UNIVERSITY OF BUCHAREST
FACULTY OF CHEMISTRY
DOCTORAL SCHOOL IN CHEMISTRY

DOCTORAL THESIS SUMMARY

BIO-COMPOSITES PRODUCED VIA THE BIOCATALYTIC TREATMENT OF WASTE LIGNINS

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2024

Bio-composites produced via the biocatalytic treatment of waste lignins

The Doctoral thesis "Bio-composites produced via the biocatalytic treatment of waste lignins" focused the synthesis of ligno-polymeric materials through the derivatization of the native lignins and oxy-polymerization of monolignols with co-monomers of industrial interest. Both alternatives were based on enzymatic catalytic protocols able to controll the generation of new materials with improved physico-chemical properties.

Lignin and functionalized lignin already found interest in a wide range of applications from biomedicine to advanced materials and energy storage. Their abundance, biocompatibility and unique properties make these and their derivatives promising candidates for sustainable and ecological solutions in several industries. The scientific reports published in the last ten years confirmed this interest demonstrating a growing effort for the development of new possible applications in fields such as the preparation of biodegradable composites or the synthesis of nanoparticles and nanostructures with antimutagenic and antioxidant activity. These applications are well related on the generated new physical and chemical properties, quit different from those provided by the nature. Thus, the polymerization by chemically controlled radical-radical coupling reactions can lead to the formation of similar C-C and C-O-C bonds as those in lignin. As an effect, it may be generated a modification of the existing structural heterogeneity with a controlled arrangement of the constituent entities and of new properties.

The thesis is structured in six chapters. The first chapter provides an overview of biomass, reviewing the commonly sources of renewable carbon. In accordance, it mainly focuses on the different lignin-type biomass considering the types of lignins found in the nature, their properties and the extraction methods.

Chapter 2 describes the main chemical reactions investigated in order to modify the lignin structure and properties. The functionalization of the lignin can take place by the transformation of the hydroxyl, carboxyl, methoxy groups or of the aromatic ring. In addition, new ligno-polymeric materials with improved properties can be generated through the oxy-polymerization reactions of the lignin monomers (monolignols) as compared with the initial lignin.

Chapter 3 focused a method for the synthesis of artificial lignins starting from coniferyl or sinapyl alcohol monolignols, using different molecules (as caffeic acid) incorporated into the polymer structure. In order to generate a polymeric structure similar to that of the natural lignin, the caffeic acid has been used as a linker for these monolignols. It corresponds to a natural, rigid molecule in which the double bond and the cycle forces flattening taking the advantage of the –OH group from the geometric favorable para-position. The introduction of such a molecule ensured the attachment of the polymer to the surface of a solid support (e.g. Amino C2/C6 Methacrylate solid support), thus generating new properties of the resulted ligno-polymer.

Chapter 4 describes the study of the biocatalytic oxy-polymerization of coniferyl alcohol with aniline, directly on the surface of a support (Amino C2 Methacrylate or Amino C6 Methacrylate) functionalized with amino-phenolic derivatives. The resulting composites were covered by a ligno-polymeric layer on the surface of the support, thus allowing the immobilization of the lipases.

Chapter 5 focused on a biocatalytic perspective of lignin derivatization with aniline by grafting the $–NH_2$ group using an enzymatic catalytic method. Thus, the process was carried out in the presence of an oxidizing agent, assisted by an enzyme biocatalyst from the peroxidase class. This method led to functionalized lignins with amine groups, allowing the control of the properties of the resulting ligno-polymer.

Finally, the chapter 6 discusses the lignin derivatization (carboxymethylation) in the presence of a carboxymethylation agent (dimethylcarbonate) and lipase, as a biocatalyst. This protocol allowed a well controlled modification of the physical and chemical properties of the initial lignin.

The general conclusions are detailed at the end of the doctoral thesis.