Progress in Polymer Science 39 (2014) 1266–1290

Contents lists available at ScienceDirect

Progress in Polymer Science

journal homepage: www.elsevier.com/locate/ppolysci

Chemical modification of lignins: Towards biobased polymers

Stéphanie Laurichesse, Luc Avérous*

BioTeam/ICPEES-ECPM, UMR 7515, Université de Strasbourg, 25 rue Becquerel, 67087 Strasbourg, Cedex 2, France

ARTICLE INFO

Article history:
Received 17 May 2013
Received in revised form
12 November 2013
Accepted 14 November 2013
Available online 20 November 2013

Keywords:
Lignin
Biopolymer
Biomass
Pyrolysis
Polyurethane foams
Epoxy resins

ABSTRACT

Lignins are now considered as the main aromatic renewable resource. They represent an excellent alternative feedstock for the elaboration of chemicals and polymers. Lignin is a highly abundant biopolymeric material that constitutes with cellulose one of the major components in structural cell walls of higher vascular plants. Large quantities of lignin are yearly available from numerous pulping processes such as paper and biorefinery industries. Lignin extraction from lignocellulosic biomass (wood, annual plant) represents the key point to its large use for industrial applications. One of the major problems still remains is its unclearly defined structure and its versatility according to the origin, separation and fragmentation processes, which mainly limits its utilization. While currently often used as a filler or additive, lignin is rarely exploited as a raw material for chemical production. However, it may be an excellent candidate for chemical modifications and reactions due to its highly functional character (i.e., rich in phenolic and aliphatic hydroxyl groups) for the development of new biobased materials. Chemical modification of lignin has driven numerous efforts and researches with significant studies during the last decades.

After an overview with some generalities concerning the main extraction techniques along with the structure and the properties of lignins, this review describes in details the different chemical modifications of lignins. They are classified into three groups: (1) lignin fragmentation into phenolic or other aromatic compounds for fine chemistry, (2) synthesis of new chemical active sites to impart new reactivity to lignin, and (3) functionalization of hydroxyl groups to enhance their reactivity. In that frame, the potential applications of lignin as precursor for the elaboration of original macromolecular architecture and the development of new building blocks are discussed. Finally, the major achievements and remaining challenges for lignin modifications and its uses as a macromer for polymer synthesis are also mentioned with emphasis on the most promising and relevant applications.

Contents

* Corresponding author. Tel.: +33 3 68852784; fax: +33 3 68852716.
E-mail address: luc.averous@unistra.fr (L. Avérous).

0079-6700/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.progpolymsci.2013.11.004

1. Introduction

The petrochemical boom of the second half of the last century has marked the strong development of the production of synthetic polymers. The availability of a growing number of monomers from fossil resources has supplanted during a period of time the use of biobased chemicals and their corresponding polymers. For different reasons, mainly economic, modest investments were devoted for a long time to the development of renewable resources in chemistry. Nevertheless, the increasing use of fossil fuels associated with the lack of availability of some petrol fractions and an increasing awareness concerning the human impacts on the environment have led to a renewed strong interest in the use of sustainable resources for energy and material [1]. This growing interest about a green and sustainable chemistry has also contributed to call attention to biomass and specifically on lignocellulosic feedstock as a promising, renewable and vast resource for chemicals, mainly without competition with food applications compared to, e.g., starch or vegetable oils. Lignocellulosic biomass is mainly composed of carbohydrate polymers (cellulose and hemicellulose), and aromatic polymers (lignin and tannin). After cellulose, lignin is the second most abundant polymer from biomass and the main one based on aromatic units. It can be isolated from wood, annual plants such as wheat straw or agricultural residues (sugar cane bagasse) by different extraction processes. Research on lignin chemistry is not recent. Progress concerning lignin characterization in the mid-nineteenth century contributed to the development of new materials based on renewable resources. Improved technologies associated with papermaking, wood processing and textile also contributed to the development of these polymers from biomass [2] that could be integrated in biorefineries [3,4] to produce a large range of outputs such as materials, power, chemicals and fuel. The following reviews the major breakthrough in lignin by mainly development of biorefinery industries and new processes to convert this biomacromolecule into value-added products.

One objective of this review is to provide overview and background information on economic aspects concerning the use of lignin from its extraction by several processes to its thermal conversion or chemical modification. Beyond the presentation of the different chemical investigations performed on lignin, special stress will be laid on potential applications for production of chemicals and polymers.

2. Lignin chemistry

2.1. Historical outline

A period of about 170 years has passed since the French chemist, Anselme Payen (1795–1871) treated wood with nitric acid and caustic soda, recovering two different products [5]. He called the first one “cellulose” and the other material with higher carbon content was considered as an *incrusting material*, in which the fiber-forming cellulose was imbedded. The Payen’s “incrustation theory” [6] marks the beginning of the history of what latter was named “lignin”, a word derived from the Latin *lignum*, meaning wood [7,8]. At that time, the nature of this abundant