

Enzyme one-pot system for the construction of artificial lignin-based composites

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Abstract: A novel and practical one-pot system was developed for artificial lignin-composites production. Monolignols such as sinapyl alcohol (SA) and coniferyl alcohol (CA) were linked together with CafAc in a polymeric net similar with natural lignin based on oxi-copolymerization process with H₂O₂ as oxidation reagent and peroxidase enzyme as biocatalyst (71.1 % and 49.8 % conversion for SA and CA, respectively). Variation of system polarity by adding a co-solvent (e.g. MeOH, EtOH and THF) affected the conversion. Additionally, the chemical structure, morphology, and properties of the bio-composites surface were investigated using different techniques, e.g. FTIR, TPD-NH₃, TGA, contact angel and SEM.

Keywords: bio-composite, artificial lignin, peroxidase.

1. Introduction

Lignin is one of the most abundant green polymer in the world together with the cellulose and hemicellulose. Beside the natural sources exploited up to maximum limit today, the pulp-paper as well as bio-refining industries are generous providers of lignin resources. As an example, the papermaking industry produces over 50 million tons of lignin wastes annually used mainly as energy source by combustion and only 2 % for polymeric industry (e.g. production of phenolic resins, polyurethane foams, bio-dispersants and epoxy resins). Considering the environmental pollution caused by paper-pulp industry and also the necessity for improving of the market competitiveness for bio-refining industry, new perspectives of lignin valorization are absolutely required.

We studied the construction of lignin-composites using monolignol fractions (e.g. SA or CA) based on the fact that lignin can be efficiently converted into a mixture of mono-/oligo-mers [1-3] with the ability to be recombined into artificial lignin [4].

2. Experimental

Solid supports S_{C2} and S_{C6} (S_{C2} - amino C2 methacrylate and S_{C6} - amino C6 methacrylate, 150-300 μm of diameter) were functionalized with CafAc for providing phenolic structures on the particles surface. For bio-composites preparation, mixture of functionalized silica particles, SA/CA, 2-1B mutant of versatile peroxidase and H₂O₂ in PBS solution was incubated over night under gentle agitation at 40 °C. Separation of bio-composite by centrifugation led also to a supernatant. Both phases were analyzed using UV-Vis and Folin-Ciocalteu approaches. Bio-composites characterization were performed using specific protocols of FTIR, TPD-NH₃, TGA, contact angel and SEM techniques.

3. Results and discussion

Oxi-copolymerization process has been developed in a heterogeneous system, i.e. SA/CA dissolved in liquid phase, while CafAc was attached on silica particles (S_{C2}/S_{C6}-CafAc). In this case, the monolignols and immobilized CafAc were linked together in a polymeric structure miming the natural lignin and attached directly on the particles surface. S_{C2}/S_{C6}-CafAc-L₁ bio-composite was produced from CA, while SA oxi-

copolymerization led to S_{C2}/S_{C6} -CafAc- L_2 . Different conversions were achieved for both functionalized supports (S_{C2} -CafAc and S_{C6} -CafAc) demonstrating that the solid support together with type of monolignol affected the co-polymerization process (S_{C2} -CafAc - 71.1 % of SA and 49.8 % of CA, and S_{C6} -CafAc - 65.7 % of SA and 36.3 % of CA). Comparing the results of the UV-Vis and Folin-Ciocalteu analysis on the supernatant demonstrated that most of the monolignols were efficiently converted to the polymeric layer of the bio-composites instead of dissolved oligomers in the supernatant. Additionally, poor reproducibility of bio-composite production for using co-solvent (e.g. MeOH, EtOH, THF) enforced to choose the H_2O alternative.

Characterization of the produced bio-composites (S_{C2}/S_{C6} -CafAc- L_1 and S_{C2}/S_{C6} -CafAc- L_2) allowed to highlight the products morphology, textural and physico-chemical properties. FTIR spectra offer clear evidence of the artificial lignin deposition on the silica beads. TPD- NH_3 analysis allowed to evaluate the bio-composite acidity related to the CafAc-functionalized support. SA monolignol allowed to prepare a bio-composite with two different acidity centers assigned by phenolic and aliphatic OH groups. Total number of acidity for SA-based bio-composite was higher than for CA-based bio-composite. This evaluation is in agreement with the conversion calculated previously for oxi-copolymerization of monolignols. Also, the lignin attachment improved the thermo-stability of the composites compared to original/functionalized support.

Investigation of surface hydrophobicity was performed using contact angle measurement of distilled water on CafAc-functionalized silica chip (S-CafAc) and the corresponding bio-composites (S-CafAc- L_1/L_2). The contact angle of the chip (S) was 29° , while the bio-composites reached to 63° for CA-based polymer or 18° for SA-based polymer. Obviously, the results indicated an enhancement of the hydrophobicity when the chip surface was covered with the oxi-copolymer L_1 belonged to CA monolignol. Similar hydrophobicity was reported in the literature for natural lignin attached on silica surfaces [5, 6]. Moreover, it has to be mentioned that the artificial lignin prepared by oxi-copolymerization is more hydrophobic than some natural lignins (e.g. soda lignin from *Triticum sp* and *Saccharum officinarum* with 35° contact angle) [7].

4. Conclusions

Beside of an innovative system for bio-composite preparation with green chemical aspects, this work gives a new alternative for valorization of lignin residues. Versatility as well as green aspects of the polymeric structure on the bio-composite surface allow easy adjustment of proposed bio-composites to different applications. In this direction, we can mention the use of bio-composites as support or carrier for biomolecules (e.g. enzymes and whole cell) when specific properties of support/carrier are requested.

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