Research Progress in the Chemical Modification of Eucalyptus

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Abstract. Eucalyptus, a main fast-growing tree species for plantation in southern China, has remarkably contributed to balance the supply and demand of wood in the country. Eucalyptus is mainly used for processing wood-based panels, including fiberboards, plywood, and chipboards, with low added value because of its poor dimensional stability and susceptibility to cracking and deformation. In this paper, the mechanisms, merits, and demerits of wood acetylation, furfurylation, and resin-related and thermal modifications were summarized. The research status of the chemical modification of eucalyptus was analyzed, and existing problems and future research directions of eucalyptus modification were stated briefly.

Keywords: eucalyptus; acetylation; furfurylation; modification with resin; thermal modification

1. Introduction

China’s wood output has decreased significantly for six consecutive years from 2012 to 2017. The timber yield of 2018 was 84.32 million cubic meters, which is slightly higher than that of 2017; however, the gap remains large. The timber yield of Guangxi has ranked first in the country in recent years¹[2] and eucalyptus has been the most important tree species for plantations in Guangxi, with a planting area over 30 million mu. The National Sharing Infrastructure on Science Data of Forestry reported that the timber yield of Guangxi in 2018 reached 31 million cubic meters; of which, eucalyptus accounted for about 70%. The eucalyptus industry is the ninth industry with annual sales of over RMB100 billion in Guangxi [3][4]. Eucalyptus trees grow rapidly and have high wood density (0.45–0.58 g/cm³), fine and beautiful texture, and other merits. However, eucalyptus easily cracks and deforms and exhibits poor machinability, corrosion resistance, etc.; as such, its utilization is severely restricted. This paper summarizes various methods of chemical modification of wood. Existing problems in chemical modification of eucalyptus were analyzed and future research direction and possible breakthroughs were prospected to regulate the supply and demand of wood in China and increase the added value of this tree.
2. Research on chemical modification of wood

Wood modification, especially chemical modification, can greatly improve wood properties that are important in processing and storage. Wood modification adopts physical or chemical methods to refine natural wood properties, such as anti-corrosion (anti-moth), mechanical strength, and dimensional stability, and extend its service life. Wood is an anisotropic porous material, and its primary components, such as cellulose, hemicellulose, and lignin, contain numerous hydroxyls, which exhibit wood reactivity and hydrophilicity. Reactivity and hydrophilicity are the main foundations for wood modification. Wood modifier enters the wood by impregnation and pressurization, leading to molecular changes in the cell wall or closing of lumen and consequently improving the properties of wood. The entry of modifier into wood and its stacking in lumen are not good for improving wood properties. The modification effect depends on whether the modifier can enter the cell wall and improve wood density; the reaction of the modifier with cell wall constituents can improve the wood and enhance its durability [5]. Various techniques can be used for chemical modification of wood; among which, wood acetylation[6], resin impregnation[7], and thermal modification[8] are the most successful.

2.1. Acetylated wood

Wood acetylation has been extensively studied and applied. Acetylated wood was first reported in 1946. Wood acetylation can significantly improve dimensional stability, water absorption resistance, decay protection, and so on [9]. The modification mechanism of wood acetylation largely depends on the reaction of anhydride with cell wall constituents, which are mainly hydroxyls on the cell wall, as well as wood expansion due to acetic anhydride, reduction of hydroxyl number, reduction of water absorption, blockage of cell wall micro pores, increased decay protection and dimensional stability, and reduction in the equilibrium moisture content [10]. The degree of wood acetylation is significantly related to the contents and distributions of cell wall constituents; it is characterized by the higher content of lignin in acetylated wood than those of hemicellulose and cellulose and the higher acetylation efficiency of low-density wood than that of high-density wood [11]. Thus, the wood of high content lignin is liable to acetylation. Although wood acetylation refines the wood absorbency, the hardness, elastic modulus, and creep resistance of acetylated wood diminish because acetic anhydride can degrade wood components, thereby decreasing the wood strength and causing difficulty in the recovery of the reaction mixture[12]. Acetylated wood is corrosive to ferrous metals and poorly resistant to blue staining fungi. The color of wood after acetylation becomes dark[13]. Acetylated wood is costly and mainly used for high-value-added products.

2.2. Furfurylated wood

Furfurylated wood is based on the in situ polymerization principle of furfuryl alcohol. Under heating and catalyst reactions, furfuryl alcohol monomers polymerize and react with lignin and become grafted in the cell wall, increasing the number of hydrophobic groups in wood [14] and improving the dimensional stability, hardness, flexure strength, anti-corrosion, insect resistance, and so on of wood. When the weight gain rate (WPG) of the modified lumber is low, furfuryl alcohol is found in the cell wall of wood but less in lumen; furfuryl alcohol monomers are abundant in lignin concentrated area. Furfuryl alcohol oligomers are impregnated with modified wood, minimal difference between cell wall and lignin is observed in the concentration of furfuryl alcohol[15]. Hadi[16] found that the WPG of furfuryl alcohol in wood is high, indicating that additional furfuryl alcohol enters the wood and leads to enhanced anti-termite performance. Furfurylated wood is not very durable underground [17].

Furfural can significantly improve the properties of wood but also has many disadvantages. First, furfurylated wood can easily get dark especially when the concentration of furfuryl alcohol is high; the color changes pronouncedly, and in severe cases, the surface is carbonized [18]. Second, the leachate from furfurylated maple is highly toxic, but the toxicity of furfurylated wood is also affected by tree species [19]. The impact strength of furfurylated wood decreases with WPG [15].
2.3. Wood modified with thermosetting resins
Thermosetting resins have been used to develop wood-based composites with commercial value. Thermosetting resins for wood impregnation primarily include urea resin (UF), phenol–formaldehyde (PF) resin, and melamine formaldehyde resin (MUF). After impregnating the wood with resin and curing at high temperature, active groups, such as hydroxyl and amino groups, in the resin can form a cross-linked structure with the cell wall constituents; the resultant hydrophobic groups permanently swells the cell wall of wood and the equilibrium moisture content and hygroscopicity of wood are reduced, thereby improving the properties of wood [20][21].

Gindl[21] found that water-soluble melamine resin can enter the cell wall (S2) of wood, and the Young modulus and lateral cell wall hardness of modified wood are improved by 33% and 115%, respectively. Resin mainly penetrates the adjacent lumen and cell wall via pits [22]. South yellow pine is impregnated with MUF or melamine–melamine–formaldehyde (MAF) resin; MAF-treated wood greatly enhances dimensional stability and flame and weathering resistance and moderately increases chemical resistance; however, the cured resin is hard and brittle, weakening the mechanical properties of wood [23]. Resin-impregnated wood exhibits improved modification effect but is costly and has environmental pollution problems (free formaldehyde).

2.4. Thermally modified wood
Thermally modified wood is an important part of industrial wood products. Thermal modification can degrade hemicellulose in wood at high temperatures. Organic acids produced during the degradation of hemicellulose accelerate the degradation of the amorphous regions of hemicellulose and cellulose, enabling the permanent chemical change of the wood components and improving the properties of wood. The most important characteristics of thermally modified wood are the higher dimensional stability, durability and lower equilibrium moisture content compared with the untreated control.

Research on thermal modification began in the early 20th century; current modification technology is relatively mature and has been applied in actual production in Finland, France, the Netherlands, and Germany. Under the same heating condition (such as 205 °C, 2 hours), wood hygroscopicity in an oxidizing environment is far below that in reducing condition; in increased temperature, the same hygroscopicity can be obtained in the reducing atmosphere. However, the original hygroscopicity of thermally modified wood can be restored by soaking in water in any heating condition; the color of thermally modified wood changes with decreasing hygroscopicity[24]. Thermally modified wood has no adverse effect on the environment, but the chemical reactions are complex and the safety of thermally modified wood should be considered. Kamdem et al.[25] investigated the toxicity of thermally modified wood and reported that the organic solvent extract of thermally modified wood produces potentially toxic compounds, such as toxic polycyclic aromatic hydrocarbons(pahs) and their derivatives as well as other types of pahs. Hemicellulose, cellulose, and lignin in thermally modified wood are partially degraded, cross-linked, and poly condensed, resulting in the dark color of thermally modified wood and reducing the mechanical properties [26].

3. Chemical modification of eucalyptus
Chemical modification of wood has been studied for years, and many methods are available; however, chemical modification of eucalyptus has been rarely reported.

Research on acetylated eucalyptus is mainly focused on producing fibers, paper, or wood-based panels. Modifying eucalyptus fibers with acetic anhydride improves the compatibility with PP and good interfacial adhesion, indicating the enhanced surface activity of the acetylated eucalyptus fibers [27]. The dimensional stability of eucalyptus, poplar, fir, and pine modified with acetic anhydride is also enhanced; however, acetylation slightly lightens the color of eucalyptus. Givenits high density and compact texture, eucalyptus is difficult to penetrate and diffuse with solutions, such as acetic anhydride.

Under the same conditions, eucalyptus is more difficult to acetylate than poplar and pine; thus, high-density wood is difficult to acetylate[18]. Therefore, a suitable acetylation process should be explored.
Similar to acetylation, furfurylation is suitable for wood species with loose structure and large cell wall pore (e.g. poplar) that can be easily modified; however, the compact texture and fine-cell pores of eucalyptus are unsatisfactory.

The pyrolysis temperature of eucalyptus modified with UF and MUF is low. The shrinkage resistance and anti-swelling of thermally modified eucalyptus combined with MUF are increased by 47% and 49%, respectively. The mechanical properties of eucalyptus modified with MUF are weaker than those of simply thermally modified eucalyptus, and MUF can refine the mechanical properties of thermally modified wood [28]. Although modification with resin can improve the dimensional stability of eucalyptus, the formaldehyde emission of the treated wood and the pyrolysis performance of eucalyptus decrease [29].

Thermal modification can improve the performance of eucalyptus. Eucalyptus is thermally modified with nitrogen as protective gas. When the temperature exceeds 200 °C, hemicelluloses degrades, reducing the crystallinity of cellulose and the equilibrium moisture content, elastic modulus, and static bending intensity of eucalyptus[30]. Pinus pinaster and Eucalyptus globulus are treated with steam at 190 °C–210 °C without air; the longer the treatment time is, the higher the mass loss rate is. Given the high content of hemicellulose in eucalyptus and different constituent monomers, the mass loss rate of eucalyptus is higher and the bending strength is lower than that of pine [31].

Zhao Zijian [32] proved that 19 types of organic compounds, including esters, furans, aromatics, and terpenes, are volatile from the thermal modification of eucalyptus. The bending strength, tenacity, dynamic elastic modulus, maximum bending stress, and compressive strength of wood during thermal modification decrease at 150 °C; the strength of wood decreases with increasing temperature [33] [34] [35] [36].

4. Problems of chemical modification
Because of many problems in wood chemical modification, it is difficult to realize mass production of modified wood. Such problems include the following: 1) modifiers as chemical reagents can pollute the environment or affect human health; 2) adverse effects of chemical modification on wood, such as wood component degradation, mechanical property reduction, and uncontrollable color change after modification; in particular, the brittleness of wood modified with resin increases with reduced water-retaining capacity and bonding strength. The hardness, elastic modulus, and creepage of acetylated wood diminishes; 3) undefined mechanism of modification. The mechanism of wood modification with resin is accepted as resin infiltrating into the lumen; however, direct evidence for cell wall infiltration is rarely found, and limited works have obtained indirect evidence by indirect methods, such as spectroscopy[37][38][39][40][41]; 4) few studies on eucalyptus; and 5) structural constraints of eucalyptus with compact texture and venturized pitting, and pit aspiration under normal conditions and difficult modifier penetration, leading to an unsatisfactory modification effect of eucalyptus.

5. Research direction of the modification of eucalyptus
Possible research directions in the future to make better use of eucalyptus include the following: (1) recycling and utilization of reaction mixture; (2) exploring environment-friendly thermosetting resins; (3) probing into thermal-modification to alleviate the decomposition of eucalyptus and reduce volatile matter; (4) improving the impregnation process, promoting the penetration of the modifier by processes, such as decompression pressure, changing the structure or composition of the cell wall, and increasing the content of modifier impregnated into the cell wall of wood.

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References

[1] 10-year Timber Yield Data, sohu-inc.com, http://www.sohu.com/a/200342459_205809.
[2] www.forestry.gov.cn, China's Timber Output of 84.32 million Cubic Meters in 2018, http://www.forestry.gov.cn/xdly/5197/20190308/083200663296440.html.
[3] Luo Laifeng. Study on the Economic Development of Eucalyptus Plantations in Guangxi[J]. Journal of Green Science and Technology, 2016(13): 57-58.
[4] Liang Linghua. Analysis on the Sustainable Development of Eucalyptus Plantations in Guangxi[J]. Journal of Green Science and Technology, 2018, (03): 103-104.
[5] Dong Youming, Zhang Shifeng & Li Jianzhang. Research Progress of Wood Modification with Cell Wall Enhanced [J]. Journal of Forestry Engineering, 2017, 2(4):34-39.
[6] Wang Yuhua, Yin Sici & Chen Yuyun. Study on the Corrosion Resistance of Acetylated Wood[J]. Journal of Nanjing Forestry University(Humanities and Social Sciences Edition), 1982, (4): 64-68.
[7] Xu Kang, Lu Jianxiong, Liu Junliang, et al. Impacts of the Post-impregnation Treatment and Drying on the Wood Modification with Impregnated Resin[J]. Scientia Silvae Sinicae, 2018, v.54(04):87-95.
[8] Tian Chunming, Gao Ming, Xu Jianzhong et al. Study on Thermal Properties of Modified Wood[J]. Journal of Hebei University (Natural Science Edition), 2009, 22(2): 141-144.
[9] Li J Z, Furuno T, Zhuo W R, et al. Properties of Acetylated Wood Prepared at Low Temperature in the Presence of Catalysts[J]. Journal of Wood Chemistry and Technology, 2009, 29(3) : 241-250.
[10] Hill C, Kwon JH. The Influence of Wood Species upon the Decay Protection Mechanisms Exhibited by Anhydride Modified Woods [C]/proceedings of 4th European Conference on Wood Modification, 2009:96-101.
[11] Sadeghifad H R, Dicke Rson J P, Argy Ropoulos D S. Quantitative 31P NMR Analysis of Solid Wood Offers An Insight into the Acetylation of Its Components[J]. Carbohydrate Polymers, 2014, 113: 552-560.
[12] Goldstein E.B, Jeroskl, A.E. Lund, and J.M. Weaver. Forest Products, 1961, 11: 363-370.
[13] Goldsteinis, J, LunA E, et al. Acetylation of Wood in Lumber Thickness [J]. Forest Products Journal, 1961, 11: 363-370.
[14] Nordstierna L, Lande S, Westin M, et al. Towards Novel Wood — Based Materials: Chemical Bonds between Lignin — like Model Molecules and Poly (furfuryl alcohol) Studied by NMR [J]. Holzforschung, 2008, 62(6): 709-713.
[15] Thygesen L G, Barsberg S, T. M. Venä s. The Fluorescence Characteristics of Furfurylated Wood Studied by Fluorescence Spectroscopy and Confocal Laser Scanning Microscopy[J]. Wood Science & Technology, 2010, 44(1): 51-65.
[16] Hadi Y S, Westin M, Rasyid E. Resistance of furfurylated wood to termite attack [J]. Forest Products Journal, 2005, 55(11) : 85-88.
[17] Alfredsen. Durability of modified wood - laboratory vs field performance [C]. European Conference on Wood Modification 2009, Stockholm, Sweden, 2009.
[18] Dong Y, Qin Y, Wang K, et al. Assessment of the performance of furfurylated wood and acetylated wood: Comparison among four fast-growing wood species [J]. Bioresources, 2016, 11(2):3679-3690.
[19] Vetter L D, Depraetere G, Janssen C, et al. Methodology to assess both the efficacy and ecotoxicology of preservative-treated and modified wood [J]. Annals of Forest Science, 2008, 65(5):504-504.
[20] Stamm AJ, Seborg RM (1962) Resin-treated laminated, compressed wood-impreg. USDA Forest Service, Forest Product Laboratory, report. 1380.
[21] Gindl W, Gupta H S . Cell-wall hardness and Young’s modulus of melamine-modified spruce wood by nano-indentation [J]. Composites Part A Applied Science & Manufacturing, 2002, 33(8):1141-1145.
[22] Chen H, Miao X, Feng Z, et al. In Situ Polymerization of Phenolic Methylolurea in Cell Wall and Induction of Pulsea Pressure Impregnation on Green Wood [J]. Industrial & Engineering Chemistry Research, 2014, 53(23):9721-9727.

[23] Jr C U P, Kim M G, Nicholas D D, et al. Wood Enhancement Treatments I. Impregnation of Southern Yellow Pine with Melamine-Formaldehyde and Melamine-Amelmine-Formaldehyde Resins [J]. Journal of Wood Chemistry & Technology, 1994, 14(4): 577-603.

[24] Stamm A J, Hansen L A . Minimizing Wood Shrinkage and Swelling [J]. Industrial & Engineering Chemistry, 1937, 7(29): 831-833

[25] Kamdem D P, Pizzi A, Triboulot M C . Heat-treated timber: potentially toxic byproducts presence and extent of cell wall of wood degradation [J]. Holz als Roh- und Werkstoff, 2000, 58(4):253-257.

[26] Shi Qiang, Lu Jianxiang, Bao Yucheng, et al. Study on the Change Regularity and Mechanisms of Properties of Thermally Modified Wood [J]. Forestry Machinery & Woodworking Equipment, 2011, 39(3):20-24.

[27] Li Y. Characterization of acetylated eucalyptus fibers and its effect on the interface of eucalyptus/polypropylene composites [J]. International Journal of Adhesion & Adhesives, 2014, 50(4):96-101.

[28] Zhang Yu, Mu Jun, Li Sijin et al. Effects of UF and MUF Resins on the Pyrolysis Characteristics of Eucalyptus[J]. Journal of Beijing Forestry University, 2014, 36(3):130-135.

[29] Bailing, Liu, Junliang, et al. Changes in dimensional stability and the mechanical properties of wood of Eucalyptus;pellita by melamine-urea-formaldehyde resin impregnation and heat treatment[J]. European Journal of Wood & Wood Products, 2013, 71(5):557-562.

[30] Wu Guofu & Huang Shengxia. Study on the Mechanical Properties of Thermally Modified Eucalyptus from Fast-growing Plantations [J]. Chinese Agricultural Science Bulletin, 2012, 28(10):59-62.

[31] Esteves B, Marques A V, Domingos I, et al. Influence of steam heating on the properties of pine ( Pinus pinaster ) and eucalypt ( Eucalyptus globulus ) wood[J]. Wood Science & Technology, 2007, 41(3):193-207.

[32] Zhao Zijian. Study on the Thermal Response of Eucalyptus and Fir During High-temperature Thermal Modification[D].Beijing: Beijing Forestry University, 2017.

[33] Hillis W E. High temperature and chemical effects on wood stability[M].Part 1.General considerations,1984:281-293.

[34] Obataya E, Shibutani S, Hanata K, et al. Effects of high temperature kiln drying on the practical performances of Japanese cedar wood(Cryptomeria japonica) II : changes in the mechanical properties of wood due to heating[J].Journal of Wood Science,2006,52(2):111-114.

[35] Yildiz S, Gezer E D, Yildiz U C. Mechanical and chemical behavior of spruce wood modified by heat[J].Building and Environment, 2006,41(12):1762-1766.

[36] Santos J A. Mechanical behaviour of eucalyptus modified by heat[J].Wood Science and Technology,2000,34(1):39-43.

[37] Suchsland O. über das eindringen des Leimes bei der Holzverleimung und die Bedeutung der Eindringtiefe fur die Fugenfestigkeit[J]. Holz Roh Werkst, 1958, 16:101-108.

[38] Furuno T, Goto T. Structure of the interface between wood and synthetic polymer [J]. Mokuzai Gakkaishi, 1975, 21: 289-296.

[39] Brady D E, Kamke F A. Effects of hot-pressing parameters on resin penetration [J]. For Prod J, 1988,38(11):63-68.

[40] Sernek M, Resnik J, Kamke F A. Penetration of liquid urea-formaldehyde adhesive into beech wood [J]. Wood Fiber Sci, 1999, 31:41-48.

[41] Harper D, Lee S H, Rials T G, et al. Adhesive penetration of cell wall of woods investigated by scanning thermal microscopy (SThM) [J]. Holzforschung, 2008, 62: 91-98.