Moreover, Ismail et al.[43] developed adhesives through the esterification of succinic anhydride, EG and LS to prepare a prepolymer to which glycerol diglycidyl or ethylene glycol diglycidyl ether were subsequently added to crosslink the structure (Scheme 4d).

Li et al.[44] replaced sodium alkanoate, a hazardous catalyst, by a greener natural catalyst, *i.e.*, choline chloride, in the esterification of LS with butyric anhydride[45]. Choline chloride disrupts the hydrogen bonds in the LS structure thus increasing its solubility and catalyzing the esterification reaction. This reaction can be considered as a green method for the esterification of a natural polymer, such as LS, as it uses cheap and environmentally friendly reagents (Scheme 4e).



Scheme 4: (a) esterification of LS and poly(ethylene-alt-maleic anhydride), (b) esterification of LS with methacrylic anhydride, (c) PET with LS as diol, (d) synthesis of LS-based adhesives, (e) the mechanism of the green butyration of LS

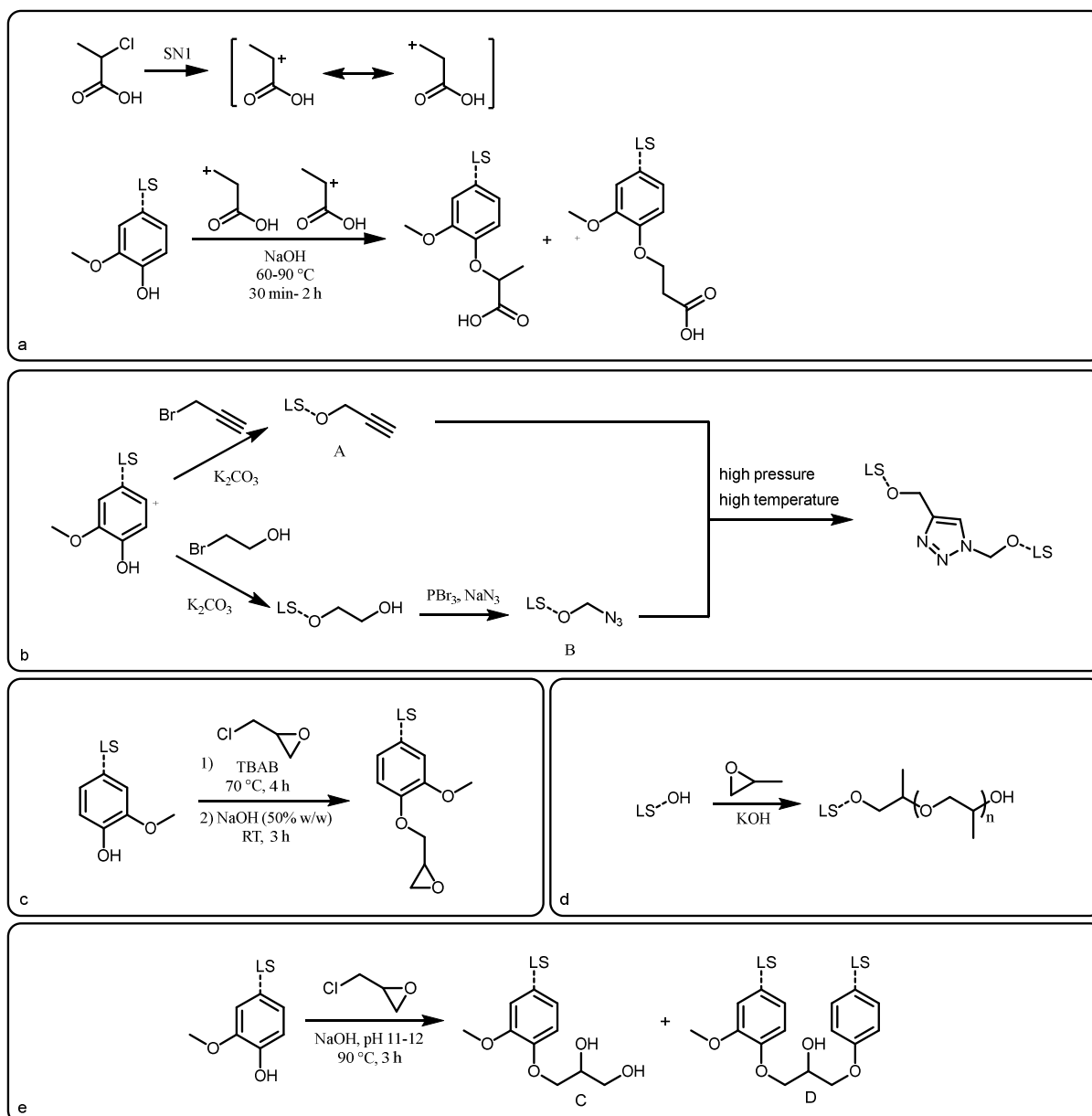
Etherification

Etherification is also a common way to functionalize LS by creating a strong carbon-oxygen bond that can withstand harsh conditions such as high pressure, high temperature, and strong acidic and basic media. Generally, halogenated compounds are used to easily create ether bonds with phenolic and aliphatic hydroxyl groups through Williamson etherification. Barhpaima et al.[46] etherified phenol-protected LS with 2-chloropropionic acid to obtain carboxyethylated LS and thus extended the possible applications of the modified LS by replacing the aliphatic groups with reactive carboxylic acid (Scheme 5a). Empire Technology Development LLC[47] developed LS-based adhesives by etherifying LS with propargyl bromide and 2-bromoethanol to form molecules A and B, respectively (Scheme 5b). The latter was reacted with phosphorus tribromide and sodium azide to transform the primary alcohol into an azide. A and B can react through click-chemistry under mild pressure conditions (Scheme 6b).

A well-explored approach to etherify LS is the functionalization of LS through glycidylation, followed by the opening of the resulting epoxide with different molecules. It is a two-step reaction: first, a phase-transfer catalyst (e.g., tetrabutylammonium bromide) is added to LS and epichlorohydrin to generate phenolates in solution, thus allowing the ring-opening of epichlorohydrin. Finally, in a second step, sodium hydroxide is added to close the

opened oxirane on LS. A SN_2 mechanism on the carbon bearing the chloride is also possible to directly obtain the resulting oxirane. Yamini et al.[26],[48] reported the glycidylation on LS to synthesize polyurethane (PU) (Scheme 6c). De Oliveira et al.[49] also used epoxide to prepare PU by oxypropylation of LS as depicted in Scheme 5d.

In an attempt to reduce the adsorption capacity of LS to use it as a dye dispersant, Yu et al.[50] used epichlorohydrin at 90 °C and under basic conditions (pH 11-12) to etherify the phenols (Scheme 5e). Other research groups focused their work on lignin at a lower temperature (70 °C),[51] to obtain epoxidized lignin which can be compared with Yu's results who assumed that when a relatively small amount of epichlorohydrin was added at low pH, the reaction between lignin and epichlorohydrin yielded product C (Scheme 5e). On the other hand, increasing the pH and amount of epichlorohydrin led predominantly to product D (Scheme 5e).[50]



Scheme 5: (a) carboxyethylation of LS, (b) synthesis of a two-component adhesive (A and B), (c) epoxidation of LS, (d) oxypropylation of LS, (e) etherification of LS by epichlorohydrin under hard conditions

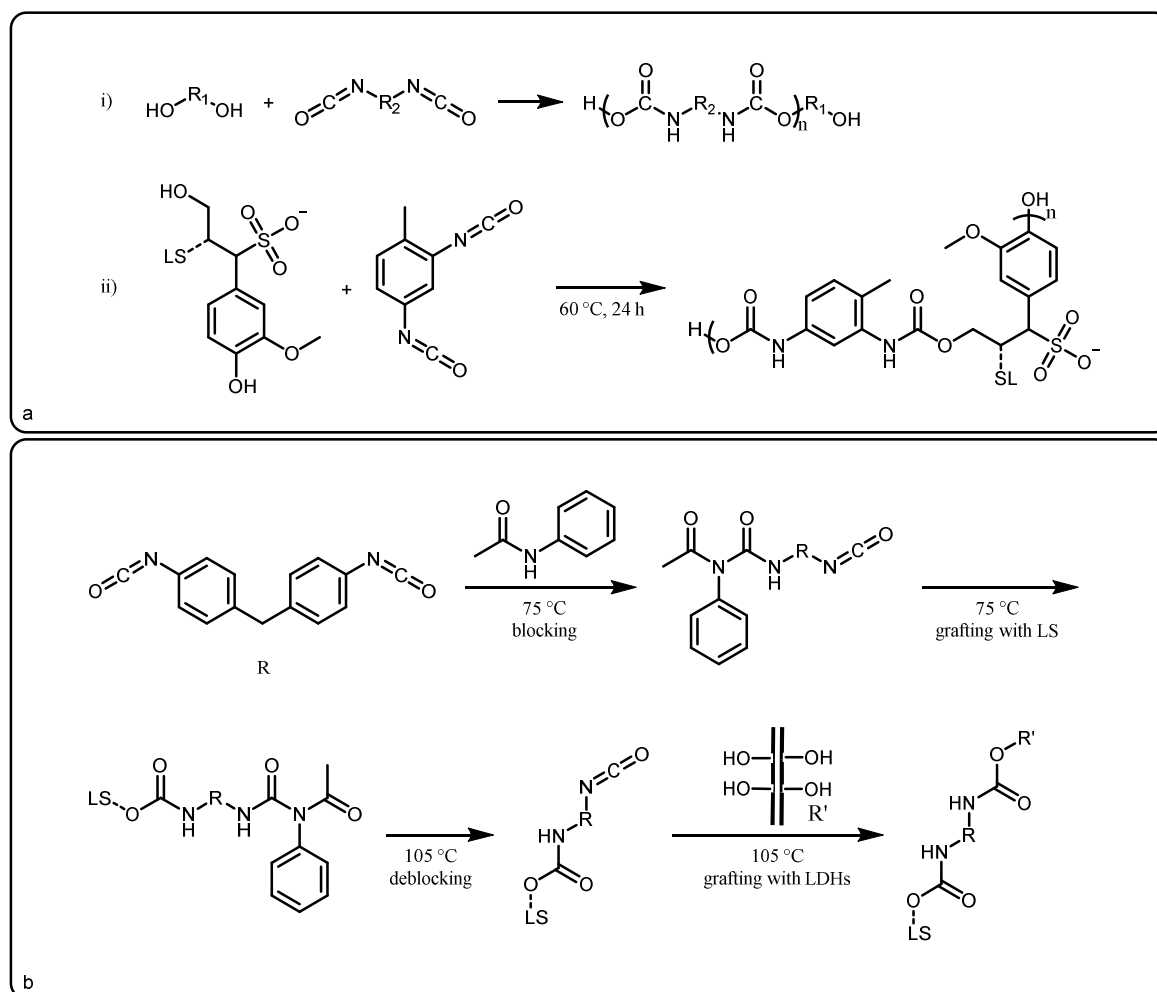
Polyurethane

PU is an efficient material used in many applications such as thermal isolation or foams. PU can be prepared by the reaction of two reactive monomers, a diol and a diisocyanate, as illustrated in Scheme 6a(i). Interestingly, Leitner et al.[52] used LS as a polyol to synthesize PU by mixing LS with toluene-2,4-diisocyanate (TDI) at 60 °C for 24 h (Scheme 7a(ii)). It was observed that not only the reaction is favored on phenols compared to aliphatic alcohols, but also the sulfonate groups act as a catalyst for the reaction. Through this approach, they built nanosized salt crystals as well as PU-based hydrogels for water absorption.

The reaction between various ethylene glycols (EG) (e.g., diethylene glycol (DEG), triethylene glycol (TEG), or polyethylene glycol (PEG)) as a diol with a common diisocyanate (e.g., methylene diphenyl 4,4'-diisocyanate (MDI)) was studied by Hatakeyama et al.[53],[54] to improve the properties of the newly formed materials such as glass transition temperature. Moreover, Lu et al.[55] used a mixture of LS, DEG and MDI to obtain flame retardant building on Hatakeyama's previous work. They observed that, by limiting the oxygen content in the matrix, phenols prevent the formation of flames. De Oliveira et al.[49] combined crude and oxypropylated-LS with OH-containing vegetable oil, such as castor oil, before reacting it with MDI. They showed that oxypropylation and such association with castor oil allow a fine-tuning of PU properties based on a difference in reactivity between crude and oxypropylated LS. This was due to a lower diversity and a better accessibility of hydroxyl groups for the polyurethanization of the latter. After prepolymer formation, the final polymerization - called "cure cycle" - required a lower temperature compared to classical polyurethanization of LS, which is a great advantage for industrial purposes.

An interesting strategy for PU synthesis was developed by He et al.[56] who grafted LS with layer double hydroxides (LDH, inorganic materials) *via* MDI, TDI or isophorone

diisocyanate (IPDI) to obtain UV additives for bitumen. They controlled the reaction with a blocking agent such as acetanilide, and changed the reaction temperature to lock or unlock the diisocyanate in order to obtain control of the polymerization, thus facilitating the study of the properties (Scheme 6b).



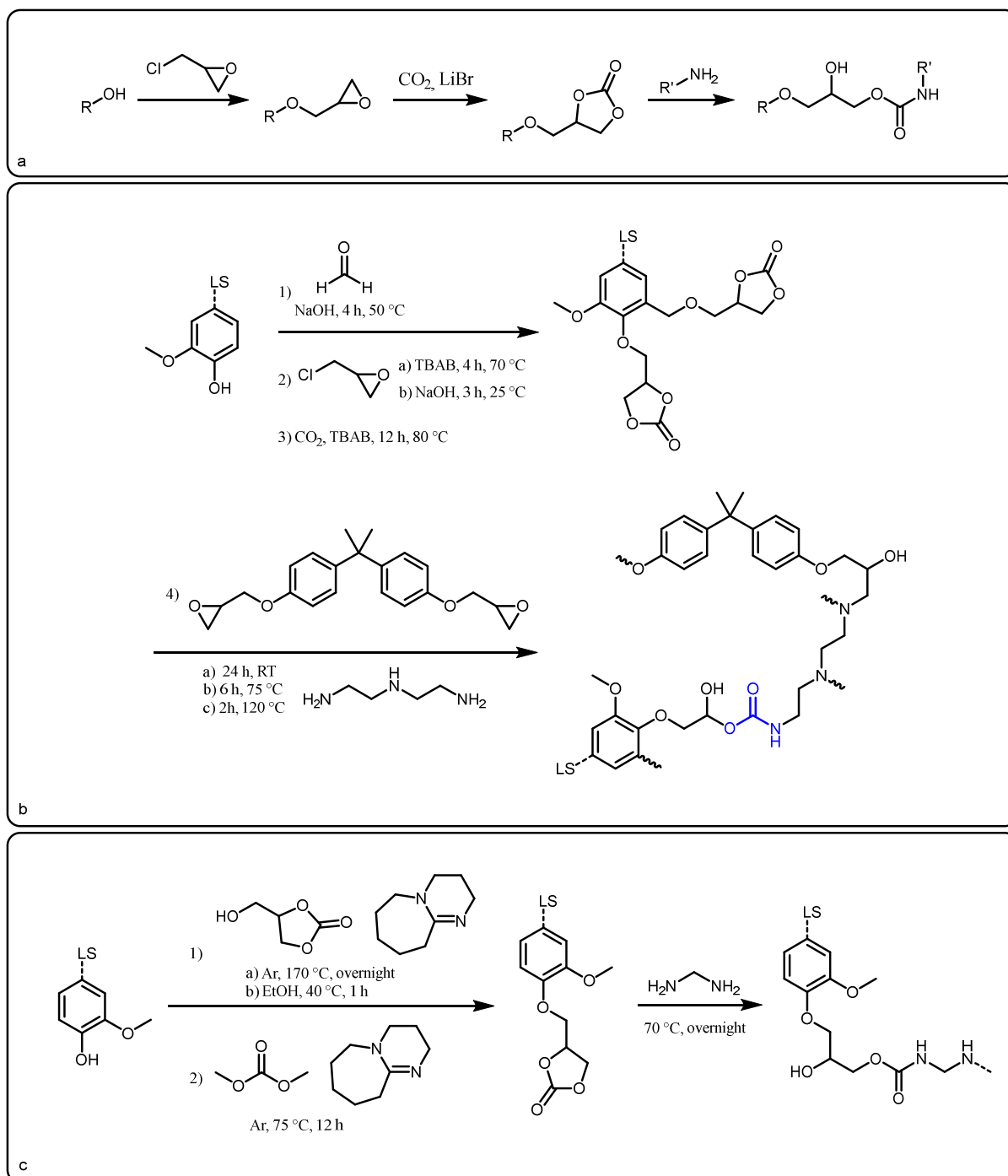
Scheme 6: (a) (i) classic polyurethanization, (ii) polyurethanization from LS, (b) polyurethanization of LS and LDH via MDI using blocking agent (acetanilide)

Due to their toxicity for humans and the environment, isocyanates need to be replaced in PU synthesis. Many research groups have been looking for greener synthetic methods and substitutes. For example, a safer and more sustainable alternative to the classical urethane bond formation was developed.[57] This strategy relies on the glycidylation of a diol, followed

by the lithium bromide-catalyzed opening of the resulting oxirane by CO₂ to obtain cyclic carbonate. Then, the latter is opened by a diamine to obtain non-isocyanate polyurethane (NIPU) (Scheme 7a). This reaction presents the advantages of being isocyanate-free, and avoids the dispersion of toxic unreacted molecules into the environment. Also, it uses CO₂ as a sustainable reagent. Unfortunately, this method is not readily industrialized as it requires pressure reactors; moreover, only a few developments were performed for this method on lignocellulosic materials, specifically on LS.[58],[59]

This method was applied by Yamini et al.[48],[26] using biobased materials such as LS to transform lignin-based industrial waste into a value-added reinforcing agent for epoxy matrix composites. To increase the hydroxyl content and thus that of carbonate groups, they methylolated, glycidylated, and carbonated LS before proceeding to the polyurethanization (Scheme 7b). The obtained resin, completely cured - which means the reaction is total after the formation of prepolymers - are eco-efficient materials with higher mechanical properties compared to classical NIPU.

Mimini et al.[60] used directly cyclic carbonate to build LS-based NIPU following another method without using epichlorohydrin which is considered a toxic compound. They performed a direct esterification reaction on LS with glycerol carbonate in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as a catalyst. This step was followed by the polymerization with hexamethylenediamine (Scheme 7c).



Scheme 7: (a) example of synthesis of NIPU, (b) synthesis of LS-based NIPU with DGEBA and DETA, (c) alternative synthetic pathway to LS-NIPU

Radical activation for free radical polymerization, enzymatic reaction and radical grafting

The use of a radical initiator to grow up chains or to graft molecules on LS is another functionalization strategy (Scheme 8a). LS could be used as an initiator by deprotonating phenols as illustrated below in this review. Several initiation methods were explored in the literature for the free radical polymerization of LS. An old method is the use of Fenton reagent (i.e., ferrous ion such as FeSO_4 or FeCl_2) as an initiator, in the presence of hydrogen peroxide, to generate a radical as depicted in Scheme 8b.[61]

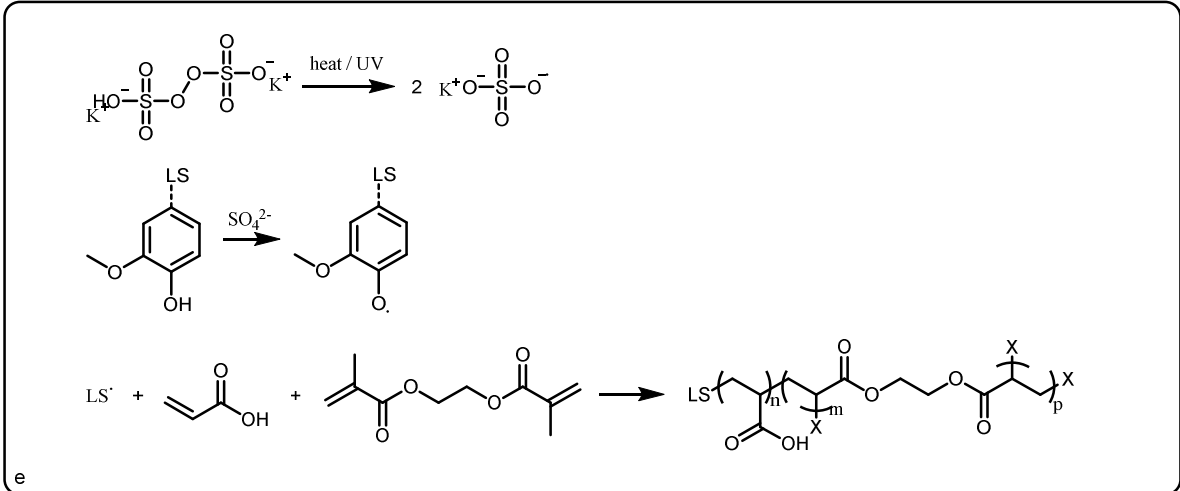
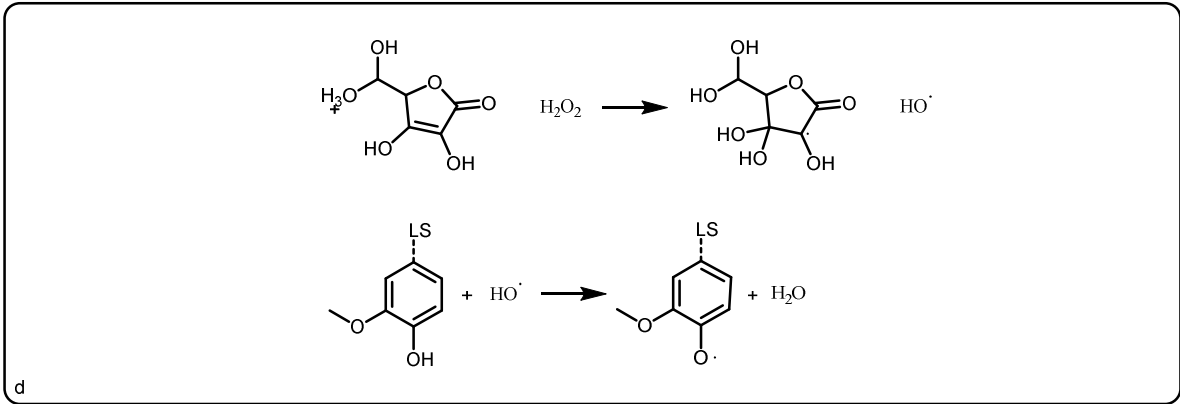
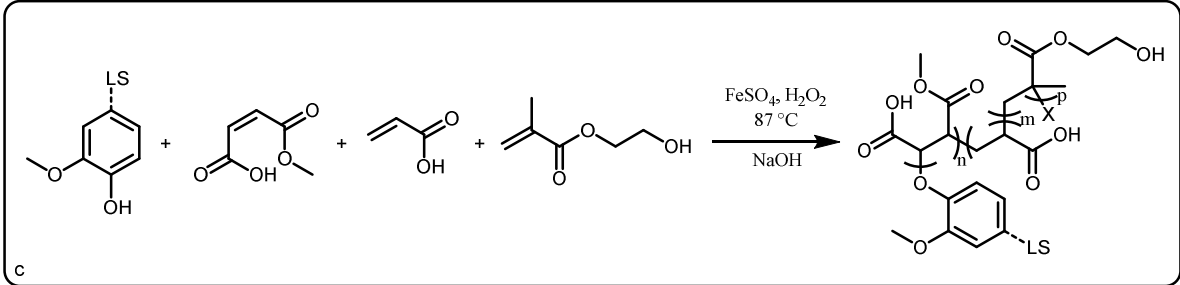
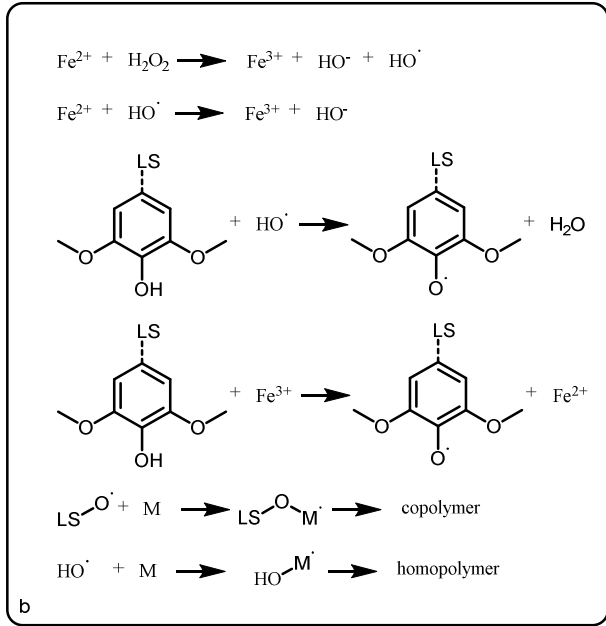
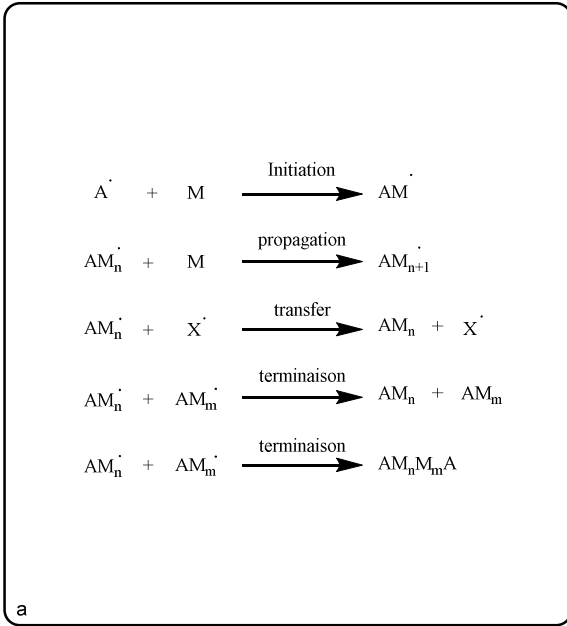
Ye et al.[61] used Fenton reagent with acrylic acid to initiate a growing acrylic chain on LS. The Texaco company[62] used a LS-co-poly(acrylic acid) to prepare a sacrificial agent for carbon dioxide foaming agents. Moreover, seeking an adjuvant to control the viscosity of water-based mud systems for deflocculation, Akzo Nobel Chemicals International[63] used Fenton-type polymerization to prepare a copolymer based on LS, monomethylmaleate, acrylic acid and hydroxymethylmetacrylate (Scheme 8c). Similarly, Liu et al.[64] made a dust depressor based on LS-co-poly(acrylic acid) using FeSO_4 . Although this method was industrialized thanks to its efficiency, it cannot be considered green because of the use of ferrous ions which can be released in the environment.

In a greener process, Zhao et al.[65] replaced Fenton reagent by a system composed of safe and naturally occurring ascorbic acid and hydrogen peroxide to synthesize LS-based hydrogels and acrylic acid with *N,N'*-methylenebisacrylamide (MBAAm) as a crosslinking agent. Ascorbic acid/hydrogen peroxide initiation mechanism is illustrated in Scheme 8d.

Abdollahi et al.[66] compared two methods of initiation: a redox system using calcium chloride and hydrogen peroxide, and a thermally-induced initiation system using persulfate potassium. They synthesized environmentally friendly additive for high salty water-based drilling fluid with a copolymer of LS and acrylamide where 13.3% of conversion was recorded

for the thermal system vs. 3.38% for the redox system. They concluded that the thermally-induced initiation system is both more efficient and more environmentally friendly for the radical polymerization of LS in comparison to a redox system using ferrous ion or chloride ions.

Concerning the radical formation by thermal activation, many researchers used potassium persulfate (KPS) to initiate classical polymerization. For instance, Xu et al.[67] made hydrogels in order to remove dyes from water by copolymerizing acrylic acid, LS and ethylene glycol dimethacrylate in a mixture of dioxane and water by thermal activation and UV (Scheme 8e). Yao et al.[68,69] also followed this method to create composite adsorbing Pb^{2+} in contaminated water by copolymerizing LS with acrylamide (AM)/NMBA, then acrylamide/maleic anhydride.



Scheme 8: (a) classic free radical polymerization mechanism, (b) mechanism of initiation via Fenton reagent, (c) example of one-pot free radical polymerization of LS via Fenton reagent for various monomers, (d) initiation of radical polymerization with LS via ascorbic acid, (e) mechanism of radical polymerization of LS and vinylic monomers via thermally-induced initiation with KPS

Thermal activation can be useful to obtain industrial products such as retarders for phosphoaluminate cement. Ma et al.[70] optimized the copolymerization of LS, itaconic acid and 2-acrylamido-2-methylpropane sulfonic acid (AMPS) via KPS at 60 °C. The sulfonic acid and carboxylic acid moieties grafted on a chain grown from LS through AMPS improve concrete properties by retarding the setting time.

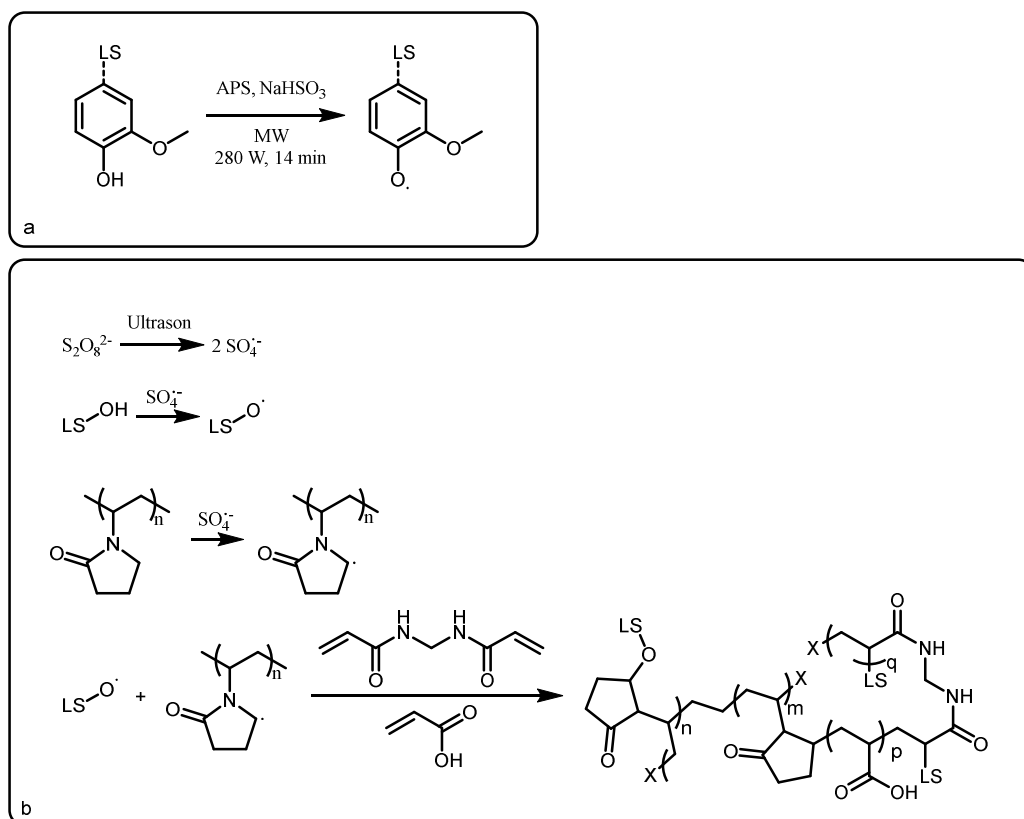
Jin et al.[41] made pH-responsive hydrogels through a two-step reaction: esterification followed by radical polymerization. In a first step, they esterified LS with methacrylic anhydride to graft a double bond as described in Scheme 4b. Then, they thermally activated this double bond via KPS to grow up the pH-responsive copolymer of itaconic acid and *N*-isopropylacrylamide (NIPAM).

Kunpeng et al.[71] thermally activated both chitosan and LS with KPS and sodium thiosulfate to create a crosslinked matrix that proved a good agent of deflocculation for water depollution. Liu et al.[72] grafted *N,N*-dimethylacrylamide and γ -methacryloxypropyl trimethoxy silane on LS via KPS and sodium bisulfite to obtain filtration reducer for water-based drilling fluid.

Another way to green up the radical polymerization of LS with vinyl monomer (e.g., acrylamide, acrylic acid) consists of using microwave or ultrasounds-activated new technology

that significantly reduces the reaction time while increasing yields. The Initiator is activated by irradiation instead of heating (Scheme 9a). Zhang et al.[73] chose microwave for copolymerizing acrylamide, dimethyldiethylammonium chloride on LS, thus creating polymers with better flocculation performances useful for dye removal. They added ethylenediaminetetraacetic acid (EDTA) into the reaction to chelate any traces of metal ions, as well as ammonium persulfate (APS) and sodium bisulfite (NaHSO_3) as thermal initiator. Zhang et al.[73] were able to produce the modified LS in 14 min compared to several hours for a reaction without microwave activation.

Other researchers, such as Hao, Zhang, Wang et al.[74],[75],[76],[77],[78] used ultrasonic reactors to copolymerize LS. Such a polymerization method is considered green and fast as it helps with the dispersion of molecules into the solvent and favors the radical activation of LS. They obtained superabsorbent hydrogels using ammonium or potassium persulfate as initiator, *N,N'*-methylenebisacrylamide (NMBA) as a crosslinker and acrylic acid, maleic acid, vinyl alcohol, and acrylamide as monomers. The reaction was heated at 53 °C and 70 °C for 2 and 3 h, respectively, both at a power of 250 W, and at a frequency of 40 kHz. They also made hydrogels for drug delivery by copolymerizing LS, acrylic acid and polyvinylpyrrolidone (PVP) also under ultrasounds at 100 W and 40 kHz (Scheme 9b).



Scheme 9: (a) microwave-assisted initiation of radical polymerization of LS, (b) example of ultrasound-assisted radical copolymerization for hydrogels synthesis

Radical polymerization can be useful for the grafting of different chemical moieties. For example, Sun et al.[79] grafted methacrylic acid (MAA), methoxy polyethylene glycol methacrylate (MPEGMA), sodium methyl acryl sulfonate (SMAS), PEG, sulfonate and carboxylic acid groups on LS to create functional polymers for the concrete industry as it will be further discussed in this review. Furthermore, Sudrajat et al.[80] simply added PEG on LS after using KPS.

LS-based free radicals can be formed by enzymes as well. Shogren et al.[81] grafted LS on starch using *Trametes versicolor* laccase catalysis in an aqueous solution. 1-Hydroxybenzotriazole (HBT) was added into the solution as a mediator to both facilitate the initiation and reduce hydrogen peroxide content (Figure 6). The combination of starch, LS, and

an enzyme is a great strategy to green up the production of an adjuvant, such as an antioxidant, as it replaces a non-environmentally friendly catalyst system by natural enzymes while employing natural polymers.

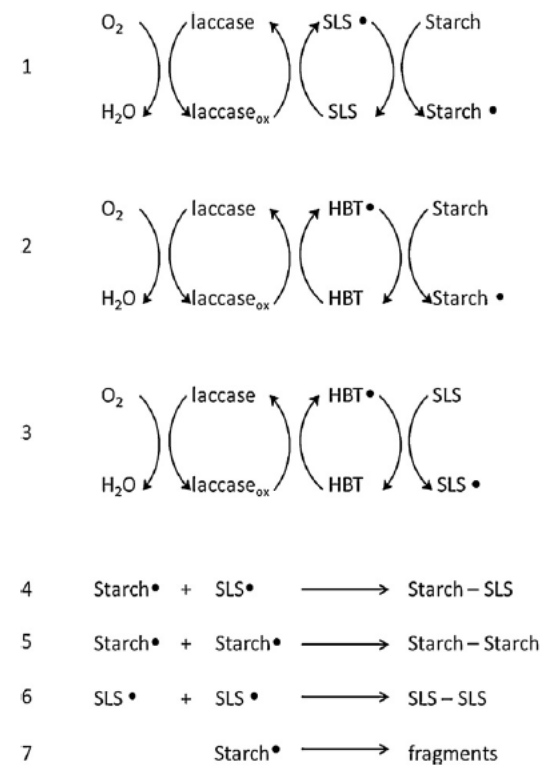


Figure 6: mechanism of enzymatic grafting of LS on starch. Copyright [81]

Pegylation

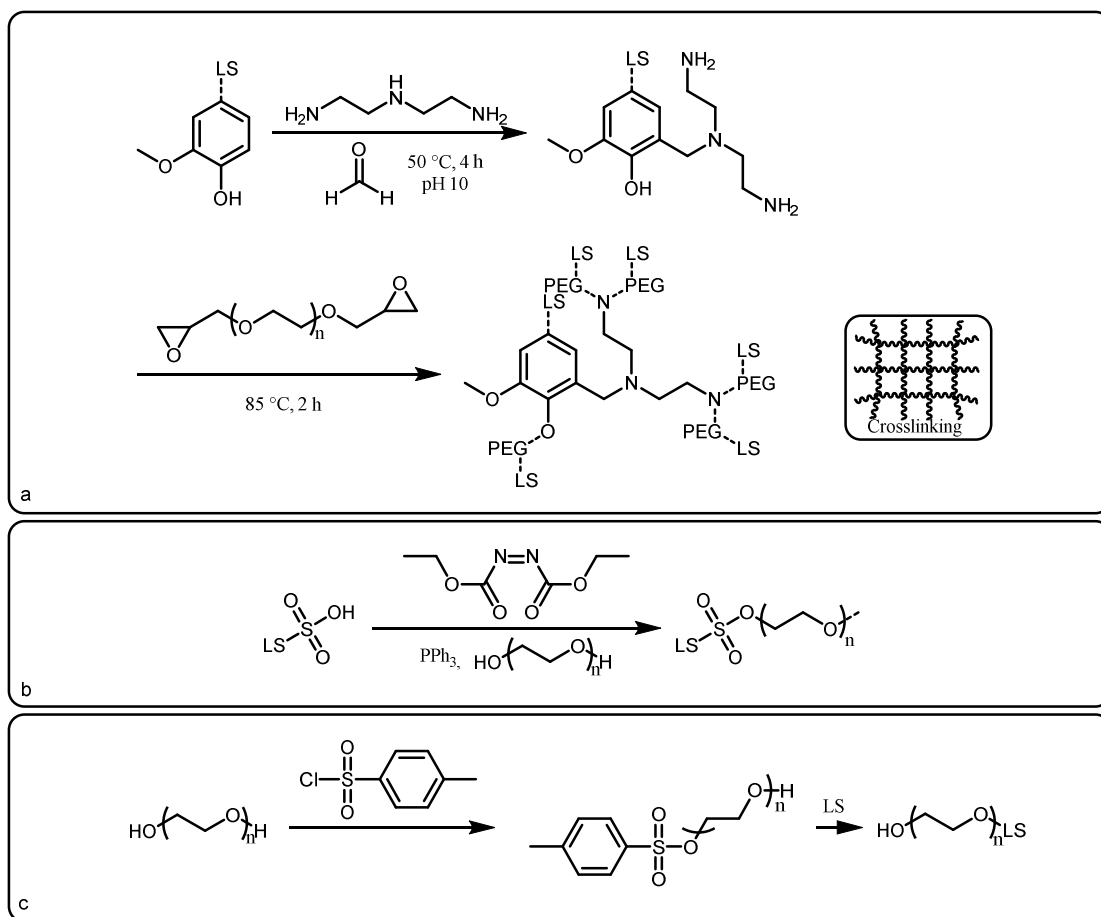
Polyethylene glycol (PEG) chains are generally helpful for different applications as they provide hydrophilicity and create entropic effect, two key properties for specific applications such as concrete. Pegylation consists of grafting PEG on synthetic or natural molecules such as LS. While different pegylation strategies have been reported in the literature, only a few were applied to LS.[82],[83],[84]

Teng et al.[85] synthesized PEG-LS-based hydrogels using a two-step reaction: Mannich reaction using formaldehyde and diethylenetriamine (DETA) to graft amine groups on the aromatic cycle, and grafting of polyethylenediglycidylether (PEGDE). In this example, both diamine and phenol can open the oxirane, thus leading to a crosslinked network (Scheme 10a).

Generally, epoxidized PEG was mainly used to be grafted on the phenol moiety (Ar-OH) through etherification. Lin et al.[82] studied the effect of LS-PEG on enzymatic hydrolysis of lignocellulose. They observed that cellulose adsorbs on lignin, thus limiting its hydrolysis. To overcome this, they proposed using LS-PEG to favor hydrolysis by preventing cellulose adsorption. To do so, they synthesized diepoxide-PEG in presence of epichlorohydrin, and $\text{BF}_3 \cdot \text{Et}_2\text{O}$ as a catalyst, and grafted the latter on LS at pH 13 at 80 °C during 3 h. Ou et al.[86] prepared LS-based polypropylene glycol diglycidyl ether, by grafting polypropylene glycol diglycidyl ether (PPGDE) on LS at 70 °C for 5 h at pH 11, to evaluate its performance as a detergent builder and more generally as surfactant by studying their emulsifying and dispersing ability.

Another possible route for the pegylation is to use directly the sulfonate groups of sulfonated lignin. Empire Technology Development LLC[83] synthesized an adhesive based on pegylated LS. Mitsunobu reaction with triphenyl phosphine and diethyl azodicarboxylate was used to add PEG on LS (Scheme 10b).

Finally, Gupta et al[84] wanted to obtain a LS-PEG plasticizer for concrete by creating a hybrid between LS and PCE which is the actual SP used in industry. To synthesize it, tosylated PEG was prepared and then grafted on LS (Scheme 10c). The performance of the new SP will be discussed later in this review.



Scheme 10: (a) creation of network with PEG and Mannich reaction, (b) Mitsunobu conditions for pegylation of LS, (c) pegylation of LS via tosylation

Grafting via nitrogen

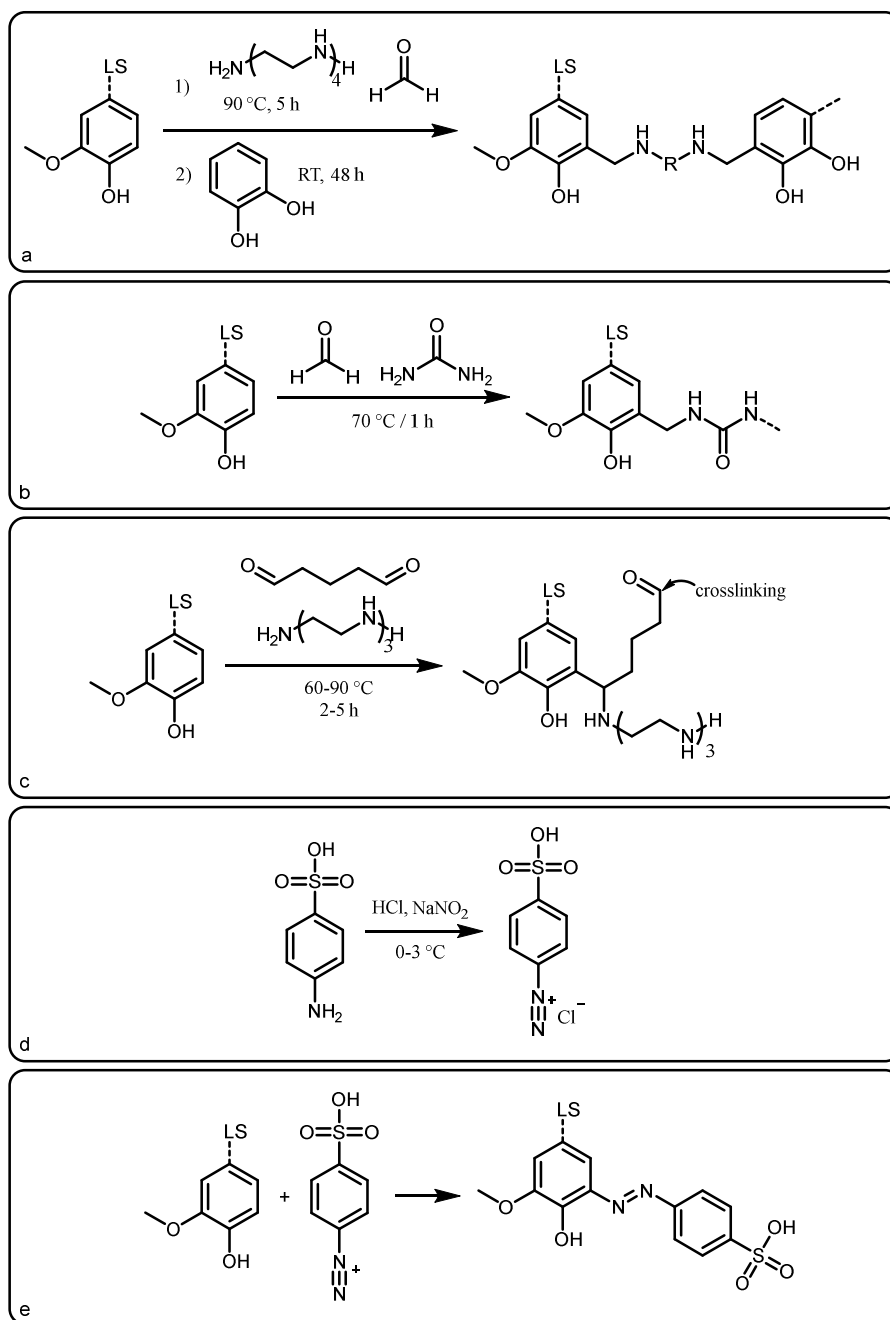
As previously shown in the section devoted to methylation, formaldehyde can be used to graft new aliphatic hydroxyl groups on phenolic structures. By combining formaldehyde and amine, other possibilities to functionalize LS were reported. Using Mannich reaction with formaldehyde and tetraethylenepentamine, Gao et al.[87] synthesized polycatecholamine-based hydrogels able to remove dyes from water through a two-step reaction: grafting of aliphatic polyamine onto LS with formaldehyde (5 h, 90 °C), and addition of the catechol in the

reaction to allow polymerization (48h, room temperature) (Scheme 11a). This functionalization strategy was also used by Teng et al.[85] and Yanhua et al.[29] to graft PEG and polyamine on LS, respectively.

Then, Bai et al.[27] applied the same concept to create urea-formaldehyde-LS microcapsules from hydroxymethylated pre-polymers to encapsulate acetochlor, a phytosanitary product (Scheme 11b).

Starting from triethylenetetramine and glutaraldehyde, Wang et al.[30] also obtained aminated LS to adsorb on dyes for water depollution. It is worthy to note that the use of glutaraldehyde - a dialdehyde - instead of formaldehyde further increased crosslinking (Scheme 11c).

In order to study the mechanical properties of the concrete mixture with modified LS as a water reducer, another nitrogen-based linkage was tested by Li et al.[88],[89] They grafted *p*-aminobenzene sulphonic acid on LS under chlorohydric acid and sodium nitrite (scheme 11d). Also, Zhang et al.[90],[91] developed drilling fluid additives from LS after nitration and oxidation of phenol. Furthermore, after methylation, Lignotech USA[92] ammoxidized LS under high pressure and temperature with ammonium hydroxide to obtain LS possessing free nitrogen as amide, nitrile and/or amine functional groups. The final modified LS was used as a dispersant for concrete.



Scheme 11: (a) copolymerization of LS and catechol, (b) creation of urea-formaldehyde-LS prepolymer, (c) crosslinking of LS-glutaraldehyde-triethylenetetramine, (d) LS grafting via azo groups

Modified LS and their application in concrete industries

In this section, a special focus will be given to the use of LS as SPs for concrete and how chemical modifications impact concrete physico-chemical properties. As explained previously, LS acts as a plasticizer through electrostatic repulsion. However, no steric effect was observed, thus leading to the formation of multilayers on the cement particles that reduce drastically its performance[2]. This results in low water reduction, high setting retardation, or/and high air-entraining which creates bubbles in the matrix. These drawbacks can be minimized by adding chemical functions on LS to trigger the steric effect, and to further improve the properties of the fresh and hardened concrete. As discussed above, grafting PEG onto LS improved the separation of cement aggregates by increasing the steric repulsion between SPs triggered by the interpenetrated “hairy”-like PEG chains.[84] They compared three mixtures of cement: without plasticizer, with LS and with LS-PEG using PEG of 900 Da. They demonstrated that PEG-grafted LS creates a steric effect and provides better plasticization of cement compared to unmodified LS. They performed adsorption measurements to understand the impact of grafting PEG on the affinity of LS for cement particles (Figure 7). A plateau was observed at concentrations ≥ 4 mg/mL which is similar to that of PCE SPs. On the other hand, when unmodified LS was employed, a continuous increase in adsorption with respect to concentration was observed (Figure 7). This difference in behavior towards the cement particles can be explained by the absence of multilayer structure when grafted PEG chains are added in the mixture, even at low PEG grafting content. Indeed, the repulsion generated by PEG chains limits the possibility to form a new layer that increases both the dispersion and water reduction capacity of the SP. Furthermore, the slump spread was increased by 20% which is dependent on the water reduction found as 20-25%. A lower value of water reduction

was observed in the case of unmodified LS, commonly less than 12%. Concerning the viscosity of the obtained concrete using pegylated LS as a superplasticizer, they also demonstrated that LS-PEG provides an effective plasticization by measuring both the storage modulus and loss modulus (i.e., viscoelastic responses of the materials).

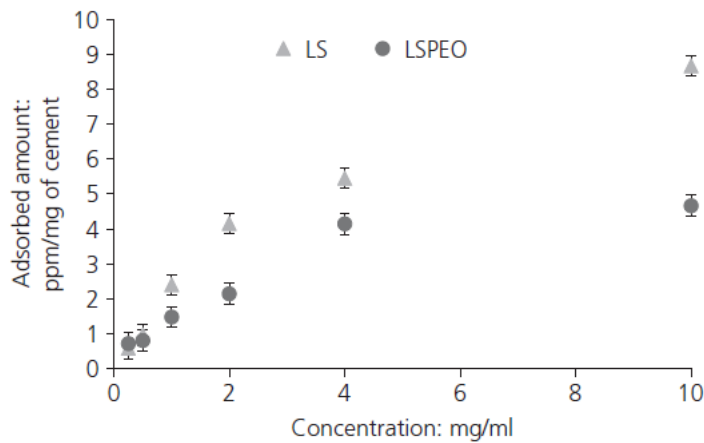


Figure 7: adsorption of LS and LS-PEG onto cement particles[84]

Yu et al.[32] and Wu et al.[33] reported strategies based on the oxidation, methylation and sulfonation reaction methods to improve the properties, especially, fluidity of the fresh concrete. Two general effects were observed: (1) the increase of the number of hydrophilic groups, such as sulfonate groups which chelate calcium ions, and modify the adsorption of LS on the surface of cement particles, (2) the narrowing of the M_w of LS which increases the repulsion potential energy between the particles. They studied the fluidity of the resulting materials with regards to different reaction conditions such as stoichiometric ratio, temperature and reaction time for each step of the process. They demonstrated that adding sulfonate groups improved the dispersing ability due to the increased content of hydrophilic groups, resulting in better fluidity. Also, they both observed a change in M_w and especially a reduction in the dispersity (\mathcal{D}) which enhances the repulsion between the particles.

By employing the Mannich reaction, Jiangsu TMS Group[93] prepared LS-based water reducer by growing aliphatic carbonyl compounds onto LS such as sulphite-acetone-formaldehyde (SAF) to enhance the properties of LS (Figure 8). The aliphatic carbonyl groups led to high water reduction despite the use of a large amount of formaldehyde which is toxic for humans and the environment. Furthermore, a strong red coloration of the concrete mixture was observed which is a critical issue for commercial use. Therefore, they decided to graft carbonyl aliphatic chains onto LS to reduce its carbonyl groups/ M_w ratio in the general polymer matrix while preserving its properties. Then, they compared properties of concretes (1) without water reducer, (2) with the aliphatic carbonyl alone, (3) with the newly grafted LS, and (4) with the cold combination of aliphatic carbonyl and unmodified LS. The viscosity was reduced in the presence of the grafted LS and the fluidity of the mixture was similar to the aliphatic product but higher than that of the cold combination. Furthermore, the water reducing ability was increased by 15% by using an aliphatic or grafted product. However, the compressive strength of the concrete containing grafted LS was inferior to that enclosing the aliphatic carbonyl but higher than the value obtained for the cold combination. Therefore, grafting aliphatic carbonyl compounds on LS avoids both the strong red coloration and the use of non-environmentally friendly reagents, while keeping similar properties. The Mannich reaction was also used by Lignotech USA[92] using polyamine with formaldehyde. All the obtained formulations showed better performance in setting retardation, water reducing ability, and air-entraining limitation compared to commercial LS.

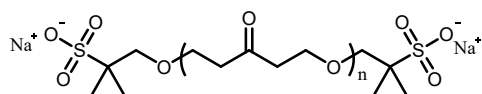


Figure 8: typical SAF molecule

As shown previously in this review, sulfonate groups are considered good hydrophilic moieties for the complexation of calcium. Under such considerations, Li et al.[88] and Pei et al.[89] explored another way to add hydrophilic groups, such as sulfonate or carboxylate groups, on LS structure by using diazonium salt (Scheme 11d). Pei et al.[89] grafted a hydrophobic aromatic group bearing sulfonate moiety to reduce the surface activity of LS, and thus decreased both air entrainment and foaming ability. The flexural and compressive strength of the (non-)grafted LS were measured after 7 or 28 days. The results showed that in the case of grafted-LS, higher dispersing ability and lower air entrainment were obtained, thus leading to higher compressive and flexural strength compared to the of unmodified LS. Li et al.[88], from the same laboratory, investigated this strategy but by using carboxylic group instead of sulfonate. They also observed a lower surface activity and better mechanical properties of the concrete than with “neat” LS. Moreover, they observed a plateau in the adsorption for the functionalized LS compared to “neat” LS which showed a growing adsorption profile, indicating the absence of the creation of multilayer structure. It is worthy to note that the LS-based plasticizer possessing carboxylates displayed better performance in terms of adsorption where a saturation plateau was registered. However, the adsorption kept in increasing when the LS bearing sulfonate groups was considered.

The influence of the copolymer of LS, AMPS and itaconic acid was tested by Ma et al.[70] for application in phosphoaluminate cement, a cement known for its rapid solidification, rapid hardening and good CO₂ resistance. They compared the properties - such as thickening time which represents the duration where the slurry remains fluid, rheology and compressive strength - of cement by adding 3% LS or 0.5% grafted LS, both with a water/cement ratio (w/c) of 0.5. The thickening time was measured with a consistometer

under high pressure and temperature, using the evolution of consistency specifically used to study retarding effects for aluminate cement,[94] until it reached a limit of 75 Bearden units. They observed that the limit was reached in 245 min at 90 °C and 3000 psi and in 274 min at 75 °C and 1500 psi. As the preferential thickening time should be generally between 4 and 6 h, these results proved to be very promising. Rheology measurements demonstrated that the grafted LS led to a good rheological behavior of the concrete thanks to the good adsorption of molecules onto cement particles which led to an increase in the flow. Finally, the compressive strength at 75 °C under 1500 psi, and at 90 °C under 3000 psi, for grafted LS was much better than that for “neat” LS but similar to that of cement alone. The grafted LS showed good potential to replace LS for fresh and hardened concrete.

Sun et al.[79] prepared copolymers of polycarboxylate and LS by using MPEGMA, MAA, LS, and sodium methyl acryl sulfonate (SMAS) to be used as SPs for concrete. They compared the resulting copolymers with cold combinations of LS and polycarboxylate (PC) at the same ratios, with a w/c about 0.29 and a quantity of water reducer about 0.2%. Fluidity was measured to obtain plasticizing properties. It was demonstrated that LS-based copolymer offers better plasticization of concrete compared to cold combinations of LS with PC. Also, at a ratio of 5 or 10% w/w of LS in the copolymer, compressive strength obtained for the solid concrete at 28 days was similar to the one with PC alone. Finally, those ratios of 5 and 10% w/w of LS resulted in water-reducing rates higher than 30%, this is similar to the one obtained for common PC.

Conclusion

In this review, we defined SP - hydrophilic molecules used in the field of building materials as high-range water reducers for concrete - and their sought properties. Through various examples on the commercially available SPs (i.e., LS, PMS, PNS and PCE), we demonstrated how LS, the non-expensive and abundant byproduct of pulp and paper industry and the only commercial SP derived from renewable resources, despite being not optimal yet, could be a good starting point for the development of new sustainable SPs via specific chemical modifications to enhance its performance as a concrete admixture. In many applications such as hydrogels for water depollution, dispersant, superadsorbant, antioxidant, or as alternatives to some existing materials such as PU, PET, or epoxy resin, modifications of LS (e.g., etherification, esterification and free radical polymerization of LS) were investigated and proved successful, owing to the diverse active functional groups grafted. A special focus has been made on the concrete application, and the importance of adsorption and dispersion mechanisms in the hydration process was highlighted. It has been concluded from the literature survey that the cement-SPs interactions are largely affected by the modified-LS structure, especially by preventing the multilayer structure formation. Researchers demonstrated that many chemical groups such as PEG or sulfonate groups can significantly impact concrete properties such as adsorption, fluidity, mechanical strength, water-reducing ability or setting retardation. In order to replace the current petroleum-based SPs with renewable, non-toxic and environmentally friendly alternatives, concrete research needs further development and exploration of tailored modifications on LS.

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Authors contribution

Damien Breilly: Investigation, Data curation, Formal analysis, Writing - original draft; **Sami Fadlallah:** Conceptualization, Visualization, Investigation, Data curation, Formal analysis, Supervision, Writing - review & editing; **Vincent Froidevaux:** Conceptualization, Supervision, Writing - review & editing; **Antoine Colas:** Conceptualization, Project administration, Funding acquisition, Supervision, Validation, Resources, Writing - review & editing; **Florent Allais:** Conceptualization, Project administration, Funding acquisition, Supervision, Validation, Resources, Writing - review & editing.

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