International Journal of Adhesion & Adhesives 48 (2014) 92–101

Contents lists available at ScienceDirect

International Journal of Adhesion & Adhesives

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

Lignin in straw and its applications as an adhesive

Seyed Hamidreza Ghaffar, Mizi Fan*

Nanocellulose and Biocomposites Research Centre, School of Engineering and Design, Brunel University, Uxbridge, Middlesex UB8 3PH, United Kingdom

ARTICLE INFO

Article history:
Accepted 30 May 2013
Available online 27 September 2013

Keywords:
Lignin
Straw
Adhesive
Lignocellulosic
Lignin-based products

ABSTRACT

The relevant information about the lignin in straw and its applications in the industry is scattered and scarce compared to the wood lignin. This review is focused on the chemical structural and composition of lignin in the straw, and its modification and uses as an adhesive. The review has showed that (1) lignin as a by-product in the pulping process and as an abundant natural and renewable product has been used and there is a great potential for many applications across various industrial sectors as a replacement for increasingly scarce and expensive petroleum based materials, including traditional products, e.g. resins, and composites, and emerging materials, e.g. biofuel and commodity chemicals. (2) The type of lignin differs not only from one to another species but also depending on the isolation protocol. However, the lack of optimising or processing technologies is significant when it comes to using technical lignin. The review has also shown a great encouragement in studying the lignin within the straw and other herbaceous crops, and the creation of the functionalities of lignin as it does with cellulose and hemicellulose could lead to radical development of lignin as bio-matrix for green composites and biomass as biofuel or other high value added applications.

1. Introduction

Straw is generally constituted of three groups of organic mixtures: cellulose, hemicellulose and lignin. These compounds account for more than 80% of the dry matter of the three most common British cereal straws: namely barley, oats and wheat [1]. The chemical content of straw varies according to the stage of maturity, soil type and fertiliser treatment Table 1 [2].

Straw also contains various other organic compounds including protein, small quantities of waxes which protect the epidermis of the straw, sugars, salts and insoluble ash including silica. The lignin content for those main straw species ranges from 12 to 21% although it varies from one to another species Table 1. The first discovery of lignin was recorded from 1838 by Anselme Payen cited by McCarthy and Islam [3]. However, the word lignin was put forward in 1865 by Schulze to describe the dissolved part of wood when treated with nitric acid [4,5]. The research on lignin has proceeded at a fast pace since 1960s when powerful modern analytical tools of biochemistry and organic chemistry were applied and therefore interesting information was gathered. Research on lignin has also attracted much attention because of the dominant pulping industries [3] and recently a large number of studies on the lignin focused on finding a higher value application [4].

Lignin is an amorphous natural polymeric material that is based on phenylpropane derivate and one of the most abundant materials and renewable resources on earth. It is well accepted that lignin is a phenolic polymer derived primarily from three hydroxycinnamyl alcohols or monolignols by free radical generation followed by chemical coupling process. The hydrocycinnamyl are *p*-coumaryl alcohol (MH), coniferyl alcohol (MG) and sinapyl alcohol (MS) [6] (Fig. 1).

Many attempts have been made to define lignin based on the constitution, structural features and mechanism of formation. However, the definition of lignin has never been as clear as that of other natural polymers such as cellulose and protein, the reason being the extremely complicated isolation, compositional analysis and structural characterisation [6]. Lignin is never defined as a compound, is a class of phenolic natural polymers with broad compositions and a variety of linkages between units. The problem of lack of precise definition for lignin is also associated with its nature; no regularly repeating multiunit structures have been found, and composition and structure of lignin vary depending on their origins [6]. In a recent review of lignin, a definition given by Brunow was cited as the most concise and comprehensive one to date [7]: lignins are biopolymers consisting of phenylpropanoid units with an oxygen atom at the p-position (as HO or O–C) and with none, one or two methoxyl groups in the o-position to this oxygen atom.

There are many review articles and book chapters available that focus on structure, composition and biosynthesis of lignin, which are mostly wood lignin [4,8,9]. Reviews on lignin in herbaceous

* Correspondence to: Department of Civil Engineering, Brunel University, UB8 3PH United Kingdom. Tel.: +44 1895 266466.
E-mail address: mizi.fan@brunel.ac.uk (M. Fan).

0143-7496/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.ijadhadh.2013.09.001

Table 1
Chemical composition of agricultural residues (% dry matter) based on [2].

Type	Lignin	Cellulose	Hemicellulose	Water-soluble	Wax	Ash	Others
Wheat straw	14.1	38.6	32.6	4.7	1.7	5.9	2.4
Rice straw	12.3	36.5	27.7	6.1	3.8	13.3	0.3
Rye straw	17.6	37.9	32.8	4.1	2.0	3.0	2.6
Barley straw	14.6	34.8	27.9	6.8	1.9	5.7	8.3
Oat straw	16.8	38.5	31.7	4.6	2.2	3.1	3.1
Rape straw	21.3	37.6	31.4	-	3.8	6.0	0
Maize stems	15.0	38.5	28.0	5.6	3.6	4.2	5.1
Corn cobs	14.6	43.2	31.8	4.2	3.9	2.2	0.1
Esparto	17.8	35.8	28.7	6.1	3.4	6.5	1.7
Bagasse	19.4	39.2	28.7	4.0	1.6	5.1	2
Rye grass	8.2	37.6	32.2	8.5	4.4	4.5	4.6
Oil palm fibre	18.7	40.2	32.1	5.0	0.5	3.4	0.1
Abaca fibre	12.4	60.4	20.8	3.7	0.8	2.5	0

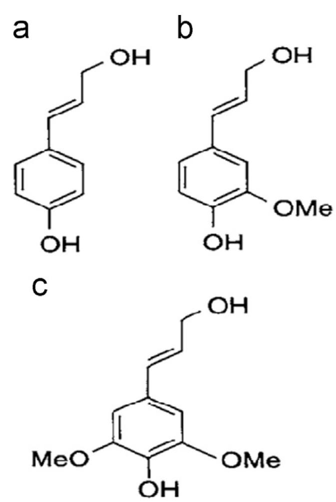

Fig. 1. Three primary lignin monomers: (a) monolignols *p*-coumaryl alcohol, (b) coniferyl alcohol and (c) sinapyl alcohols [7].

plants are limited. It is evident that the interest in herbaceous crops and their lignin is increasing and will increase further due to the importance of bioethanol production from annually renewable biomass. Hence this paper reviews the structural characterisation of lignin in straw and the process for purification and isolation of lignin. The focus of the review is centered on the applications of lignin in the engineering industry, e.g. for the development of construction materials, such as the use of lignin as adhesives for strawboard, particleboard, fibreboard, oriented strand board and wood fibre insulation board.

2. Why utilising lignin in engineering?

Renewable resources in engineering industry are very essential, and the creative design and wise application of innovative technology for the optimisation of such resources is one of the new research topics. Using a system-based approach to design technology for the sustainable development, management and conservation of our natural resources is what researchers are keen to develop. Using renewable resources in many aspects means a reduction of energy consumed synthesis and harmful substances from end product. For example manufacturers of medium density fibreboard (MDF), particleboard (PB), plywood and oriented strand board (OSB) are under pressure to reduce production costs and harmful formaldehyde emissions from the petroleum derived adhesives, and to improve product recyclability. Innovative approaches to minimise the amount of binder while ensuring product quality is vital for the industry. The transition from petroleum based chemical processes to bioprocesses based on renewable raw materials provides considerable environmental gains and such the maintenance of economic growth.

The oil crisis during the 1970s turned attention towards the utilisation of renewable resources and towards lignocellulosic materials in specific, hence biotechnical utilisation of lignocellulosic wastes from agriculture and forestry gained priority. This was a logical step to take since one of nature's most important biological reactions is the conversion of wood and other lignocellulosic materials to carbon dioxide, water and humic substances [10]. Since lignocellulosic plants constitute the raw material for the forest industries, there should be plenty of opportunities to use biotechnology to improve both the production and the use of these resources. Biotechnical utilisation and conversion of lignocellulosic materials mean the production of inexpensive products on a large scale. Biotechnological utilisation of lignocellulosic materials is therefore a very difficult task and the commercial utilisation of this technology has only recently gained momentum. Lignin in straw is receiving increasing attentions, the reason being its annual renewability and herbaceous plants have the largest annual biomass stock (1549 million tons/year worldwide) [11]. The main difficulty for the utilisation of herbaceous crops biomass is the complete separation of lignin–carbohydrates complexes (LCC) which shield cellulose from enzymatic hydrolysis and fermentation. The enzymatic digestibility of the biomass for production of bio products and biofuels depends mainly on its lignin content [12,13]. Consequently, the extraction of lignin from straw is important and the utilisation of extracted lignin could lead to the industrial production of treasured industrial products such as vanillin, ferulic acid, vinyl guaiacol and optically active lignans, the dimers of monolignols.

3. Types and variations of straw lignin

Lignin is found as a cell wall component in all vascular plants [4]. The lignin content in plant stems varies between 15 and 40%. Lignin acts as water sealant in the stems and plays an important role in controlling water transport through the cell wall. It also protects plants against biological attack by hampering enzyme penetration and acts as permanent glue, bonding cells together in the plant stems and thus giving the stems their well-known rigidity and impact resistance [14]. Most industrial lignin is obtained as a waste product during the paper pulping process, but it can be found in all plants. While cellulose is used for paper production and natural oils are mainly used in the food industry, the industrial applications of lignin are rather limited, despite its widespread availability. In 1998 about 1% of all lignin generated in paper production worldwide was isolated and sold [3]. The remaining 99% was either burned in an energy recovery step for the pulping process or disposed of in waste streams. Extrapolating this 1% lignin leads to a worldwide production of more than 10 million tons per year of available renewable raw material [15]. A number of studies on lignin focused on finding a higher value application [16–18].

The lignin within the straw is known to be structurally different from hardwood and softwood lignin; one of the significant differences is the monomeric composition. Straw lignin comprises all three H, G and S subunits. On the other hand, wood lignin contains mainly G and S subunits (except for compression wood which contains H and G units) [17]. The physicochemical properties of straw lignin are known to possess characteristic alkali solubility [19]. Alkali treatments have been used to increase the digestibility of various straws and to manufacture paper [20,21]. The solubility of straw lignin in alkali has been attributed mainly to the presence of significant amounts of *p*-hydroxyphenyl (H) residues, which are bound to lignin as *p*-coumarate units