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VALUABLE POLYMERIC PRODUCTS FROM LIGNOSULPHONATES

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ABSTRACT

Lignosulfonates (LS) are by-products of sulphite pulping that find various applications, e.g., as binders, flavours, surfactants, and dispersants, among others. The chemical modification of LS allows new range of products with improved properties. In this study, modified LS from Mg base acid sulphite cooking of eucalyptus wood were examined as modified polymeric materials in applications such as concrete plasticizers to substitute petroleum-based superplasticizers, in novel adhesives and sensor materials. Thus, it was found that LS performance as dispersants for concrete formulations can be improved substantially by their modification with epoxidized oligomer derivative of poly(propylene glycol) (PPG). In addition, LS were used as unmodified polyols in the formulation of polyurethane (PU) adhesives with addition of PEG_{200}, which contributed positively both to the homogenization of the reaction mixture and better crosslinking of the polymeric network. The adhesion strength of the ensuing LS-based PU was comparable to a commercial white glue. LS were also used as polyols in PU network doped with 1.0% w/w multiwalled carbon nanotubes (MWCNTs) yielding a unique conducting copolymer composite that was employed as a sensitive material for all-solid-state potentiometric chemical sensors selective to Cr(VI) and the Fe(II)/(III) redox pair at pH 2.

KEYWORDS: Adhesives, conductive composites, dispersants, lignosulphonates, polyurethanes, sensors.

INTRODUCTION

The rising awareness of climate change and scarcity of fossil resources has drawn attention to the relevance of the biorefinery concept worldwide and as a result to the potential of renewable materials. Among technical lignins, LS are sulphonated technical lignins present in sulphite spent liquor (SSL) from the sulphite pulping. Worldwide, over one million tons of LS are produced annually representing ca. 88% of the global lignin market [1]. Besides burning for energy recovery, the potential applications of LS depend on their good water solubility hence LS are usually marketed as dispersants for concrete formulations, for animal feed, paint and oil industries, and agriculture, among other applications, which is the reason for the world market being mostly restricted to these technical lignins [1].

About 60–90% of these LS are employed as plasticizers and/or water-reduction agents in concrete formulations to obtain concrete with improved workability, lower water/cement ratio and higher compressive strength [2,3]. Although LS compete with petroleum-based superplasticizers, such as polycarboxylates (PCAs), their plasticizing and water reducing effects are still limited and depend on the sugar content, molecular weight, and type of counteraction [4]. PCAs are more efficient than LS; however, PCAs are up to 10 times more expensive than LS. Therefore, some strategies have been used to improve LS performance including (but not only) increasing their molecular weight whilst preserving their solubility in water by an enzymatic modification treatment [5] or synthesizing lignin-based non-ionic polymeric dispersants (amphiphiles) by reacting the lignin with different commercial epoxidized oligomer derivatives of poly(ethylene glycol) (PEG) and poly(propylene glycol) (PPG) [6].

Lignins have potential as adsorbents for removing metals from water due to their acid sites, namely, carboxylic and phenolic groups, though the phenolic groups exhibit a higher affinity for metal ions than the carboxylic ones [7]. Lignin-based sensing polymeric membranes have been developed through covalent immobilization of the lignin inside a polymer matrix. In particular, the production of lignin-based PU membranes through co-polymerization of different technical lignins, including LS, with toluene diisocyanate-terminated poly(propylene glycol) (PPGDI) has been reported [8]. Considering that LS are soluble in water and contain ionogenic (sulphonic) groups, LS are considered as potentially interesting technical lignins to produce conductive polymer matrices for sensor applications. Therefore, LS-based PUs doped with MWCNTs yield composites with increased electrical conductivity with a prospective application as ion-selective membranes for potentiometric chemical sensors. Yet, the sensor properties are strongly dependent on the lignin origin hence exhibiting different sensitivities to alkali, alkali-earth, and transition metal cations ions [8].

Finally, due to the high amount of phenolic and aliphatic hydroxyl moieties in their structure, technical lignins can also act as macropolyols in PU synthesis and be used as such or after chemical modification to obtain a more reactive lignin, alone or in combination with other polyols [9,10]. Usually, lignins act both as a network former (due to its functionality being higher than 2) and as a reinforcing component (due to the high content of condensed aromatic rings) in PU formulations. To counterbalance the stiff character of lignin, other polyols can be used as soft segments, such as PEG and PPG [11], or bio-based polyols [11,12] yielding grafted or cross-linked PUs with the possibility of controlling their flexibility and/or rigidity. SSL, which is mainly composed of LS, xylo-oligosaccharides, among others [13,14], could be used as a bio-based polyol to substitute petroleum-based polyols in the formulation of PU adhesives and to reduce costs associated with LS purification.

EXPERIMENTAL SECTION

Materials

LS were purified by dialysis against distilled water from *Eucalyptus globulus* acidic magnesium-based SSL kindly supplied by CAIMA S.A. (Constância, Portugal) and contain 17.1% wt.% of HSO_3 groups, 2.4 wt.% of phenolic and 5.5 wt.% aliphatic OH groups [14]. Laccase Novozym® 51003 was kindly supplied by Novozymes (Bagsvaerd, Denmark) and was used without further purification. Two commercial petroleum-based superplasticizers, naphthalene sulfonate formaldehyde polycondensate (NSF) and copolymer polycarboxylate ethers (PCE), were kindly supplied by Sika Portugal Company (Ovar, Portugal). Multiwall carbon nanotubes (MWCNTs) Nanocyl-3150 (purity >95%, length 1–5 µm, and diameter 5–19 nm) were supplied from Nanocyl S.A. (Sambreville, Belgium). Oligomeric isocyanate 4,40-methylene diphenyl diisocyanate (pMDI) (Voranate M229) with 31.1% of NCO, a functionality of 2.7, a viscosity of 190 mPa·s (at 25 ºC) and an isocyanate equivalent of 135 was kindly supplied by Dow Chemicals (Estarreja, Portugal). Commercial poly(vinyl acetate) (PVA) glue (white glue) was purchased in the local market. All other chemicals were of analytical grade and were purchased from either Acros Organics or Sigma-Aldrich (Madrid, Spain).

Synthesis of LS-Based Dispersants for Concrete Formulations

The enzymatic treatment of LS consisted of adding laccase (loadings ranging from 42 to 500 $U \cdot g^{-1}$ of LS) to 10 ml of a 100 $g \cdot l^{-1}$ LS solution (pH adjusted to 4.3) in a reaction vessel equipped with a magnetic stirrer and a heating jacket connected to circulating water bath. The reactions were carried out at 40°C under pure oxygen bubbling for 90–120 min. The laccase oxidative treatment of LS using polyoxometalates as mediators was performed as followed: 200 µL of a 0.1 M $SiW_{11}Mn$ aqueous solution were added to 10 mL of a 100 $g \cdot L^{-1}$ LSF solution and the methodology proceeded as described above. The same procedure was carried out using 0.1 M $PMo_{10}V_2$ and $PMo_{11}V$ solutions [16]. The workability/fluidity of the cement pastes was assessed by the flow table test at Sika Company (Ovar, Portugal) according to the standard procedure EN 12350-5:2009 [17].

LS-Based Polyurethane Polymer Synthesis

In a typical trial, LS powder (500 mg) or a mixture of LS powder with a certain proportion of MWCNT (0.1, 0.2, 0.5, 0.8, 1.0, and 1.4% w/w in relation to the total mass of the mixture) was placed in a 25 mL jacketed glass reactor equipped with an overhead mechanical stirrer and a heated circulating water bath. Then, PPGDI (4 mL) was added, and the mixture was stirred for 45–60 min at 60 °C under a nitrogen atmosphere to obtain a homogeneous viscous mixture. Next, dibutyltin dilaurate (DBTDL, ca. 2% w/w in relation to the PPGDI) was added. The homogeneous mixture was stirred for a further 5–10 min until it started to thicken. At this point, the mixture was removed from the reactor and poured into a flat PTFE mold. The films were cured for 4 h at 60 °C. For the preparation of sensors, after the homogeneous mixture thicken, instead of preparing films, a thin layer of the LS-based polymer was used to coat the working electrode of SPE. The sensors were cured for 4 days at room temperature [18]. Electrochemical measurements were carried out in the following galvanic cell: Ag|AgCl, KClsat|sample|polymer membrane|PANI|carbon. Electromotive force values, Emf, were measured vs. an Ag/AgCl reference electrode with a precision of 0.1 mV using a custom-made multichannel voltmeter, with high input impedance, connected to the PC for data acquisition and processing. Calibration measurements were carried out as described elsewhere [18].

Synthesis of LS-Based Adhesive Synthesis

For all formulations, purified LS powder (500 mg) was first dissolved in water (400 µL) or a mixture of water with PEG_{200} (0, 50, 100 and 150 µL) to form the base solution, in a glass vessel with screw cap with a magnetic stirring bar, at room temperature. The volume of water used was initially optimized to ensure full solubilization of LS and ease of stirring. The mixture was kept under constant magnetic stirring for 5 min and then 50 µL of DBTDL was added as the catalyst. Finally, 900 or 1000 mg of crosslinker pMDI was introduced in the reaction mixture and the reaction proceeded for a certain time ranging from 30 s to 5 min depending on the application. For all formulations, the quantities of LS, water and DBTDL were kept constant (500 mg, 400 µL and 50 µL, respectively) while only the contents of PEG_{200} and pMDI were varied. The strength development of LS-based adhesives was assessed using the automated bonding evaluation system (ABES, Corvallis, OR, USA) at the Department of Wood Engineering, Polytechnic Institute of Viseu (Portugal), according to a method described elsewhere [15].

RESULTS AND DISCUSSION

In this work, purified eucalypt LS were used to produce polymeric formulations for three different applications: LS-based products with improved dispersant properties for concrete formulations, LS-based adhesives for biocomposites and LS-based conductive composite membranes for potential applications in sensors.

LS-Based Dispersants for Concrete Formulations

To improve LS dispersion efficiency towards the substitution (partially or completely) of commercial petroleum-based superplasticizers for concrete formulations, such as polycarboxylates, different chemical modification strategies were used to achieve this purpose, including (but not only) (1) increase of the molecular weight of LS through laccase-catalysed oxidative polymerization with and without mediators and (2) modification of LS using two different epoxidized oligomer derivatives, poly(ethylene glycol) and poly(propylene glycol) diglycidyl ethers, PEGDE and PPGDE, respectively, to yield non-ionic (amphiphilic) species.

The first strategy consisted in the laccase-catalysed oxidative polymerization of eucalyptus LS, which under optimized conditions allowed a significant increase in LS Mw up to 11-fold from 3240 Da to a maximum of 36 800 Da without the use of mediators in a considerably short reaction time (90 min) [19]. These results are in agreement with the literature where it was shown that laccase polymerization of commercial LS without using mediators led to a significant Mw increase including the reduction of phenolic hydroxyls along with only minor structural changes [5]. The mechanism of the oxidative polymerization process includes radical coupling of laccase-catalysed one-electron oxidized phenolic units, leading to the formation of new aryl ether and biphenyl bonds, with the former being the most frequent [19]. Although the total amounts of carbonyl and carboxyl groups increased, it remained moderate. At the same time, part of syringyl structures were degraded leading to some decrease in the S/G ratio after the oxidation of LS in the presence of laccase, from 79:21 down to 70:30. It is noteworthy that part of the newly formed bonds of unknown origin formed via oxidative polymerization are temperature labile and cleaved during concentration of modified LS at pH 4 and 80°C during evaporation under vacuum, which led to a noticeable reduction in the Mw of the modified lignin [19]. Since polyoxometalates (POMs) can be used as inorganic mediators in lignin oxidation by laccase [20], in this study, $SiW_{11}Mn$, $PMo_{11}V$ and $PMo_{10}V_2$ were used. However, reactions were not as successful as using only laccase, since only a slight increase of Mw was observed with slight structural changes in LS [16].

The second strategy to enhance the dispersant properties of LS was the synthesis of LS-based non-ionic polymeric dispersants using epoxidized oligomer derivatives of PEG and PPG, PEGDE and PPGDE, respectively [16]. Grafting PEG moieties onto lignin occurs via nucleophilic substitution through phenolic hydroxide groups usually under moderately alkaline pH conditions ($pH > 11$) [6,21]. However, in the present study, alkaline pH could not be considered since it compromises the water-solubility of acidic LS due to its partial desulphonisation. Therefore, experiments were carried out at an initial pH of 2.5 (LS solution) before adding PEGDE or PPGDE. Quantitative ^{13}C NMR analysis of the products (data not shown) confirmed that PPG-grafting occurred at least via reaction of phenolic hydroxyl groups in G/S structures with epoxy moieties of PPGDE while suggesting that the reaction of LS with PEGDE resulted only in a negligible modification of LS with no relevant changes in LS structure [16]. In fact, the content of phenolic OH groups in G structures present in PPG-modified LS is 15 per 100 C6 against 26 per 100 C6 in LS clearly confirmed that some of these groups reacted with PPGDE.

The fluidity/workability of cement pastes prepared with the different modified LS was determined to assess the dispersing performance of the samples and compared with the results obtained for cement pastes prepared with unmodified LS and two different commercial petroleum-based superplasticizers, PCE and NSF (Figure 1) [16]. The results show clearly that unmodified LS/SSL, modified LS, and superplasticizers, display different dispersant behaviour. Both PCE and NSF yielded the highest cement paste spreading reaching about 300 mm, clearly indicating their super-plasticizer ability with PCE exhibiting the best results. Although the molecular weight of PPG-modified LS increased only slightly, it was the only LS-based product exhibiting relevant enhanced dispersant efficiency compared to unmodified LS and laccase-modified LS but not as relevant as the dispersion efficiency of the superplasticizers. The dispersant properties of PPG-modified LS are probably due to the presence of polyether chains (just like in PCEs) that are responsible for the steric hindrance effect combined with electrostatic repulsion (caused by the ionizable groups such as sulfonic groups). These results suggest that this study is well on the way to obtaining improved dispersants based on LS.

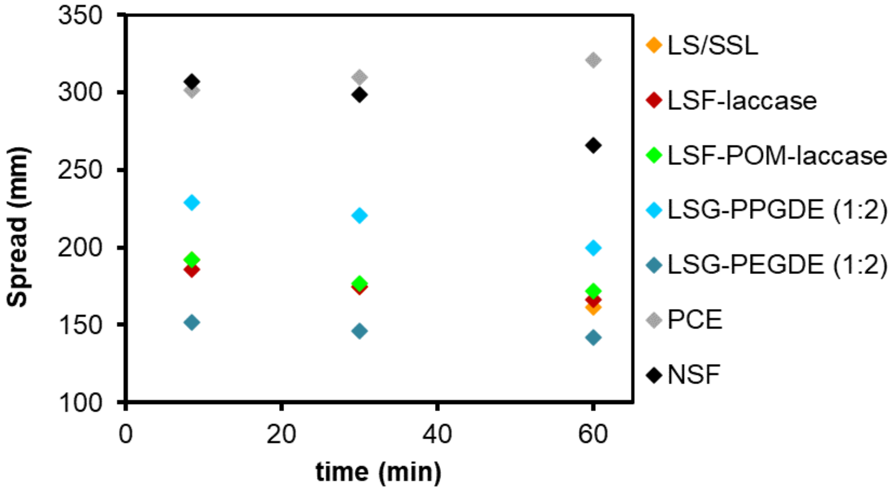

Figure 1. Spread values of cement paste determined by the flow table test (relative errors did not exceed 5%).

LS-Based Conducting Flexible Polymeric Membranes for Liquid Sensing Applications

Another goal of this project was the development of conducting polymeric formulations for the preparation of all solid-state potentiometric chemical sensors for the detection of transition metals in aqueous solutions. For this purpose, LS-based PU flexible membranes doped with different amounts of MWCNTs were synthesized.

LS-based composite containing 1% w/w MWCNTs displayed relevant electrical conductivity being suitable for sensing applications [18]. This sensor exhibited no response to Na^+, NH_4^+, and Pb(II) but displayed a near-Nernstian or super-Nernstian response to a wide range of transition metals, including Cu(II), Zn(II), Cd(II), Cr(III), Cr(VI), Hg(II), and Ag(I) at pH 7 (Figure 2) and Cr(VI) at pH 2 (Figure 3). It also exhibited a redox response to the Fe(II)/(III) redox pair at pH 2. Unlike other lignin-based potentiometric sensors in similar composite materials, this LS-based flexible polymeric membrane did not show irreversible complexation with Hg(II). The super-Nernstian behaviour displayed by the LS-based PU membrane is probably due to the presence of strong anionic sites in the composite [22], such as LS sulfonic acid groups. Hence, this work puts in evidence the decisive role of the lignin's nature (including the wood source and pulping conditions) in the response of the corresponding potentiometric sensors.

Considering the interesting sensing results obtained with MWCNTs as nanofillers in the LS-based composite, the impact of other carbon nanofillers was evaluated. Unlike LS-based composites comprising MWCNTs, those doped with graphene oxide (GO), reduced GO, and graphite did not reveal the same electrical conductivity, even with loads up to 10% w/w, in the polymer composite [18]. This fact is associated, at least partially, with the different filler dispersion abilities within the polymeric matrix. MWCNTs bind readily to LS forming bundles with a highly entangled structure; thus, forming a continuous conductive network within the composite matrix; on the contrary, this occurrence was not observed when using the other nanofillers.

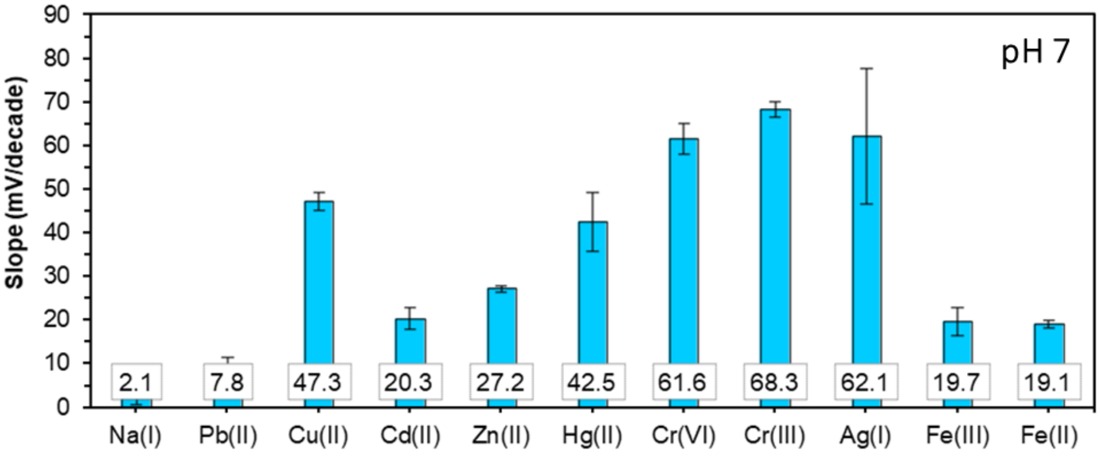

Figure 2. Slopes of the electrode function of the LS-based PU sensor doped with 1% w/w MWCNTs at pH 7 (mean values of at least three calibrations with their respective standard deviations).

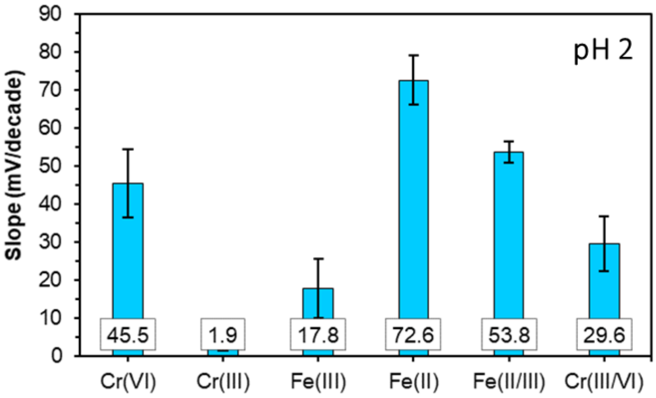

Figure 3. Slopes of the electrode function of the LS-based PU sensor doped with 1% w/w MWCNTs at pH 2 (mean values of at least three calibrations with their respective standard deviations).

LS-Based Polyurethane Adhesives

Finally, the third goal of this project was to use LS as macropolyols in PU formulations for adhesive purposes. Purified LS were dissolved in water to simulate their concentration in SSL and then reacted with pMDI [15]. It is known that the polycondensation of unmodified lignins with isocyanates with large molecular structures like pMDI is unlikely to occur without the addition of catalysts due to the lack of reactivity, which is related to the steric hinderance of OH groups in lignin and of NCO groups in pMDI as well as low diffusion due to the high viscosity of the reaction medium [23]. Therefore, DBDTL was used as a catalyst. Also, in the presence of water, the reactivity of pMDI with lignin is hampered by isocyanate competition reactions with the formation of the corresponding amines [24]. Therefore, it can be expected that a polymeric network of low crosslinking will result from the reaction of pMDI and LS alone. The addition of highly reactive water-soluble polyol to the reaction system can increase crosslinking between polymer chains and, if a polyol is polar enough to improve segmental movement of the resulting network, it can positively contribute to the adhesive properties of the final synthetic glue. Therefore, PEG with low molecular weight (Mw 200, PEG_{200}) can be used as soft crosslinking segment to overcome, at least partially, drawbacks such as limitations in the accessibility/reactivity of hydroxyl groups in LS in the reaction with pMDI and difficulties in effective homogenization of the reaction mixture. Based on these considerations, a series of formulations were synthesized using LS, pMDI and PEG_{200} [15].

ABES testing was performed to evaluate the strength of adhesion of the LS-based PU adhesives and to assess the effect of PEG_{200} amount on the adhesion results. Additionally, results were compared with those obtained using a commercial white glue (Figure 4). ABES testing measures the force in tensile mode needed to break the adhesive bond and shear strength gives an indication of the strength of an adhesive. Therefore, the higher is the force needed to break the bond, the higher is the shear strength value. At first glance, all LS-based PU adhesives showed adhesion strengths somewhat lower or similar to those obtained using commercial white glue. This means that LS-based PUs displayed variable adhesive properties depending on the formulation composition, but still comparable to the commercial adhesive. Another fact is that the errors associated to each strength value are quite high. It should be noted that each formulation was prepared in duplicate (suggesting that there are significant differences between duplicates of the same formulation) and, for each formulation, a minimum of three sets of bonded strips were prepared. Therefore, these results indicate that, for the same formulation, the samples applied on the wood strip are different from one another, possibly due to poor reagents mixing. Furthermore, only 10 mg of adhesive was applied to the strip, which may not be fully representative of the entire product. As expected, the best adhesion results were obtained with the addition of 100 µL of PEG_{200} as this polyol provides flexibility and promotes further crosslinking extension contributing positively both to the homogenization of the reaction mixture and better crosslinking of the polymeric network, as well as to the interface interactions and adhesive strength. The results suggested that the addition of PEG_{200} in the LS-pMDI reaction mixture favoured the interfacial interaction between the

LS-based PU adhesive and the glued material (wood strips). The latter was comparable to the adhesive strength recorded for a commercial white glue with shear stress values of almost 3 MPa.

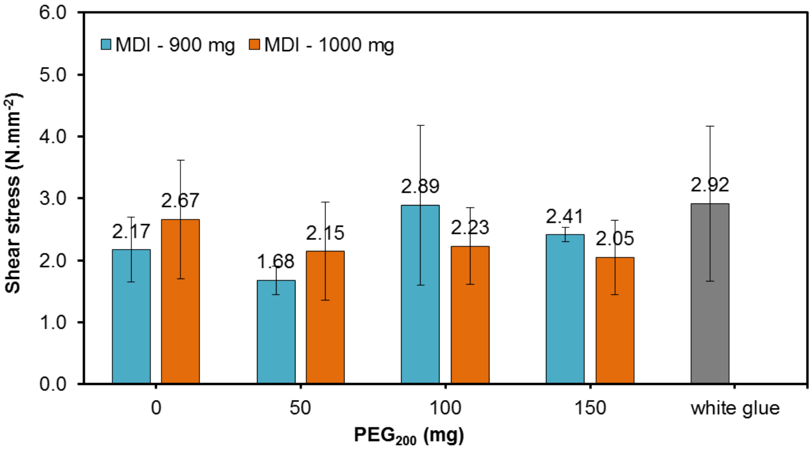

Figure 4. Shear strength values for each LS-based PU formulation as a function of the content of PEG_{200} against the shear strength of commercial white glue (each value correspond to the average of a minimum of three values).

CONCLUSIONS

The results of this study clearly showed that modifying LS eucalyptus is a suitable way to improve their consumer value in conventional and advanced applications. In particular, the hydrophilic-hydrophobic balance of LS can be adjusted by modifying them with non-ionic polymeric extenders that provide improved dispersant properties for concrete formulations. LS can be used as unmodified polyols in reaction with PEG_{200} and diisocyanates (e.g., pMDI) in the formulation of PU adhesives that exhibited adhesion strength comparable to a commercial white glue. LS also can be used as polyols to obtain conductive polyurethane membrane composites to be employed as a sensitive material for all-solid-state potentiometric chemical sensors. In this case, LS act as a sensitive element responsible for triggering mechanisms translated into a potentiometric signal.

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REFERENCES

1. Bajwa, D. S., Pourhashem, G., Ullah, A. H. & Bajwa, S. G. A concise review of current lignin production, applications, products and their environment impact. *Ind. Crops Prod.* **139,** 111526 (2019).
2. Miyake, N., Ando, T. & Sakai, E. Superplasticized concrete using refined lignosulfonate and its action mechanism. *Cem. Concr. Res.* **15,** 295–302 (1985).
3. Plank, J. Applications of biopolymers and other biotechnological products in building materials. *Appl. Microbiol. Biotechnol.* **66,** 1–9 (2004).
4. Arel, H. Ş. & Aydin, E. Effects of Ca-, Mg-, K-, and Na-lignosulfonates on the behavior of fresh concrete. *Constr. Build. Mater.* **157,** 1084–1091 (2017).
5. Areskogh, D., Li, J., Gellerstedt, G. & Henriksson, G. Investigation of the molecular weight increase of

commercial lignosulfonates by laccase catalysis. *Biomacromolecules* **11,** 904–910 (2010).

6. Aso, T., Koda, K., Kubo, S., Yamada, T., Nakajima, I. & Uraki, Y. Preparation of novel lignin-based cement dispersants from isolated lignins. *J. Wood Chem. Technol.* **33,** 286–298 (2013).

7. Guo, X., Zhang, S. & Shan, X. Q. Adsorption of metal ions on lignin. *J. Hazard. Mater.* **151,** 134–142 (2008).

8. Rudnitskaya, A., Evtuguin, D. V., Costa, L. C., Graça, M. P. F., Fernandes, A. J. S., Correia, M. R. P., Gomes, M. T. S. R. & Oliveira, J. A. B. P. Potentiometric chemical sensors from lignin-poly(propylene oxide) copolymers doped by carbon nanotubes. *Analyst* **138,** 501–508 (2013).

9. Alinejad, M., Henry, C., Nikafshar, S., Gondaliya, A., Bagheri, S., Chen, N., Singh, S. K., Hodge, D. B. & Nejad, M. Lignin-Based Polyurethanes: Opportunities for Bio-Based Foams, Elastomers, Coatings and Adhesives. *Polymers (Basel).* **11,** 1202 (2019).

10. Ma, X., Chen, J., Zhu, J. & Yan, N. Lignin-Based Polyurethane: Recent Advances and Future Perspectives. *Macromol. Rapid Commun.* **42,** 2000492 (2021).

11. Cinelli, P., Anguillesi, I. & Lazzeri, A. Green synthesis of flexible polyurethane foams from liquefied lignin. *Eur. Polym. J.* **49,** 1174–1184 (2013).

12. Carriço, C. S., Fraga, T. & Pasa, V. M. D. Production and characterization of polyurethane foams from a simple mixture of castor oil, crude glycerol and untreated lignin as bio-based polyols. *Eur. Polym. J.* **85,** 53–61 (2016).

13. Marques, A. P., Evtuguin, D. V., Magina, S., Amado, F. M. L. & Prates, A. Chemical Composition of Spent Liquors from Acidic Magnesium–Based Sulphite Pulping of Eucalyptus globulus. *J. Wood Chem. Technol.* **29,** 322–336 (2009).

14. Magina, S., Mendes, I. S. F., Prates, A. & Evtuguin, D. V. Changes in sulfite liquor composition while re-profiling mill from paper-grade to dissolving pulp production. *J. Wood Chem. Technol.* **42,** 193–203 (2022).

15. Magina, S., Gama, N., Carvalho, L., Barros-Timmons, A. & Evtuguin, D. V. Lignosulfonate-based polyurethane adhesives. *Materials (Basel).* **14,** 7072 (2021).

16. Magina, S., Barros-Timmons, A. & Evtuguin, D. V. Synthesis of lignosulfonate-based dispersants for application in concrete formulations. *Materials (Basel).* **14,** 7388 (2021).

17. BS EN 12350-5. Testing fresh concrete - Part 5: Flow table test,. *Br. Stand.* 1–14 (2009).

18. Magina, S., Rudnitskaya, A., Soreto, S., Costa, L. C., Barros-timmons, A. & Evtuguin, D. V. Lignosulfonate-based conducting flexible polymeric membranes for liquid sensing applications. *Materials (Basel).* **14,** 5331 (2021).

19. Magina, S., Barros-Timmons, A. & Evtuguin, D. V. Laccase-catalyzed oxidative modification of lignosulfonates from acidic sulfite pulping of eucalyptus wood. *Holzforschung* **74,** 589–596 (2020).

20. Kim, S., Silva, C., Evtuguin, D. V., Gamelas, J. A. F. & Cavaco-Paulo, A. Polyoxometalate/laccase-mediated oxidative polymerization of catechol for textile dyeing. *Appl. Microbiol. Biotechnol.* **89,** 981–987 (2011).

21. Perkins, K. M., Gupta, C., Charleson, E. N. & Washburn, N. R. Surfactant properties of PEGylated lignins: Anomalous interfacial activities at low grafting density. *Colloids Surfaces A Physicochem. Eng. Asp.* **530,** 200–208 (2017).

22. Amemiya, S., Bühlmann, P. & Umezawa, Y. A Phase Boundary Potential Model for Apparently 'Twice-Nernstian' Responses of Liquid Membrane Ion-Selective Electrodes. *Anal. Chem.* **70,** 445–454 (1998).

23. Evtuguin, D. V., Andreolety, J. P. & Gandini, A. Polyurethanes based on oxygen-organosolv lignin. *Eur. Polym. J.* **34,** 1163–1169 (1998).

24. Pizzi, A. in *Lignocellul. Fibers Wood Handb. Renew. Mater. Today's Environ.* (eds. Belgacem, N. & Pizzi, A.) 277–303 (Scrivener Publishing LLC, 2016). doi:10.1002/9781118773727.ch10