VALUABLE POLYMERIC PRODUCTS FROM LIGNOSULPHONATES

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ABSTRACT

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. It is known that technical lignins can be functionalized and directed to various applications as dispersants, adhesives, plastics, resins, conducting polymeric composites, including many others. Among technical lignins, lignosulphonates (LS) are sulphonated lignin-derived by-products present in sulphite spent liquors (SSL) from acidic sulphite pulping, which can be used after purification from SSL without further treatments (i.e., as such) to produce value-added products.

In this work, purified eucalypt LS were used to produce polymeric formulations for three different applications. The first goal was to improve LS dispersion efficiency for concrete formulations to substitute (partially or completely) the commercial petroleum-based superplasticizers, such as polycarboxylates. Different chemical modification strategies were used to achieve this purpose, including (but not only) (1) increasing the molecular weight of LS through laccase-catalyzed oxidative polymerization, which yielded a modified LS with increased Mw (11-fold from initial Mw of LS) and some structural changes (such as decreased of the S/G ratio compared to unmodified LS), and (2) the synthesis of LS-based non-ionic polymeric dispersants using epoxidized oligomer derivatives of PPG to yield the targeted enhanced dispersant properties. Although the molecular weight of this later product increased only slightly, it was the only product exhibiting relevant enhanced dispersant efficiency compared to unmodified LS and the other modified LS but not as relevant as the dispersion efficiency of the commercial petroleum-based superplasticizers. Yet, the results suggest that this study is well on the way to obtaining improved dispersants based on the LS.

The second goal 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 polyurethane (PU) flexible membranes doped with different amounts of MWCNTs were synthesized. The LS-based composite containing 1 % w/w MWCNTs displayed relevant electrical conductivity being suitable for sensing applications. These sensors showed sensitivity to a series of transition metals, such as Cu(II), Zn(II), Cd(II), Cr(III), Cr(VI), Hg(II), and Ag(I) at pH 7, exhibited a response to the Cr(VI)/Cr(III) redox pair at pH 2 and a weak but not negligible response toward ionic liquids, [C2mim]Cl and ChCl. The results suggested that the response is highly dependent on the type of lignin used (including the wood source and pulping conditions).

Finally, the third goal was to use LS as macropolyol in PU formulations for adhesive purposes. Due to some limitations in the accessibility/reactivity of hydroxyl groups in LS in the reaction with pMDI and difficulties in effective homogenization of the reaction mixture, the addition of PEG with low molecular weight (Mw 200, PEG_{200}) seems to be advantageous to overcome, at least partially, these drawbacks. The results suggested that the addition of PEG_{200} in the LS-pMDI reaction mixture favored the interfacial interaction between the LS-based PU adhesive and the glued material (wood strips). The adhesion strength of LS-based PU was comparable to a commercial white glue.

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