DEVELOPMENT OF CROSSLINKED PVA–CHITOSAN COMPOSITE MEMBRANES INCORPORATING KRAFT OR ORGANOSOLV LIGNIN FOR ENERGY CONVERSION AND STORAGE APPLICATIONS

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Poly(vinyl alcohol) (PVA) is a cost-effective, environmentally friendly polymer widely investigated for energy applications [1]. However, its low ionic conductivity, excessive swelling, and high permeability currently limit its performance [2]. Blending PVA with the abundant biopolymer chitosan (CS) can improve conductivity and physico-chemical stability, while enhancing the sustainability of the membranes [3]. Further property enhancement is achieved by cross-linking with sulfosuccinic acid (SSA), which forms covalent bonds and introduces sulfonic acid groups that facilitate water retention and ion transport [4].

This study investigates the optimisation of a PVA/CS blend (60:40) containing 20 $wt\%_{CS}$ of the plasticiser glycerol and 30 $wt\%_{PVA}$ of SSA [5] using two hot-press cross-linking conditions (110 °C for 2 h or 120 °C for 3 h, both at 25 kg/cm^2) and the addition of 5 $wt\%_{CS}$ kraft lignin (KL) or organosolv lignin (OL) as filler. Overall, this strategy aims to develop sustainable polymer membranes tailored for advanced energy-related applications.

Lignin incorporation into the PVA/CS composite matrix is confirmed by the visual presence of lignin particles on the membrane surface and increased characteristic infrared absorbance. Lignin addition increases water uptake due to disruption of the hydrogen-bonding network, resulting in a looser amorphous structure [6].

Thermal cross-linking with sulfosuccinic acid (SSA) during hot pressing significantly reduces water uptake by decreasing the availability of polar functional groups and reducing the inter-chain volume, particularly under more severe conditions (120 °C for 3 hours), indicating a higher degree of cross-linking. The resulting three-dimensional network of covalent bonds restricts the polymer chain mobility, which reduces the glass transition temperature (T_g), and limits radical accessibility, thereby improving the oxidative stability of the composites in Fenton's reagent.

Lignin particles actively participate in the cross-linking reaction, further compacting the polymer network and reducing water retention. Consequently, cross-linked composites containing KL and OL exhibit lower water evaporation peak temperature in thermogravimetric and calorimetric studies, indicating weaker water retention due to a reduced number of hydrophilic sites. These membranes also show higher onset temperatures for polymer degradation (~240 °C) and improved durability against accelerated degradation induced by proton transport, consistent with the formation of a stronger cross-linked network. KL-containing composites exhibit greater hydroxyl group consumption after cross-linking and a higher incorporation of acidic functionalities ($-SO_3^-$) resulting in enhanced proton diffusion.

Overall, the combination of lignin incorporation and controlled thermal cross-linking provides a promising strategy for the develpoment of highly functional, low-cost, and sustainable PVA/CS membranes for energy-related applications.

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