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Review

Isolation, structural characterization, and potential applications of hemicelluloses from bamboo: A review

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ABSTRACT

Bamboo is one of the mostly fast growing natural resources and has great potential to be used as a valuable feedstock for biorefinery. The hemicelluloses, next to cellulose, represent a diverse group of polysaccharides in plant cell wall. Elucidation and understanding of the hemicelluloses from bamboo play an important role in the efficient conversion of bamboo into biofuels and bioproducts. This review summarized the recent reports on hemicelluloses from bamboo, including immunohistochemical localization, focused on extraction and purification methods, chemical components, characterization of structural features, as well as physicochemical properties. In addition, attention was also paid to derivatives prepared from bamboo hemicelluloses and to potential applications of bamboo hemicelluloses in a variety of areas such as biomaterials, biofuel, and food.

Contents

1. Introduction

The challenges faced by society's dependence from petroleum-based resources will be the growing environmental issues and diminishing fossil fuel reserves. As an alternative to replacement of limited fossil resources, there is presently a great interest in

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developing strategies for utilization of renewable raw material. Plant biomass is generally viewed as one of the sustainable sources since it is renewable, abundant, and distributed widely in nature. Effective conversion of the biomass into biofuels, chemicals, and biomaterials has received increasing attention (Corma, Iborra, & Velty, 2007; De Lasa, Salaices, Mazumder, & Lucky, 2011; Huber, Iborra, & Corma, 2006; Kopetz, 2013; Navarro, Peña, & Fierro, 2007; Ohlrogge et al., 2009; Zakrzewska, Bogel-Łukasik, & Bogel-Łukasik, 2010; Zakzeski, Bruijnincx, Jongerius, & Weckhuysen, 2010). As we all know, biomass is primarily made up of three main types of biopolymers: cellulose (45–55%), hemicelluloses (25–35%), and lignin (20–30%), in which hemicelluloses are used to describe a class of heteropolysaccharides and define as xylans, mannans, β-glucans, and xyloglucans according to their primary structure.

After cellulose, hemicelluloses are the next most abundant polysaccharides family in the primary and secondary layers of the plant cell wall. The average degree of polymerization (DP) of hemicelluloses is in a range of 80–200. They are closely associated with the cellulose fibrils and act as a coat between and around cellulose fibrils, which give rigidity to the plant tissue. Generally, in hardwood species, the majority of hemicelluloses are *O*-acetyl-4-*O*-methylglucurono-β-D-xylans. In softwoods, the most hemicelluloses are acetylated galactoglucomannans, while arabinoxylans are the main hemicelluloses of Gramineae. Depending on the botanical sources and structural variations of hemicelluloses, the classification of hemicelluloses has been well reviewed by many authors recently (Deutschmann & Dekker, 2012; Ebringerová, Hromádková, & Heinze, 2005; Ebringerová, 2005; Gírio et al., 2010; Peng, Peng, Xu, & Sun, 2012). Although hemicelluloses currently represent a relatively large amount of polysaccharide fraction in lignocellulosic biomass, they are still wasted during the processes of bio-based industries such as pulping, cellulosic ethanol, and lignophenol-formaldehyde resins. On the other hand, hemicelluloses have many excellent properties including biodegradability, biocompatibility, bioactivity, and so on, enabling their native or modified forms applications in a variety of areas such as food (e.g., xylitol and sugar) (Otieno & Ahring, 2012; Yi & Zhang, 2012), medicine (e.g., XOS) (Bian et al., 2013; Weeks & Perez, 2009), energy (e.g., fuel and H_2) (Olcay et al., 2013), chemicals industry (e.g., furfural) (Gürbüz et al., 2013), polymeric materials (e.g., film, hydrogel, and carrier) (Karaaslan, Tshabalala, Yelle, & Buschle-Diller, 2011; Ruiz et al., 2013), biosurfactant (e.g., glycolipids) (Foley, Phimphachanh, Beach, Zimmerman, & Anastas, 2011), and papermaking additive or flocculant agent (e.g., cationic hemicelluloses) (Landim et al., 2013). Undoubtedly, those are the reasons why the hemicelluloses are particularly interesting to be investigated by researchers.

As one of the most important biomass resources, bamboo is the common term for member of a particular taxonomic group of large woody grass (subfamily Bambusoideae, family Poaceae), ranging from 10 cm to 40 m in height (Scurlock, Dayton, & Hames, 2000). Bamboos are widely distributed in China (about 300 species), Japan, and South-East Asian countries. It is now known that bamboos encompass 1250 species within 75 genera and share the desirable characteristics with high productivity and fast-growing (Choudhury, Sahu, & Sharma, 2012), which allow them possible to be a potential source of lignocellulosic feedstocks. In the last decades, more and more attention has been paid to the chemical components and structural characterization of bamboo hemicelluloses as well as their potential applications for the value-added utilization of bamboo resources.

In this paper, a review will focus on the isolation methods, chemical components, structural features, and physicochemical properties of hemicelluloses from bamboo. Special attention will also be devoted to the modification of the isolated bamboo hemicelluloses and the potential applications of the hemicelluloses and their derivatives.

2. Isolation of bamboo hemicelluloses

2.1. Immunohistochemical localization of bamboo hemicelluloses

Prior to isolation of bamboo hemicelluloses, an observation of immunohistochemical localization is necessary to understand the distribution and clarify the function of hemicelluloses in the ultra-structures of bamboo internodes at various stages. Suzuki, Kitamura, Sone, and Itoh (2003) firstly provided a detailed insight into the localization of hemicelluloses in bamboo culm (*Phyllostachys aurea* Carr) throughout its developmental stages using immunolabelling techniques. The internodes were identically classified into three developmental phases: primary wall stage (phase I), unlignified secondary wall stage (phase II), and lignified wall stage (phase III). The distribution of $(1\rightarrow3,\ 1\rightarrow4)$-$\beta$-glucans in each internode is shown in Fig. 1A. $(1\rightarrow3,\ 1\rightarrow4)$-$\beta$-Glucans were distributed in nearly all tissues in an actively elongating stage. Limited amounts of β-glucans were deposited in primary walls and the middle lamellae, but were limited to the phloem in secondary walls. This suggested that the function of β-glucans might be different in phloem vis-à-vis other tissues. Highly branched glucuronoarabinoxylans were located in nearly all tissues of early phase I, but had disappeared in all tissues immediately before lignification (Fig. 1B). In contrast, low-branched xylan epitopes (Fig. 2A) were present only in the protoxylem in phase I, but were present in all tissues immediately prior to lignification in phase II. In phase III, the epitopes were densely localized in lignified walls, implying that the substitution of xylans is closely related to maturation. However, xyloglucans were largely distributed in the phloem and in lignified tissues (Fig. 2B), indicating that they might be closely correlated with maturation.

Recent developments of specific plant cell wall probes, such as monoclonal antibodies and carbohydrate binding modules, allow researchers to detect specific polysaccharides in define locations of cell walls (Chang, Chang, Chang, & Yeh, 2013; Knox, 2008; Lee, Marcus, & Knox, 2011). It has been reported that sets of plant cell wall probes have been proven to specifically detect individual polysaccharides in primary or secondary cell walls, such as LM5 for galactan (Chang et al., 2013), LM11 for xylan (McCartney, Marcus, & Knox, 2005), LM15 for xyloglucan (Chang et al., 2013), LM19 for homogalacturonan (Chang et al., 2013), and LM21 for glucomannan (Marcus et al., 2010). Thereafter, various plant-polysaccharide-specific immunoprobes were applied to give information about the distributions of cell wall components from bamboo (*Dendrocalamus latiflorus* Munro) shoot at different growing stages by Chang et al. (2013). The results showed that xylans together with lignin and crystalline cellulose were preferentially accumulated at later stage of developments. Meanwhile, it was also found that the deposition of xyloglucan was spatially associated with that of pectin and xylan and possibly masked with each other, whereas galactan and mannan existed as minor constituents of bamboo shoots, and galactan was likely masked by other polysaccharides.

2.2. Extraction of bamboo hemicelluloses

The content and chemical composition of hemicelluloses in bamboo are influenced by the conditions of species, age, climate, harvest, etc. As previously reported, the average contents of hemicelluloses (total of xylan, mannan, arabinan, and galactan) were 27.5%, 27.7%, 26.9%, 27.7%, and 26.5% for bamboos *P. bissetii*, *P. bambusoides*, *P. nigra*, *Phyllostachys heterocycla*, and *P. reticulata*, respectively (Higuchi, 1957; Scurlock et al., 2000). For same species

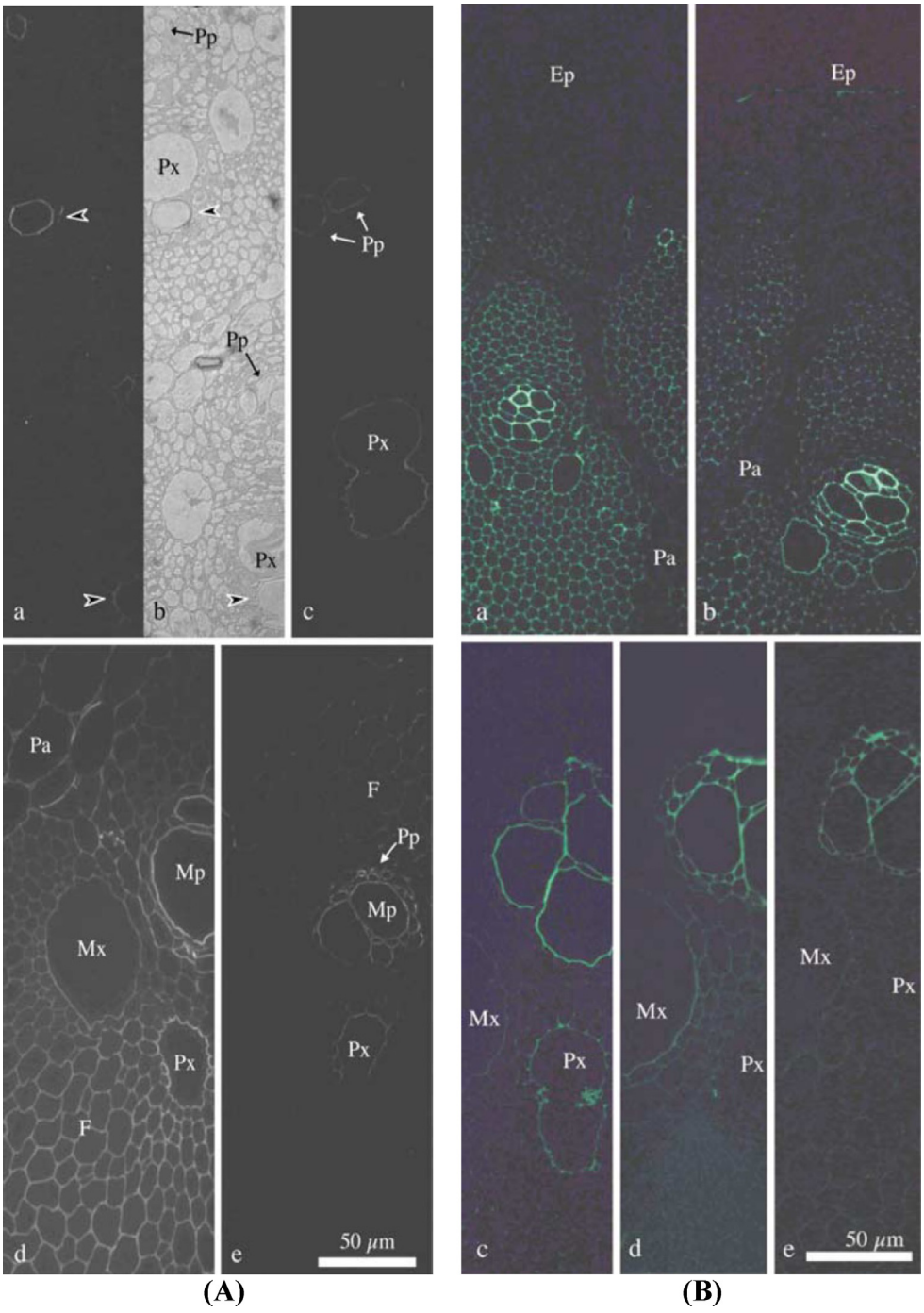

Fig. 1. (A) Localization of (1 → 3, 1 → 4)-β-glucans in bamboo internodes. In phase I-E, a number of β-glucans are distributed in the protoxylem (a). (b) A light microscope image of the section shown in (a) showing the regions labeled in the protoxylem (arrowheads). In phase I-M, the distribution in the protoxylem is extended to all walls surrounding protoxylem lacuna (c). In phase I-L, β-glucans are present at almost all tissues (d). In phase III, deposition of β-glucans is slight in the metaxylem and fiber and deposition in the protoxylem is absent from fiber walls surrounding the lacuna (e, phase III-E). (B) Localization of low-branched xylans in bamboo internodes. In phase I-E, labeling is limited to the secondary thickening in the protoxylem (a, arrowheads). (b) Shows a light microscope image of the section shown in (a) and shows the secondary thickening in the protoxylem (arrowheads). In phase II, xylans were also distributed in the metaxylem and fibers just prior to lignification (c). In phase III, localization of the xylans is similar to that in phase II, but labeling in lignified fibers and metaxylem is abundant (d). F, Fiber; Mp, Metaphloem; Mx, Metaxylem; Pp, Protophloem; Px, Protoxylem (Suzuki et al., 2003).

of bamboo, the contents of hemicelluloses show variances with age and fraction of harvest. For example, the contents of hemicelluloses were 27.7%, 27.2%, and 25.8% for whole fractions of *P. nigra* 1 year, 2 years, and 4.5 years, respectively (Scurlock et al., 2000), while the contents of hemicelluloses were 28.5% and 29.1% in internodal and nodal fractions of bamboo *Chusquea culeou* Desv., respectively (Poblete, Cuevas, & Diaz-Vaz, 2009). More recently, Li, Jiang, Fei, Cai, and Pan (2014) reported that the contents of hemicelluloses were 23.1%, 24%, and 25.1% in fractions of bamboo (*Phyllostachys heterocycla*) green, timber, and yellow, respetively. Furthermore, the order of hemicelluloses contents in height of bamboo (*Phyllostachys pubescens*) was conformed as bottom > middle > top (Saito, Ishii, & Sato, 2013). Interestingly, the immature bamboo (*Phyllostachys pubescens* Mazel) was cut into 6 portions (No. 1–6) from bottom

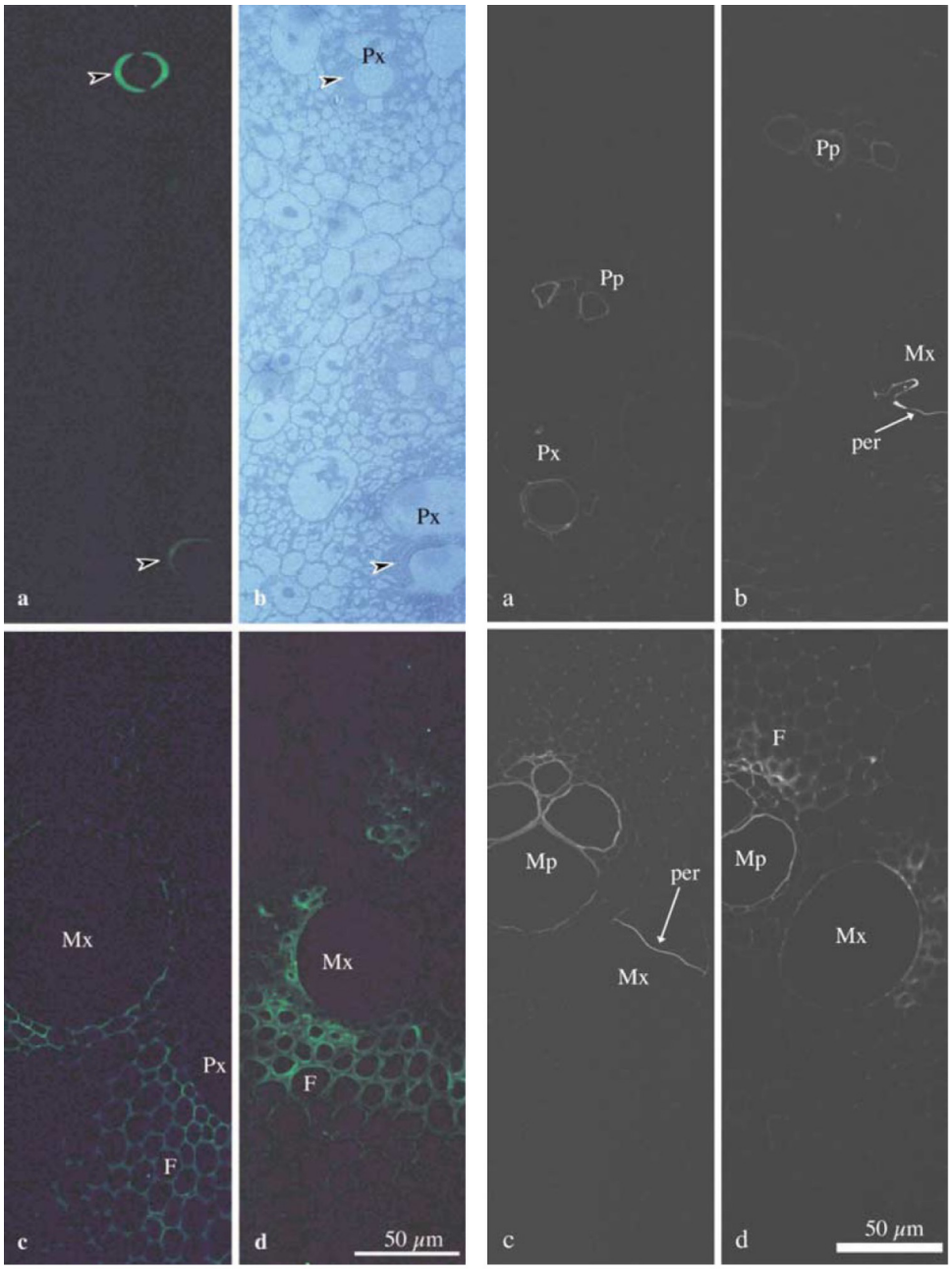

Fig. 2. (A) Localization of highly branched glucuronoarabinoxylan (hsGAX) in bamboo internodes. In phase I-E, labeling was observed in nearly all tissues, but not in the epidermis (a). However, labeling also appears in the epidermis in phase I-M (b). In phase I-L, the distribution of hsGAX is absent from fibers (c). In phase II, labeling in the protoxylem is eliminated (d). In phase III, distribution of hsGAX is limited to the phloem and a few tissues (e, phase III-L). (B) Localization of XGs in bamboo internodes. In phase I-E, labeling is distributed in the protophloem and protoxylem (a). In phase I-M, labeling in the protoxylem is lost (b). In phase I-L, labeling is limited to the phloem and the perforation plate in the metaxylem (c, arrowhead indicates perforation plate). In phase III, labeling is extended to lignified tissues (d, phase III-L). Ep, Epidermis; F, Fiber; Mp, Metaphloem; Mx, Metaxylem; Pa, Parenchyma; Pp, Protophloem; Px, Protoxylem; per, Perforation plate (Suzuki et al., 2003).

to the top of culm and their chemical comositions were then analyzed by Fujii et al. (1993). They observed an increase in pentosan contents from 24.5% (No. 1) to 34.3% (No. 2) and then a decrease from 34.3% (No. 2) to 5.1% (No. 6). In summary, as a general rule, we can say that the orders of hemicelluloses contents in same species of bamboo are young > old, bamboo yellow > timber > green, nodal > internodal, and bottom > middle > top. On the other hand, differences between the chemical compositions of hemicelluloses from immature bamboo are very samll, they shara similar structures of glucuronoarabinoxylans, which will be reviewed later.

The extraction of hemicelluloses is restricted by the physical and/or covalent interactions with other cell-wall constituents. Up to now, multiple forms of bonding between hemicelluloses and other constituents have been suggested to exist in bamboo plants. It is known that a ferulic acid forms covalent feruloyl ester-ether bridges between hemicelluloses and lignin or diferulic acid in the form of diester cross-links between polysaccharides chains would also be etherified to lignin (Ishii, 1997; Jeffries, 1990), whereas hemicelluloses tether to cellulose microfibrils by hydrogen bonds, which enable hemicelluloses to form a highly resistant

coextensive load-bearing network with cellulose microfibrils (Agger et al., 2014). Several studies have shown that xylan and xyloglucan can adsorb to cellulose forming a partial outer coating to mirofibrils (Hayashi, Marsden, & Delmer, 1987; Vincken, de Keizer, Beldman, & Voragen, 1995). However, there is still a lack of molecular level characterization of these structures because of the high complexity of the cell wall. What is more, how do the hemicelluloses compositions affect the effective interactions with cellulose fibrils and what do the substantial roles of hemicelluloses play in the stability of the primary cell wall from point of a molecular view? Recently, Silveira, Stoyanov, Gusarov, Skaf, and Kovalenko (2013) addressed the effect of hemicelluloses composition on primary cell wall nanoscale forces that control cell wall strength by using the 3D-RISM-KH molecular theory of solvation, which provided statistical-mechanical sampling and molecular picture of hemicelluloses arrangement around cellulose. The results showed that the main effect of hemicelluloses composition arose from the presence of basic groups (e.g., arabinose, galactose and glucuronic acid) but was not due to stereochemistry. Among hemicelluloses, the branches of arabinose, glucuronic acid, and especially glucuronate strengthen the primary cell wall by strongly coordinating to hydrogen bond donor sites on the cellulose surface. Extending to other classes of hemicelluloses, such as galactoglucomannans, the effect of galactose, glucose, and mannose would be rather weak and the largest contributions would arise from the carboxylate groups of random glucuronate substitutions (Silveira et al., 2013). The significant of these findings is that it provides directions for genetic modulation of plants and pretreatment design to render biomass more amenable to processing.

On the other hand, hydroxycinnamic acids (ferulic and *p*-coumaric acids) and acetyl groups are attached at *O*-5 and *O*-2 of the L-arabinofuranosyl (Ara*f*) residues in the arabinoxylan from bamboo (Ishii & Hiroi, 1990; Ishii, Hiroi, & Thomas, 1990; Ishii, 1991a, 1996), respectively. It should be pointed out here that Ara*f* residues are required for normal plant growth, development, and reproduction. Konishi and Ishii (2012) used RNAi to suppress UDP (uridine diphosphate)-L-arabinopyranose (Ara*p*) mutase that catalyzed the interconversion of UDP-Ara*p* and UDP-Ara*f* expression in plants. It was found that several transgenic plants had reduced proportions of Ara*f* in their cell walls together with a decrease in the extent of substitution of the xylan backbone and a reduction of between 25% and 80% in ferulic acid and *p*-coumaric acid contents. Subsequently, the results showed that transgenic plants with over 25% reduction in Ara*f* residues were dwarfed and infertile. At present, depending on the extraction process, the extraction methods can be mainly divided into chemical and biological methods. Chemical method includes alkali, organosolv, steam explosion, and autohydrolysis or hydrothermal, while biological method refers to the use of enzyme for hydrolysis of bamboo cell-walls.

One of the most commonly chemical methods is alkali extraction, which can be further dived into direct extraction with aqueous alkali and pre-treatment followed by alkali extraction from bamboo. Generally, the bamboo powder should be pre-extracted with toluene-ethanol (2/1, v/v) and hot water for the removal of the lipophilic and starch components before alkali extraction, respectively (Peng, Peng, Bian, Xu, & Sun, 2011). The extraction of hemicelluloses from bamboo with alkali directly was proven to be feasible in one step. Alkali-soluble hemicelluloses were respectively extracted from de-waxed bamboo (*Bambusa rigida*) with 1 M NaOH, KOH, LiOH, $NH_3{\cdot}H_2O$, $(CH_3CH_2)_3N$, $Ca(OH)_2$, and $Ba(OH)_2$ at 50 °C for 3 h by Wen et al. (2011), and the yields of the hemicelluloses ranged from 5.0 to 7.2% (relative percent of the de-waxed sample). The results suggested that strong alkali had the tendency to dissolve more hemicelluloses from bamboo cell wall. Saturated-lime-water was also used to extract the crude hemicelluosic polysaccharides of the leaves of bamboo (*Sasa senanensis* Rehd) (Suzuki, Saito, Uchiyama, & Akiya, 1968). Meanwhile, the sequential alkali or ethanol/alkali-extractions in multi-steps have been carried out for the extraction of bamboo hemicelluloses with a higher yield. Various treatments with the sequential alkali-based methods have been concerned by our research group. Peng, Peng, Bian, Xu, Sun, and Kennedy (2011) reported that the hemicelluloses were isolated by sequential extractions with distilled water, 0.5% and 1% NaOH, 60% ethanol containing 1% NaOH, 3%, 5%, and 8% NaOH at 60 °C for 3 h from dewaxed bamboo *Phyllostachys incarnate* Wen. The yields of seven fractions together achieved about 80.1% of total available hemicellulosic polysaccharides. The effect of sequential ethanol/NaOH mixtures was also examined on the extraction of bamboo hemicelluloses with some success as well by Shi, Xiao, Deng, Xu, and Sun (2011) and Sun et al. (2012). In addition, a β-D-glucan and a xyloglucan were obtained by the successive extractions with 4% and 24% potassium hydroxide from the shoot of Moso-chiku (Kato, Shiozawa, Takeda, Ito, & Matsuda, 1982). Compared with the alkali extraction in one-step, the sequential alkali extractions in multi-steps with the feature of increasing alkali concentrations in gradient mode show some advantages of higher yields and various hemicelluloses available.

Another alkali approach is pre-treatment followed by alkali extraction. The pre-treatment methods, including acidic sodium chlorite, ultrasonic irradiation, cold alkali, organic acid, and ionic liquid, have previously been applied for facilitating bamboo hemicelluloses production. Clearly, the aim of pre-treatment is to decrease the contents of lignin, break the bonds among the components, and expose cellulose and hemicelluloses. The classical procedure of delignification is that the dewaxed bamboo materials are treated with acidic sodium chlorite at 75 °C for 2 h, after which the resulting holocellulose is extracted with alkaline. In many cases, hemicelluloses from bamboo were obtained by NaOH or KOH extraction from the holocellulose (Fengel & Shao, 1984; Luo et al., 2012; Maekawa, 1976; Peng, Hu, Yu, Zhang, Liu, & Wan, 2012; Peng, Wang, Hu, Yu, Liu, & Zhang, 2012; Peng, Zhang, Liu, Liu, Yu, & Wan, 2012; Peng, Zhou, Yu, Zhang, Ruan, & Wan, 2013; Wen, Sun, Xu, & Sun, 2010; Yoshida, Kuno, Saito, Aoyama, & Kusakabe, 1998). Ultrasonic irradiation is a potential pre-treatment method for effective extraction of polysaccharides. The mechanisms of ultrasonic irradiation are generally believed to the propagation of ultrasound pressure waves, resulting in the phenomenon of cavitation. When the pressure waves pass through the biomass materials, the cavitation bubble will implode and cause microfractures, which lead the cell wall of plants swell and diffusion. Positive effects of ultrasonic irradiation in combination with cold NaOH/urea system on the extraction of bamboo (*Neosinocalamus affinis*) hemicelluloses were reported by Li, Fan, Xu, and Sun (2011). Additionally, organic acid was also employed to pre-treat bamboo shoot for extraction of cell-wall polysaccharides. Edashige and Ishii (1998) utilized the CDTA (*trans*-1,2-cyclohexanediamine-*N,N,N′,N′*-tetraacetic acid) to treat cell-walls of bamboo shoot, which then were subjected to sequential extractions with Na_2CO_3 and KOH solutions to obtain hemicellulosic polysaccharides. In recent years, ionic liquids (ILs, the so called “green solvents”) have attracted a lot of attention due to some advantages such as recyclability, physicochemical and thermally stability, and outstanding solvation (Brandt, Gräsvik, Hallett, & Welton, 2013; Pinkert, Marsh, Pang, & Staiger, 2009). According to Yang, Zhong, Yuan, Peng, and Sun (2013) the ball milled bamboo (*Phyllostachys sulphurea*) was firstly dissolved in 1-allyl-3-methylimidazolium chloride ([Amim]Cl) and regenerated with distilled water, followed by consecutively extraction with NaOH for receiving cellulose, lignin, and hemicelluloses fractions. After alkali extraction, the filtrate is usually adjusted to pH 5.0–5.5 with HCl or HAc for ethanol precipitation or further purification.

On the other hand, steam explosion and hydrothermal or autohydrolysis treatments have been developed for the effective

solubilization of bamboo hemicelluloses (oligo- and monosaccharides) (Ando et al., 2003, 2004; Aoyama & Seki, 1999; Aoyama, Seki, & Saito, 1995; Aoyama, 1996; Cheng, Jiang, & Zhang, 2013; Garrote, Dominguez, & Parajó, 1999; González, Santos, & Parajó, 2011; Luo et al., 2013; Shao, Wen, & Jin, 2008; Xiao et al., 2013). During steaming with rapid explosion procedure, bamboo is treated with high pressure saturated steam, and then the pressure is suddenly reduced, causing the materials to undergo explosive decomposition. Early studies on solubilization of bamboo xylan have shown that 55% of xylan present in the culm of *S. senanensis* could be recovered as a mixture of xylose and xylo-oligosaccharides (XOS) by steaming and subsequent water extraction (Aoyama, Seki, & Saito, 1995; Aoyama, 1996). Thus, research focused on employing catalysts to reduce temperature requirements for the steaming treatment and improve solubilization of the xylan in the substrate. The effects of the various acid catalysts on the recovery of solubilized sugars were investigated by Aoyama and Seki (1999). Culms of bamboo grass (*Sasa senanensis* Rehd.) were treated with saturated steam at a range of temperatures between 170 and 197 °C for 10 min in the presence of catalysts including Lewis acids, inorganic salts, and organic acids. The results showed that the use of low levels of Lewis acids or $CaCl_2$ had the advantage of a substantial reduction in temperature required. The solubilized sugars were mainly composed of xylose, arabinose, and xylo-oligosaccharides with low molecular weight. Chemical changes in cell wall components of bamboo (*Phyllostachys pubescens*) internode during steam explosion process were also investigated by Shao et al. (2008). It was found that more than 30% of xylose on initial mass was solubilized after steam explosion treatment. Apart from steaming, hydrothermal or autohydrolysis treatment well-suited for the "biomass refining" philosophy provides a successful approach for fractionating lignocellulosic materials (LCM) into their main components. Autohydrolysis (hydrothermal) is a technology based on the utilization of water and LCM as the only reagents at high temperature and pressure, the hydronium ions from both water and in situ-generated compounds such as acetic, uronic and phenolic acids catalyze the hemicelluloses depolymerization (Garrote, Dominguez, & Parajó, 1999). González et al. (2011) reported that 62.6% of the initial hemicelluloses present in the raw material were converted into oligosaccharides during the autohydrolysis of bamboo process (treatments with hot, compressed water). Fraction A mainly composed of xylose, xylooligosaccharides, and water-soluble lignin was extracted from bamboo (*P. pubescens* MAZEL) powder with hot-compressed-water at 200 °C using a percolating reactor by Ando et al. (2004). Recently, the autohydrolysis of bamboo culm (*Dendrocalamus giganteus* Munro) showed that the maximum yield of xylo-oligosaccharides was 47.49% at 180 °C for 30 min (Xiao et al., 2013). Meanwhile, the relatively low levels of xylose (4.73%), arabinose (0.20 g/l), galactose (0.19 g/l) and other byproducts (HMF 0.15 g/l, furfural 0.36 g/l, acetic acid 0.64 g/l, and formic acid 0.26 g/l) were also detected. Although steam explosion and hydrothermal or autohydrolysis treatments have the benefits of environmentally friendly character and ability for causing a selective solubilization of hemicelluloses, the disadvantage of the methods is that the solubilized hemicelluloses appear mainly in mon- and oligomeric forms. Similar problem is also present in the treatment of bamboo with acids, such as sulfuric acid (Alves et al., 2010; Vena, Görgens, & Rypstra, 2010), phosphoric acid (Hong, Xue, Weng, & Guo, 2012), and oxalic acid (Hong, Xue, Guo, & Weng, 2013), which is hardly used for the extraction of hemicelluloses from bamboo.

At the same time, researchers have focused on the removal of hemicelluloses from biomass using subcritical or supercritical fluid (SCF) with or without catalysts. In fact, the hydrothermal treatment is one type of pre-treatment technologies employing subcritical water, which is defined as liquid water at temperatures between the boiling point and the near critical point (373–647 K). The properties of subcritical water exhibiting lower dielectric constant, weaker hydrogen bonds, and a higher isothermal compressibility than ambient liquid water make subcritical water a very promising reaction medium for decomposing the lignocellulosic materials. In some cases, subcritical water is also called superheated water. Based on the extraction using superheated water, microwave-assisted technology was submitted to the extraction of hemicellulosic polysaccharides since its main advantage is the ability to rapidly heat the sample solvent mixture. Therefore, the extraction by microwave can be performed at elevated temperature accelerating the mass transfer of target compounds from the sample matrix. Recently, microwave superheated water extractions of arabinoxylans, galactomannans and arabinogalactans, and mannans from brewers spent grain (BSG) (Coelho, Rocha, Saraiva, & Coimbra, 2014) and spent coffee grounds (SCG) (Passos & Coimbra, 2013; Passos, Moreira, Domingues, Evtuguin, & Coimbra, 2014) were proposed at temperature ranges from 140 to 210 °C during 2 min, with ratios of mass of SCG to water from 1:5 to 1:30 (g/ml) at 200 °C, and with the number of extractions between 1 and 5, respectively. The results confirmed that the sequential microwave superheated water extraction was feasible and efficient technology for the quantitative recovery of hemicelluloses from BSG and SCG. For supercritical water, due to its severer condition (T_c = 374.0 °C, P_c = 221.0 bar), few literature has been reported to remove hemicelluloses from biomass by supercritical water. As an alternative to the subcritical and supercritical water processes, the addition of CO_2 to aqueous solutions can form weak acid catalyst with water for degradation of hemicelluloses. Among SCFs, both subcritical CO_2 and supercritical CO_2 are attracting growing attention because CO_2 is non-toxic and friendly to the environment, leaves no residue, and is inexpensive, and readily available. The subcritical CO_2 (pressure < 7.36 MPa) has been successfully used to separate the hemicelluloses from sugarcane bagasse at temperatures 140–160 °C by Zhang and Wu (2013). Meanwhile, the effect of subcritical CO_2 pre-treatment on removal of hemicelluloses at various pressures, times, and temperatures were also investigated. The results showed that 3.16 g xylose and 12.62 g xylo-saccharides per 100 g raw material were obtained at 5 MPa CO_2 and 160 °C for 80 min (Zhang & Wu, 2013). More recently, da Silva, Morais, and Bogel-Łukasik (2014) investigated the CO_2-assisted autohydrolysis of wheat straw at 180–210 °C and an initial CO_2 pressure of 60 bar. In comparison to CO_2-free pre-treatments under the same conditions, the in situ formed carbonic acid caused by CO_2 was found to result in a higher dissolution of xylose as well as XOS. Additionally, they also studied the effects of temperature and CO_2 density on the pre-treatments, the CO_2-assisted autohydrolysis toward the formation of XOS at elevated amounts under much less severe conditions was proposed. This work was devoted to enhance the selectivity of the dissolved hemicelluloses fraction. While the pre-treatment with supercritical CO_2 (SC-CO_2) (T_c = 31.0 °C, P_c = 73.8 bar) is another interesting approah for removal of hemicelluloses. Under the supercritical conditions, the fluid of CO_2 shows perfect properties of partition coefficients and solubility (even up to 100-fold changes). What is more, because most biomass substractes have some nascent moisture content, the introduction of SC-CO_2 will result in the formation of carbonic acid. Thus, "explosive comminution" and weak acid are responsible for the dissolution of hemicelluloses during SC-CO_2 process, which lead many authors to claim important advantages for the use of SC-CO_2 in the pre-treatment of biomass for removal of hemicelluloses. For example, Kim and Hong (2001) investigated the SC-CO_2 pretreatments of aspen and yellow pine (moisture contents, 0–73%) for enzymatic hydrolysis of cellulose at 3100 and 4000 psi and at 112–165 °C for 10–60 min. The pre-treatment resulted that the final sugar yields of 84.7 and 27.3% (w/w) of theoretical maximum for aspen and

yellow pine, respectively, were obtained when the lignocellulose with moisture content 73% at 3100 psi and 165 °C for 30 min. However, comparison with the process of subcritical CO_2, the supercritical CO_2 need high resist reaction equipments, which limit the extensive use of SC-CO_2 pretreatment. More importantly, when the biomass does not contain moisture, any significant changes are not caused by the pre-treatment of pure SC-CO_2. In order to address the issue, SC-CO_2 with water (SC-CO_2/H_2O) as co-solvent was applied to pre-treatment of lignocellulosic biomass for removal of hemicelluloses (King et al., 2012; Luterbacher, Tester, & Walker, 2010). Unfortunately, as far as we know, up to now there is few literature report about the removal of hemicelluloses from bamboo by SCFs. Summarizing, SCFs will be widely used as high efficient solvents for extraction of hemicelluloses from plant cell wall, although there is still a wide range of improvements in larger scale and reaction equipments for hemicelluloses extraction.

The main drawbacks of using chemical methods are the partial cleavage of the side chains (e.g., deacetylation) and degradation of hemicelluloses. In order to avoid the above drawbacks, enzymatic strategy is suggested especially for the extraction of hemicellulosic polysaccharides from bamboo shoot. Ishii's group has made great contributions in structural studies of polysaccharides obtained by hydrolysis of bamboo shoot cell walls with Driselase (Ishii & Hiroi, 1990; Ishii et al., 1990; Ishii, 1991b). A typical procedure is as follows: the cell walls (20 g) of bamboo shoot were suspended in 1.0 L of distilled water and incubated for 16 h at 30 °C after addition of 3 ml of a 60 mg/ml solution of Driselase, and the pH of the suspension was adjusted to pH 5.0 with HAc. Then the suspension was heated for 15 min in a boiling-water bath to stop the reaction, and then centrifuged. The supernatant solution was concentrated and precipitated by addition of 5 volumes of EtOH, after which the polysaccharides were obtained by centrifugation.

2.3. Purification of bamboo hemicelluloses

It is necessary to purify the extracted hemicellulosic fractions for further utilization since they are still mixtures of various polysaccharides containing some inorganic salts. Washing with 70% ethanol (Sun et al., 2012) and dialysis (Kato et al., 1982) are simple approaches for removing inorganic salts and polymers with low molecular weights. In dialysis, the neutralized filtrate with acids after alkali extraction is transferred to a dialysis bag (MWCO < 5000) and dialyzed against plenty of deionized water. Fehling's solution was also suggested to selectively separate crude hemicelluloses from bamboo (Suzuki et al., 1968; Wilkie & Woo, 1976, 1977). Generally, the crude hemicelluloses are dissolved in 3–4% sodium hydroxide solution, to which freshly prepared Fehling's solution is added dropwise until the copper complex is formed completely. The gelatinous precipitate is collected by centrifugation, washed twice with distilled water and then dispersed in ice-water, and 6 M hydrochloric acid is added. The complex gives a clear solution which yields a precipitate on addition to ethanol. The precipitate is dissolved in water after slight acidification with HCl, the solution is added to ethanol, the precipitate is recovered, and the dissolution and precipitation procedures repeat twice. Finally, the resulting white precipitates (purified hemicelluloses) dissolved in water are treated with dialysis for 3 days and obtained by freeze-drying.

Column chromatography including diethylaminoethyl (DEAE) cellulose column chromatography, ion-exchange column chromatography, and gel-permeation column chromatography is usually employed to separate hemicellulosic polysaccharides from bamboo into several pure sub-fractions. DEAE-cellulose column chromatography was utilized to purify hemicellulosic polysaccharides from bamboo (*Sasa senanensis* Rehd) leaves by Suzuki et al. (1968). Ten percent solution of the polysaccharides was applied onto a column of DEAE-cellulose (acetate type: 5 cm × 30 cm), then eluted to obtain different sub-fractions by following sequence: water, 0.2 M NaOAc, 0.2–1.0 M NaOAc linear gradient elution, and 1.0 M NaOH (or water, 0.05 M NaOAc, 0.05–0.2 M NaOAc in linear gradient, and 0.2 M NaOAc). The eluates were combined and concentrated, then dialyzed against water and precipitated by the addition of four volumes of ethanol. Edashige and Ishii (1998) were successful in purifying (1 → 3, 1 → 4)-β-D-glucan from 1 M KOH extract of bamboo shoot cell-walls using QAE-Sepadex A-25 anion-exchange chromatography. At the same time, xyloglucan from the 4 M KOH extract of bamboo shoot cell-walls was further purified on a Bio-Gel A-5 m gel-permeation column to give three fractions. For the xyloglucan and arabinoxylan oligosaccharides from hydrolysis of bamboo shoot with Driselase, the preparative/reversed-phase HPLC with a 2.0 (i.d.) × 25 cm column, analytical normal-phase HPLC with a 0.6 (i.d.) × 15 cm column, Sephadex LH-20 column (4.4 cm × 85 cm), and Sep-Pak C18 cartridge were reported to effectively purify these Driselase digestion-products (Ishii & Hiroi, 1990). The method of column chromatography can provide a better procedure of polysaccharides purification. However, from industrial point view, column chromatography would be less economical since it can take a very long time.

Recently, graded ethanol precipitation as a valuable tool has been successfully used for the purification of bamboo hemicelluloses. Peng, Peng, Bian, Xu, and Sun (2011) reported that the alkali-extractable hemicelluloses from holocellulose of the bamboo (*Phyllostachys bambusoides* f. shouzhu Yi) were purified by graded precipitation at final ethanol concentrations of 15%, 30%, 45%, 60%, and 75% (v/v). The results revealed that the molar ratios of Ara/Xyl and Glc/Xyl increased with ascending ethanol concentrations and all sub-fractions showed the relatively narrow molar mass distribution. In comparison with other methods of purification, graded ethanol precipitation exhibits several advantages of being efficient, low-cost, simple manipulation, and ethanol recovery. Additionally, iodide-complex (Edashige & Ishii, 1998; Gaillard, 1961), ammonium sulfate precipitation (Kato et al., 1982), and starch-block zone electrophoresis (Suzuki et al., 1968) were also suggested to purify bamboo hemicelluloses. What is more, it should be noted that purification of bamboo hemicelluloses could be carried out by a combination of various methods. For example, attempt to fractionate xyloglucan from bamboo by a combination of anion-exchange chromatography, selective precipitation with iodide, and gel permeation chromatography was reported by Edashige and Ishii (1998).

3. Structural characterization and physicochemical properties

3.1. Structural characterization

At present, various pathways toward structural characterization of bamboo hemicelluloses have been developed. The applications of the analytical methods including chromatographic and/or spectroscopic analysis will be discussed below in detail.

3.1.1. Chromatographic analysis

The determination of mono- and/or oligo-saccharides compositions after degradation of hemicelluloses plays an important role in calculating the backbone and side-chains of molecular structure. In general, the degradation products could be obtained by acid hydrolysis, enzymatic hydrolysis, and Smith degradation of bamboo hemicelluloses, in which the classical acids include sulfuric acid, oxalic acid, and trifluoroacetic acid. The conditions of acid hydrolysis widely used are described as follows: bamboo hemicelluloses (5 mg) are treated with 1 M H_2SO_4 (1.475 ml) at 105 °C for 2.5 h (Peng, Peng, Bian, Xu, & Sun, 2011), yet a

sample (10 mg) is heated with 25 mM oxalic acid (3 ml) at 100 °C for 18 h (Wilkie & Woo, 1976), or 20 mg samples are hydrolyzed using 3 M trifluoroacetic acid (TFA) at 120 °C for 3 h (Peng, Zhang, et al., 2012). After acid hydrolysis, the excess sulfuric acid and oxalic acid are usually neutralized with barium carbonate or diluted with water, while the TFA is removed by evaporation. Rabemanolontsoa, Ayada, and Saka (2011) evaluated the sulfuric acid, TFA, and acid methanolysis methods for determination of monosaccharide composition in bamboo. It was found that sulfuric acid was suitable to determine amorphous xylanic saccharides, TFA could not achieve complete hydrolysis of xylooligosaccharides, while acid methanolysis was considered appropriate to determine monosaccharide in amorphous hemicelluloses. Moreover, enzymatic hydrolysis also has the capability of structural analyses of the polysaccharides from bamboo. Four arabinoxylo-oligosaccharides and two glucuronoxylo-oligosaccharides were identified from the hydrolysate of the bamboo (*Sasa senanensis* Rehd.) xylan with β-xylanase of streptomyces olivaceoviridis E-86 by Yoshida et al. (1998). More recently, lytic polysaccharide monooxygenase (LPMO) from *Neurospora crassa*, namely *Nc*LPMO9 C, was firstly discovered to degrade various hemicelluloses (xyloglucan, $(1\rightarrow 3)$, $(1\rightarrow 4)$-β-D-glucan, and glucomannan), in particular xyloglucan, by Agger et al. (2014). The nature copper-dependent redox enzymes called LPMOs are well known to carry out oxidative cleavage of glycoside bonds in the most recalcitrant and crystalline of these polysaccharides (cellulose and chitin). As the authors claim, this finding dramatically widens the scope of LPMOs and oxidative processes in plant cell wall degradation and biorefining. It would be a significant new insight into the biological roles of LPMOs and extend the enzyme toolbox available for studying hemicelluloses structures. In order to improve the efficiency of enzymes for degrading hemicelluloses, some enzyme engineering strategies (e.g., random mutagenesis, site-directed mutagenesis, and recombinant DNA) have been applied. Meanwhile, the coordinated action of various hemicellulases was also investigated to significantly improve hemicelluloses hydrolysis (Guo, Zheng, Wu, Tian, & Zhou, 2013; Zhang, Tuomainen, Siika-aho, & Viikari, 2011). In addition, Smith degradation was used to decompose the bamboo xylan and the hydrolyzate was neutralized with Amberlite IR 45 (CO_3^-) exchange resin (Maekawa, 1976). Subsequently, the hydrolyzates containing monomeric and/or oligomeric sugars were subjected to various chromatographies.

Paper chromatography is a simple method for the qualitative analysis of the sugar components with a phenol-sulfuric acid reagent (Dubois, Gilles, Hamilton, Rebers, & Smith, 1956) and seems inefficient by today's standards. The gas liquid chromatography (GLC) or gas chromatography–mass spectrometry (GC–MS) is suggested as a good candidate for the analysis of acetylated or trimethylsilyl sugar monomers. The accurate determination of sugar component by GLC or GC–MS has been improved comparable to paper chromatography. However, the preparation of their derivatives is a time-consuming step. Recently, the development of high performance anion exchange chromatography (HPAEC) coupled with a pulsed amperometric detector (PAD) has attracted much attention and become popular method for the qualitative and quantitative measurement of neutral monomeric sugars and uronic acids due to its advantages of be rapid, reliable, and reproducible. It was suggested that mono- and oligo-saccharides could be efficiently separated and analyzed by HPAEC-PAD with columns of PA-20 and PA-100 using a sodium acetate/NaOH eluent system in gradient mode, respectively (Peng, Peng, Bian, Xu, & Sun, 2011). According to the results of mono- and/or oligo-saccharides analysis from the most research, it has been suggested that the hemicelluloses from bamboo culms share the similar chemical structure and are composed mainly of glucuronoarabinoxylans(GAX)-type polysaccharides. In GAX, the linear β-(1,4)-D-xylopyranose backbone is substituted by α-L-arabinofuranosyl units at the positions *O*-2 and/or *O*-3 and by 4-*O*-methyl-α-D-glucopyranosyl uronic unit at the position *O*-2 (Peng, Peng, Bian, Xu, & Sun, 2011; Shi et al., 2011; Sun et al., 2012; Wen et al., 2010). In addition, the bamboo xylan contains acetyl groups (6.5%) (Maekawa, 1976) and arabinofuranosyl residues of GAX may also be esterfied with *p*-coumaric acid and/or ferulic acid (Ishii, 1997). In general, the arabinose (A) to xylose (X) ratio in degradation products is considered to be a measure for the degree of linearity or branching of arabinoxylans, a high A/X ratio indicates a short-chain polymer with a large amount of branching, while a low A/X ratio suggests a linear hemicellulosic polymer with a small amount of side chains. The substitution pattern of the GAX from bamboo depends on the source materials and is usually affected by the methods of extraction and purification. The culms of the bamboo *Phyllostachys reticulata* C. Koch gave hemicelluloses containing 4-*O*-methyl-D-glucuronic acid, arabinose, and xylose in a molar ratio of 1:1.3:25 (Maekawa, 1976). An arabinoxylan with a Xyl:Ara ratio of about 17:1 in bamboo *Phyllostachys makinoi* Hay (Fengel & Shao, 1984). and 8:1 in *Bambusa arundinace* (Guha & Pant, 1967) were reported respectively. More published data about the composition of arabinose, glucuronic acid, and xylose in bamboo hemicelluloses are listed in Table 1. Apart from GAX, other hemicellulosic polysaccharides such as arabinogalactan, xyloglucan, and β-D-glucan were also found in bamboo leaves and/or shoots (Wilkie & Woo, 1976, 1977).

The size of bamboo hemicelluloses is usually characterized by the weight-average (M_w) and number-average (M_n) molecular weights determined by gel permeation chromatography (GPC) on a PL aquagel-OH 50 column with a refractive index detector (RID), which is eluted with 5 mM sodium phosphate buffer (pH 7.5) containing 0.02 N NaCl at a flow rate of 0.5 ml/min and kept at 30 °C (Peng, Peng, Bian, Xu, & Sun, 2011). The other method is sedimentation equilibrium and osmotic pressure measurement for determination of M_w and M_n, respectively. For instance, M_n estimated from osmotic pressure measurement was 25,700 for the acetate of bamboo xylan (F2A) by Maekawa (1976). It should be noted that the M_w and M_n values of bamboo hemicelluloses show considerable variations depending on the method of their estimation (Table 1).

High performance liquid chromatography (HPLC) is frequently used to analyze the solubilized sugars in liquors after autohydrolysis or steaming of bamboo. Researchers reported that an HPX 87P column (300 mm × 7.8 mm, Bio-Rad) was employed for analysis of neutral sugars after hydrolysis of the extract, whereas an HPX 42 C column (300 mm × 7.8 mm, Bio-Rad) was used to determine the XOS present in the hot water extract (Aoyama & Seki, 1994). On the other hand, HPLC is also applied to estimate the phenolic acids and aldehydes, which were liberated during the alkaline nitrobenzene oxidation of the lignin associated with the bamboo hemicelluloses (Li et al., 2011; Wen et al., 2011). A ZORBAX Eclipse XDB-C_{18} column (250 mm × 4.6 mm) together with DAD is suggested to be well-suited for the detection of those oxidation products.

Methylation analysis based on GC–MS is the most powerful method in the determination of glycosidic linkage composition and substitution pattern of bamboo hemicelluloses. Current methylation analysis includes the conversion of free hydroxyl groups into methoxyls followed by acid hydrolysis, then the hydrolyzed monomers are reduced and acetylated to give volatile PMAA (partially methylated alditol acetate), which can be submitted to GC–MS analysis (Chaikumpollert, Methacanon, & Suchiva, 2004; Petzold, Günther, Kötteritzsch, & Heinze, 2008; Revanappa & Salimath, 2010). Briefly, the process of methylation analysis of bamboo hemicelluloses is described as follows: the dried sample (10 mg) is dissolved in 2 ml of DMSO under nitrogen and then methylated with 0.2 ml of CH_3I and 40 mg of NaOH powder. PMAA

Table 1
Hemicelluloses from bamboo: Extraction and purification methods, chemical compositions, molecule weights, as well as structural features.

Bamboo	Extraction		Purification	Fraction	Yield (%)	Monosaccharide composition (%)					M_w	M_n	Structure features	References
						Ara	Gal	Glc	Xyl	GlcA				
Bambusa rigida	Direct extraction with alkali	Extraction with 1 M NaOH, KOH, LiOH, $NH_3{\cdot}H_2O$, $(CH_3CH_2)_3N$, $Ca(OH)_2$, and $Ba(OH)_2$, respectively, at 50 °C for 3 h	Washing with 70% EtOH	H_1	6.4	6.90	1.15	7.56	78.39	6.00	53,070	24,770	The hemicelluloses consist of a backbone of β-(1 → 4)-linked D-xylopyranosyl units having branches of arabinose and 4-*O*-methyl-D-glucuronic acid	Wen et al. (2011)
				H_2	6.0	5.43	0.86	7.34	81.82	4.54	26,840	20,280		
				H_3	7.2	6.11	0.76	10.09	77.41	5.63	41,740	25,980		
				H_4	5.0	5.57	2.79	23.06	65.38	3.19	9790	9480		
				H_5	6.1	5.37	3.12	25.29	63.26	2.96	9240	8780		
				H_6	4.2	6.18	1.73	19.06	69.32	3.71	8250	8200		
				H_7	5.2	5.68	0.93	9.85	78.81	4.73	25,360	18,660		
Leaves of *sasa senanensis* Rehd		Saturated-lime-water	Dialysis DEAE-cellulose column chromatography Fehling's solution CM-Sephadex C-50 NH_4^+ column Starch-block zone Electrophoresis	p-Fr. I-(A) Fr. I-(B) p-Fr. III		17.1 26.3 16.7	trace 32.4 26.7	19.5 12.2 21.8	63.4 29.1 34.5	non – 1.2			Neutral polysaccharide consisting of L-arabinose, D-xylose and D-glucose Acidic polysaccharide consisting of L-arabinose, D-xylose, D-glucose, D-galactose, and uronic acid	Suzuki et al. (1968)
Shoot of Moso-chiku		Successive extraction with 4% and 24% potassium hydroxide	Dialysis Successive washing with water, ethanol, and acetone	HC-IA HC-IB HC-IIA HC-IIB	2.02[a] 24.30[a] 0.22[a] 14.30[a]	23.5 19.9 16.8 23.2	11.5 9.2 11.8 9.7	19.4 37.2 19.9 15.7	45.6 33.6 51.6 51.4				β-D-Glucan, xyloglucan	Kato et al. (1982)
Phyllostachys incarnata Wen		Sequential extractions with 0.5% and 1% NaOH, 60% ethanol containing 1% NaOH, and 3%, 5% and 8% NaOH at 60 °C for 3 h	Washing with 70% EtOH	$H_{0.5}$ H_1 $H_{60\text{-}1}$ H_3 H_5 H_8	1.85 2.82 1.75 7.93 2.95 1.52	9.48 7.17 9.16 6.25 5.97 6.02	2.14 0.94 1.50 0.38 0.33 0.28	14.53 16.00 11.64 9.17 5.10 4.43	69.28 71.44 68.40 80.82 85.73 86.03	4.57 4.44 9.29 3.37 2.86 3.24	26,140 30,140 21,780 27,550 32,830 36,000	14,990 17,830 13,910 17,080 20,890 25,340	*O*-Acety-(4-*O*-methylglucurono)-arabinoxylans	Peng, Peng, Bian, Xu, Sun, and Kennedy (2011)
D. brandisii		Sequential extractions with 60% ethanol containing 0.25, 0.5, 1, 2, 3, and 5% NaOH at 80 °C for 3 h	Washing with 70% EtOH	H_4 H_5 H_6 H_7 H_8 H_9	1.50 2.90 6.30 2.30 1.40 1.60	10.04 6.85 3.77 4.83 4.93 4.46	3.80 2.02 0.87 2.35 2.42 ND	49.94 48.28 40.75 35.48 21.90 21.20	26.21 37.54 50.85 52.42 64.88 70.28	6.95 3.73 3.36 3.45 4.74 3.53	35,700 35,910 41180 31320 23,220 22,870	18,240 25310 27200 22470 19,120 20,470	A linear (1→4)-β-linked xylopyranosyl backbone attachment with α-L-arabinofuranose units and/or 4-*O*-methyl-glucuronic acid via α-(1→3) and/or α-(1→2) linkages	Shi et al. (2011)
Neosinocalamus affinis		Sequential extractions with 0.2 and 0.5 M NaOH, 70% ethanol containing 0.6 M NaOH, and 1.0 and 2.0 M NaOH at 50 °C for 3 h	Washing with 70% EtOH	H_3 H_4 H_5 H_6 H_7	6.1 3.2 2.6 5.6 2.7	6.69 4.70 4.74 4.45 4.05	0.82 0.22 0.33 0.13 0.09	17.87 10.80 6.74 3.19 1.92	73.53 83.06 87.29 91.40 92.65	1.09 1.20 0.90 0.84 1.29	68,770 65,750 41,200 45190 42790	29,030 32,510 26,620 30650 26610	A linear (1→4)-β-D-xylopyranosyl main chain substituted by a small amount of L-arabinofuranosyl at C-2 and/or C-3 together with a minor quantity of 4-*O*-methylglucuronic acid at C-2	Sun et al. (2012)
Pyllostachys makinoi Hay.		Extraction with 5% NaOH for 2 h at 20 °C	Ion exchanger	NaOH extract	21.2	6.1		7.9	85.2				Arabinoxylan with a Xyl: Ara ratio of 17:1	Fengel and Shao (1984)

Table 1
(*Continued*)

Bamboo	Extraction		Purification	Fraction	Yield (%)	Monosaccharide composition (%)					M_w	M_n	Structure features	References
						Ara	Gal	Glc	Xyl	GlcA				
Phyllostachys reticulata C. Koch	Pretreatment followed by alkali/DMSO extraction	Delignification with acidic sodium chlorite Successive extraction with 5 and 18% NaOH	Fehling's solution	F2 F2A F2B F3 F3A	16.7[b] 15.6[b] 1.0[b] 3.4[b] 3.0[b]	5.6 4.8 10.1 5.9 4.5	0.9 1.0 5.3 0.3 1.3	2.4 3.9 22.6 5.5 4.3	91.1 90.3 62.1 88.4 89.9			25,700[c]	A 1,4-linked linear structure of D-xylopyranose residues and attachments of single side units such as the residues of L-arabinose and 4-*O*-methyl-D-glucuronic acid	Maekawa (1976)
Bambusa rigida		Delignification with acidic sodium chlorite Sequential extraction with 1 M KOH and 1 M LiOH for 3 h	Washing with 70% EtOH	H_5 H_6	19.1[d] 5.58[d]	5.52 4.07	1.10 1.07	2.03 4.39	85.6 88.5	5.80 2.03	44,450 35,200	21,600 24,260	The (1 → 4)-linked *β*-D-xylopyransyl backbone with 4-*O*-methyl-α-D-glucuronic acid attached to *O*-2 of the xylose residues and L-arabinose attached to *O*-3 of the xylose residues	Wen et al. (2010)
Phyllostachys bambusoides f. shouzhu Yi		Delignification with acidic sodium chlorite Extraction with 8% NaOH at 25 °C for 16 h	Graded ethanol precipitation	HA H_{15} H_{30} H_{45} H_{60} H_{75}	3.7[b] 1.8[b] 3.2[b] 5.1[b] 4.8[b] 1.5[b]	5.75 5.84 6.44 5.86 7.40 9.65	0.04 0.04 0.13 0.17 0.65 1.05	8.36 9.05 10.29 17.01 35.18 24.27	84.30 83.26 81.10 74.58 53.33 61.60	1.55 1.81 2.04 2.38 3.44 3.43	24,400 21,300 33,000 55,000 67,500 26,900	17,500 16,300 20,800 34,300 32,800 19,000	*O*-Acetylated 4-*O*-methyl-glucuronoarabinoxylans consisting of a linear (1 → 4)-*β*-D-xylopyranosyl backbone decorated with branches at *O*-3 of α-L-arabinofuranosyl (5–12 mol %) or at *O*-2 of 4-*O*-methylglucuronic acid units and acetyl groups (0.8–11 mol %)	Peng, Peng, Bian, Xu, and Sun (2011)
Leaves of *Phyllostachys pubescens* Mazel		Delignification with acidic sodium chlorite Extraction with 2% NaOH at 55 °C for 2.5 h	Graded ethanol precipitation	BLH_{20} BLH_{40} BLH_{60} BLH_{80}	0.89 4.27 4.58 0.97	45.21 7.22 43.14 36.35	8.24 2.09 7.99 16.61	14.45 4.23 1.62 1.42	30.38 85.33 43.97 40.47	1.28 2.09 1.43 2.03			Arabinoxylans, arabinogalactans, and *β*-D-glucans having (1 → 3)- and (1 → 4)-glucosidic linkages	Peng, Zhou, et al. (2013)
Neosinocalamus affinis		Ultrasonic irradiation in combination with cold NaOH/urea system Extraction with DMSO	Washing with 70% EtOH	F0 F1 F2 F3	4.0 3.4 3.3 3.4	2.21 1.99 2.32 2.17	0.50 0.43 0.38 0.33	50.82 53.69 54.67 52.93	43.99 42.30 41.07 43.08	2.39 1.49 1.48 1.40	6360 5950 6650 6480	3560 3670 3700 3930	(1 → 4)-Linked α-D-glucan from amylase and (1 → 4)-linked *β*-D-xylan attached with minor amounts of branched sugars from hemicelluloses	Li et al. (2011)
Shoots of *Phyllostachys edulis* A. and C. Riv.		Pretreatment with CDTA Sequential extraction with 0.05 M Na_2CO_3, 1 and 4 M KOH	Ion-exchange chromatography Selective precipitation with iodide Gel-permeation chromatography	Na_2CO_3-I Na_2CO_3-II 1 M KOH-I 1 M KOH-II 4 M KOH-I 4 M KOH-II	3.6 1.1 7.3 15.5 7.2 3.0	19.1 15.0 6.8 27.5 13.8 15.2	22.3 6.2 1.6 10.4 7.4 7.6	23.4 48.6 75.4 24.9 54.7 52.8	23.8 27.6 16.0 31.3 22.0 21.9	1.3 0 0 0 0 0			Arabinoxylan, (1 → 3, 1 → 4)-*β*-D-glucan, xyloglucan, glucomannan	Edashige and Ishii (1998)

Phyllostachys sulphurea (Carr.) A. et C. Riv		Pretreatment with [Amim]Cl Consecutive extraction with 0.5 M NaOH and 70% ethanol containing 1.0 M NaOH	Dissolution in water and precipitation in 3 vol. of 95% ethanol twice	IL-H_1 IL-H_2	5.78[b] 0.87[b]	7.04 3.03	0.31 0.14	8.53 42.75	80.52 52.97	3.60 1.10	16,110 10,020	11,180 7770	4-*O*-Methyl-α-D-glucurono-α-L-arabino-*β*-D-xylan	Yang et al. (2013)
Sasa senanensis Rehd.	Steaming-hot water extraction	Treatment with saturated steam at a range of temperatures between 170 and 197 °C for 10 min in the presence of various acid catalysts			1.0–17.1	0.8–1.3[e]			0.4–6.8[e]				The solubilized sugars mainly composed of xylose, arabinose and low molecular weight xylo-oligosaccharides	Aoyama and Seki (1999)
Bamboo fiber	Autohydrolysis	Treatments with hot, compressed water at 180–230 °C											The liquors containing mainly hemicellulose-derived products (oligo- and mono-saccharides)	González et al. (2011)
P. pubescens MAZEL		Extraction with hot-compressed water at 200 °C			75 (% fraction A)								The decomposed products mainly contained xylose and xylooligosaccharides (xylobiose, xylotriose, xylopentaose) and their concentrations were in the interval 4–6 μg/ml each	Ando et al. (2004)
Shoots of *Phyllostachys edulis*	Enzymic hydrolysis	Hydrolysis with Driselase at 30 °C for 16 h	Sephadex LH-20 Reversed-phase HPLC Analytical normal-phase HPLC	1 2	0.039 mg/g of cell walls 0.016 mg/g of cell walls								Xyloglucan oligosaccharides containing ferulic acid Arabinoxylan oligosaccharides containing *p*-coumaric acid	Ishii and Hiroi (1990)
Shoots of *Phyllostachys edulis*		Hydrolysis with Driselase	Sephadex LH-20 Sep-Pack C18 cartridge	1	23 μg/g of cell walls								Diferuloyl arabinoxylan hexasaccharide	Ishii (1991b)

[a] From 80.0 g of crude cell-wall materials, g.
[b] Percent based on the original air-dried defatted bamboo meal.
[c] Estimating from osmotic pressure measurement.
[d] Percent based on the dry holocellulose.
[e] Percent based on dry materials.

Table 2
GC–MS results of methylation analysis of bamboo hemicellulosic subfractions (Peng, Peng, Bian, Xu, & Sun, 2011).

Glycosyl residue	Methylated sugar	Mass fragments (*m/z*)	Type of linkage	Molar ratio					
				HA	H_{15}	H_{30}	H_{45}	H_{60}	H_{75}
Galactose	2,3,4,6-Me_4-Gal[a]	43, 45, 71, 87, 101, 117, 129, 145, 161, 205	*β*-D-Gal*p*-(1→	0.1	0.1	0	0	2.4	2.7
	2,3,6-Me_3-Gal	43, 45, 71, 87, 99, 101, 113, 117, 129, 233	→4)-*β*-D-Gal*p*-(1→	0.2	0.1	0.8	0.2	0.2	0.2
Arabinose	2,3,5-Me_3-Ara	43, 45, 71, 87, 101, 117, 129, 161, 233	α-D-Ara*f*-(1→	24.8	22.5	33.8	45.7	55.0	59.1
	2,3-Me_2-Ara	43, 87, 101, 117, 129, 189	→5)-α-D-Ara*f*-(1→	0	0	0	0	0.2	0.5
	3,5-Me_2-Ara	43, 45, 71, 87, 99, 101, 117, 129, 161, 233	→2)-α-D-Ara*f*-(1→	0.2	0	0	0.7	0.3	0.7
Xylose	2,3,4-Me_3-Xyl	43, 45, 87, 101, 117, 129, 161	*β*-D-Xyl*p*-(1→	3.5	2.1	1.2	0.8	3.2	0.3
	2,3-Me_2-Xyl	43, 87, 101, 117, 129, 189	→4)-*β*-D-Xyl*p*-(1→	21.1	9.7	9.1	5.5	6.7	2.1
	3-Me-Xyl	43, 45, 87, 99, 101, 129	→4)-*β*-D-Xyl*p*-(1→ 2 ↑	0.3	0.1	0.3	0.3	1.5	0.1
	2-Me-Xyl	43, 85, 101, 117, 127, 159, 261	→4)-*β*-D-Xyl*p*-(1→ 3 ↑	1.3	0.7	1.4	0.8	1.6	0.2
Glucose	2,3,4,6-Me_4-Glc	43, 45, 71, 87, 101, 117, 129, 145, 161, 205	*β*-D-Glc*p*-(1→	0.1	0.1	0.1	0.2	0.7	0.2
	2,4,6-Me_3-Glc	43, 45, 71, 87, 101, 113, 117, 129, 161, 233	→3)-*β*-D-Glc*p*-(1→	0.8	0.8	0.9	1.5	1.3	1.1
	2,3,6-Me_3-Glc	43, 45, 71, 87, 99, 101, 113, 117, 129, 233	→4)-*β*-D-Glc*p*-(1→	3.8	3.1	3.4	5.3	4.1	2.0
	2,3-Me_2-Glc	43, 58, 85, 87, 101, 117, 127, 142, 159, 161, 201, 261	→4)-*β*-D-Glc*p*-(1→ 6 ↑	0.4	0	0	0.3	2.0	0.4
	2,3,4-Me_3-Glc	43, 58, 87, 99, 101, 117, 129, 161, 189, 233	→6)-*β*-D-Glc*p*-(1→	0	3.2	3.5	3.7	1.1	0.2

[a] 2,3,4,6-Me_4-Gal = 2,3,4,6-tetra-O-methyl-1,5-di-*O*-acetyl-D-glucitol, etc.

is obtained by acid hydrolysis of fully methylated sample with 1 M H_2SO_4 at 105 °C for 2.5 h, and the reduction of the hydrolysate is carried out using $NaBH_4$, followed by acetylation with acetic anhydride. A HP-5MS capillary column (30 m × 0.25 mm × 0.25 μm) and the conditions of GC–MS analysis including an initial temperature of 80 °C for 2 min, then to 200 °C at 25 °C/min, further to 270 °C at 10 °C/min, and finally to 280 °C at 10 °C/min for 5 min were used to indentify and quantitative determination of PMAA from bamboo hemicelluloses by Peng, Peng, Bian, Xu, and Sun (2011). The results (Table 2) showed that approximately 0.8–11% of the xylose units were monosubstituted by 4-*O*-methylglucuronic acid and acetyl groups at the *O*-2 position, while 5–12% of the xylose residues were monosubstituted at the *O*-3 position by arabinose units. Additionally, it was found that the side chains of α-L-Ara-(1 → 2)-α-L-Ara-(1 → 3) were attached on the water-soluble arabinoxylan backbones by methylation analysis.

3.1.2. Spectroscopic analysis

Spectroscopic methods as the main tools of modern chemistry are widely used to determine and confirm molecular structures of bamboo hemicelluloses. Most essential methods are the Fourier-transform infra red (FT-IR) and nuclear magnetic resonance (NMR) spectroscopy. In the FT-IR spectra of bamboo hemicelluloses, several important absorptions have been attractive to obtain structural information of arabinoxylans. The arabinoxylans usually show the main band maximum at about 1045 cm^{-1} due to COH bending mode (Kačuráková et al., 1999). A band at about 1160 cm^{-1} arises from C—O and C—O—C stretching with some contribution of OH bending (Kačuráková, Capek, Sasinková, Wellner, & Ebringerová, 2000). The C—C stretching gives the absorption at about 1116 cm^{-1}, while the peak intensity ratios at 1164 (1164/1048 and 1164/1158) and 990 (990/1380 and 990/1040) cm^{-1} could be suggested as an index of arabinofuranosyl contribution (Kačuráková, Ebringerova, Hirsch, & Hromadkova, 1994). The most important band is at about 898 cm^{-1}, corresponding to the glycosidic C_1-H deformation mode with ring vibration contribution for the *β*-anomer form of the pyranoid ring, which indicates *β*-glycosidic linkages between the sugar units. Furthermore, the weak absorptions at about 1735 and 1247 cm^{-1} are due to the acetyl groups of bamboo hemicelluloses (Robert, Marquis, Barron, Guillon, & Saulnier, 2005).

^1H and ^{13}C NMR spectroscopy are usually employed in order to reveal the structural features of bamboo hemicelluloses. The signals on the ^1H and ^{13}C NMR spectra of the hemicelluloses from bamboo *Phyllostachys incarnata* Wen were assigned by Peng, Peng, Bian, Xu, Sun, and Kennedy (2011), and the detailed data are summarized in Table 3. Recent reports also suggested that 2D ^1H–^{13}C heteronuclear single quantum correlation (HSQC) NMR spectroscopy could provide a better signal resolution (Bian et al., 2012; Sun, Wen, Ma, & Sun, 2013) and allow the estimation of the relative ratio of X/A in bamboo hemicelluloses by the integration of the corresponding anomeric C_1-H_1 correlation signals (Wen et al., 2010). A HSQC spectra of hemicellulosic subfraction HA from bamboo *Phyllostachys bambusoides* f. shouzhu Yi is shown in Fig. 3 as an example of compositional analysis (Peng, Peng, Bian, Xu, & Sun, 2011). Based on the above results of structural characterization, alkali-extracted hemicelluloses (GAX) from bamboo clums can be mainly proposed as 1,4-*β*-D-[4-*O*-Me-α-D-Glc*p*A-(1 → 2)][α-L-Ara*f*-(1 → 2) and/or (1 → 3)]-xyl*p*. Other types of bamboo hemicelluloses are also summarized in Table 1. In addition to the above-mentioned methods, the structure of hemicelluloses and their derivatives or degradation products could be characterized by 1D and 2D-double quantum filtered correlation spectroscopy (DQF-COSY), 2D-total correlation spectroscopy (TOCSY), heteronuclear multiple bond correlation (HMBC), and electrospray-ionization mass spectrometry (ESI-MS) (Dourado, Cardoso, Silva, Gama, & Coimbra, 2006; Ishii et al., 2010).

Scanning electron microscope (SEM) and atomic force microscopy (AFM) are utilized to describe the morphologies of bamboo hemicelluloses. The hemicelluloses from bamboo (*Phyllostachys pubescens* Mazel) were analyzed with SEM by Peng, Wang, et al. (2012). It was found that bamboo hemicelluloses displayed flat particles with compact surfaces and the particle sizes were more than 100 nm. To obtain information on the general shape of the aggregates, the bamboo hemicelluloses were visualized with AFM by Peng, Wang, et al. (2012), Peng, Zhang, et al. (2012). As seen in Fig. 4A, the island aggregations and rod aggregations were observed, and the AFM images clearly showed chains, which were believed to be hemicellulose molecules and congregated through hydrogen bond and Van der Waals force. In Fig. 4B, the arrow-pointed length was about 165.84 nm, the

Table 3
$^{1}H/^{13}C$ NMR chemical shifts in ppm (measured at 400 MHz in D_2O; relative to an internal D_2O, δ_H 4.700 ppm) of constituent monosaccharide residues in hemicellulosic fraction H_3 (Peng, Peng, Bian, Xu, Sun, & Kennedy, 2011).

Structural	Residue[a]	Chemical shift (ppm)							
		H/C-1	H/C-2	H/C-3	H/C-4	H/C-5a	H-5e	OCH_3-4	COOH
	ß-X_{red}	4.58/n.d.	3.23/n.d.	3.60/n.d.	3.76/77.80	3.34/66.50	n.d.[b]		
	X_{int}	4.42/102.06	3.29/73.06	3.51/74.45	3.73/76.09	3.37/63.26	4.06		
	X_{term}	4.40/n.d.	3.25/74.02	3.49/76.90	3.72/70.54	3.35/66.61	4.03		
	$X_{MeGlcA2}$	4.64/103.55	3.56/78.39	3.65/73.47	3.80/n.d.	3.38/n.d.	4.19		
	X_{A23}	4.56/n.d.	3.53/n.d.	3.62/74.60	3.65/76.98	3.32/n.d.	n.d.		
	X_{Ac2}[c]	4.63/100.97	4.63/n.d.	3.76/72.53	3.87/n.d.	3.40/63.95	4.19		
	X_{Ac23}	4.76/100.42	n.d./72.51	5.14/73.97	n.d./n.d.	3.54/n.d.	4.20		
	A_2	5.23/109.34	4.20/82.49	n.d./79.25	n.d./86.24	3.73/61.67	3.85		
	A_3	5.28	4.25	n.d.	n.d.	3.73	3.87		
	MeGlcA	5.27/97.55	3.58/72.31	3.87/73.76	3.23/n.d.	n.d./n.d.		3.46/59.72	177.10

[a] The following designations are used: ß-X_{red}, ß-Xyl reducing end; X_{int}, Xyl internal; X_{term}, Xyl terminal end; $X_{MeGlcA2}$, MeGlcA 2-*O*-linked Xyl; X_{A23}, Ara 2-*O*- and 3-*O*-di-substituted Xyl; X_{Ac2}, 2-*O*-acetylated Xyl; X_{Ac23}, 2,3-di-*O*-acetylated Xyl; A_2, 2-*O*-linked Ara; A_3, 3-*O*-linked Ara; MeGlcA, 4-*O*-methylglucuronic acid.
[b] Not detectable.
[c] The chemical shift was observed for the 2-*O*-acetyl groups at δ_H 2.11 ppm.

calculated average distance of helix was 41.46 nm, and the average diameter of helix was 66.94 nm.

3.2. Physicochemical properties

3.2.1. Rheological properties

Knowledge on the dynamic viscosity and modulus of bamboo hemicelluloses is important in the elucidation of their rheological properties, but also interesting in their possible applications. Currently, more detailed investigation on the rheological behaviors of hemicellulosic derivatives varying in concentrations and DS from bamboo (*Dendrocalamus membranaceus* Munro) has been carried out (Peng, Ren, Zhong, & Sun, 2012; Peng, Ren, Zhong, Sun, Shi, & Hu, 2012). The rheological properties of the glycidyl methacrylate hemicellulosic (GMH) derivatives at concentrations of 0.5%, 1.0%, and 2.0% (wt%) were measured by an AR2000 rheometer at 25 °C. The results indicated that the GMH showed shear-thinning performance and elasticity in aqueous solution at high frequency. Meanwhile, the elastic modulus and loss modulus of GMH solution increased with the increasing concentration and DS. In addition, the viscoelasticity of amphoteric xylan-type hemicelluloses increased with the increasing DS and concentration, which were due to strong electrostatic attraction or intermolecular interactions.

3.2.2. Thermal behavior

Thermogravimetric analysis (TGA) and derivative thermogravimetry (DTG) are the most common techniques for rapid investigating the mass loss during pyrolysis of materials. The

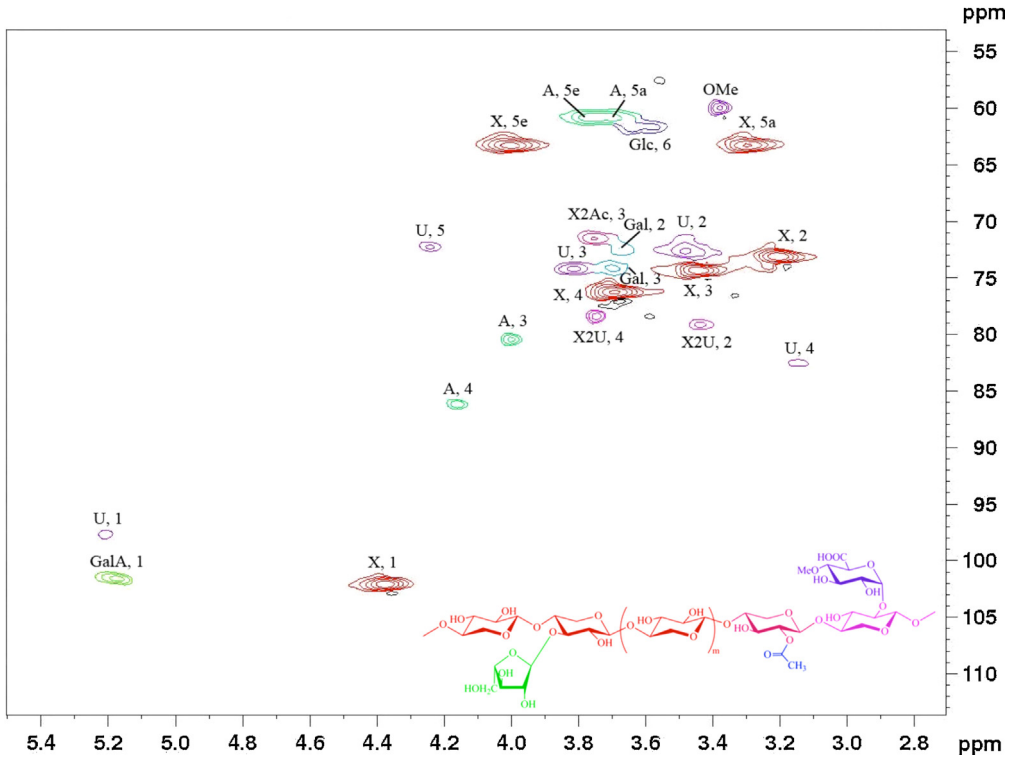

Fig. 3. HSQC (D_2O, 25 °C) spectra of hemicellulosic subfraction HA. Designations are as follows: X, Xyl*p* unit; A, Ara*f* unit; U, 4-*O*-Me-α-D-Glc*p*A unit; Gal, →4)-ß-D-Gal*p*-(1→ unit; Glc, (1→4)-linked α-D-Glc*p* unit. GalA, (1→4)-α-D-GalA (Peng, Peng, Bian, Xu, & Sun, 2011).

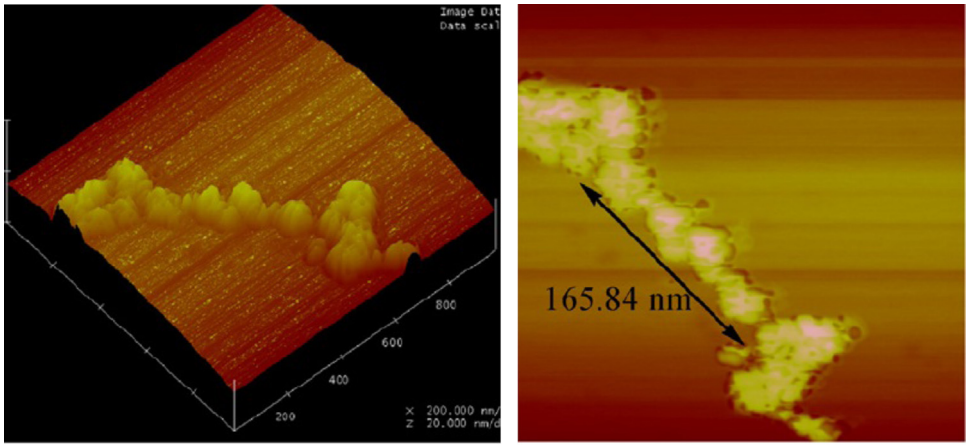

Fig. 4. AFM images of hemicellulosic fraction H_2 adsorbed on mica at concentration of 0.01 mg/ml: (A) the 3D image and (B) the corresponding plane image (Peng, Wang, et al., 2012).

measurement of thermal behavior is essential for the application of bamboo hemicelluloses as biomaterials. In recent years, the thermal behavior of bamboo hemicelluloses has been extensively investigated by TGA and DTG. In general, the thermal degradation of bamboo hemicelluloses could be simply divided into three stages with the increase of temperature. The fist stage (about < 200 °C) is ascribed to the loss of moisture and volatile ingredients, the second stage (about 200–350 °C) is attributed to fast thermal decomposition of xylans, and the third stage (about > 350 °C) represents the degradation of volatile components and further charring processes of the residues (Peng, Hu, et al., 2012). Correspondingly, the rate of maximum degradation is usually observed in DTG curve between 200 and 300 °C (Peng, Peng, Bian, Xu, Sun, & Kennedy, 2011). Studies have shown that the thermal behavior of bamboo hemicelluloses is supposed to be affected by the presence of lignin, structural features as well as molecular weight. In addition to TGA and DTG, differential thermal analysis (DTA) curves were also depicted to display endothermic and exothermic behaviors of bamboo polysaccharides (Li et al., 2011).

4. Potential applications of bamboo hemicelluloses

The potential applications of hemicelluloses have attracted a growing volume of research during the last decade because of their biodegradability, excellent biocompatibility, and physico-chemical properties. Interesting works of biorefineries and bioconversions of hemicelluloses for fuel ethanol have been well reviewed by Gírio's group (Carvalheiro, Duarte, & Gírio, 2008; Gírio et al., 2010). At present, research activities in the field of bamboo hemicelluloses have been aimed mainly at utilizing them by conversion into biomaterials, biofuels, and food. These potential applications will open up new window for the utilizations of bamboo resources.

4.1. Modification of bamboo hemicelluloses

In order to improve the hydrophobic, thermoplastic, and functional properties of hemicelluloses, chemical modification is necessary and plays a key role in maximally exploiting the hemicelluloses applications. A great deal of effort has been made to investigate the derivatives of bamboo hemicelluloses by our research group (Peng, Ren, & Sun, 2010; Peng, Ren, Zhong, & Sun, 2012; Peng, Ren, et al., 2012; Peng, Peng, et al., 2012), and the pathways of modification are shown in Fig. 5. The esterification of bamboo hemicelluloses was carried out in various ways. A novel type of derivative containing carbon—carbon double bonds (C=C) was synthesized by transesterification reaction of bamboo hemicelluloses and glycidyl methacrylate (GMA) in DMSO. The reaction mechanism was confirmed by the presence of methacryloyl groups on the hemicellulosic chains and glycidol in the reaction mixture solution. Various catalysts (DMAP, TEA, NBS, PB, pyridine, and lipase) were also investigated to estimate the influence of catalysts on DS. The results exhibited that the catalysis effect increased in this order: lipase < pyridine < NBS < TEA < PB < DMAP. Under the optimum reaction condition (20 wt% DMAP, the GMA/anhydroxylose units molar ratio of 9:5, 40 °C for 36 h), the resulting methacrylated hemicelluloses with a maximum DS value of 0.94 could be obtained (Peng, Ren, et al., 2012). Interestingly, the unsaturated double bonds can act as active and polymerizable sites for the further modification or cross-linking. Therefore, the introduction of vinyl groups into bamboo hemicelluloses is an important strategy to further prepare the functional polymer as a versatile platform. Moreover, the functional derivative with unsaturated double bonds and carboxyl groups was prepared by homogeneous esterification of bamboo hemicelluloses with maleic anhydride in IL 1-butyl-3-methylimidazolium chloride ([BMIM]Cl) in the presence of LiOH and the DS ranged from 0.095 to 0.75 (Peng, Ren, & Sun, 2010). In this work, the chemical modification of bamboo hemicelluloses in IL as the satisfactorily homogeneous media was proven to be an efficient way.

The etherification of hemicelluloses is another important approach to prepare functional polymers. A kind of amphoteric polymer was successfully synthesized by sequential incorporation of carboxymethyl and quaternary ammonium groups into the backbone of bamboo hemicelluloses in the presence of NaOH under microwave irradiation (Peng, Ren, Zhong, & Sun, 2012). The maximum DS of carboxymethyl groups under the optimum reaction condition was 0.90, while the corresponding DS of quaternary ammonium groups was 0.44. Amphoteric macromolecules containing both anionic and cationic groups possess polyampholyte characteristics and pH or salt-sensitivity, nonspecific adsorption resistance, and functionality from the pendant charged groups. Such properties have made the amphoteric derivatives possible to be applications in the fields of biomaterials, adsorbents, cosmetic, biomedicine, etc. More recently, cyanoethyl hemicelluloses (CEH) were successfully synthesized by nucleophilic addition reaction of bamboo hemicelluloses and acrylonitriles in aqueous sodium hydroxide (Cao, Sun, Peng, Zhong, & Sun, 2013). A series of CEH with DS ranging from 0.23 to 1.64 were obtained. Hence,

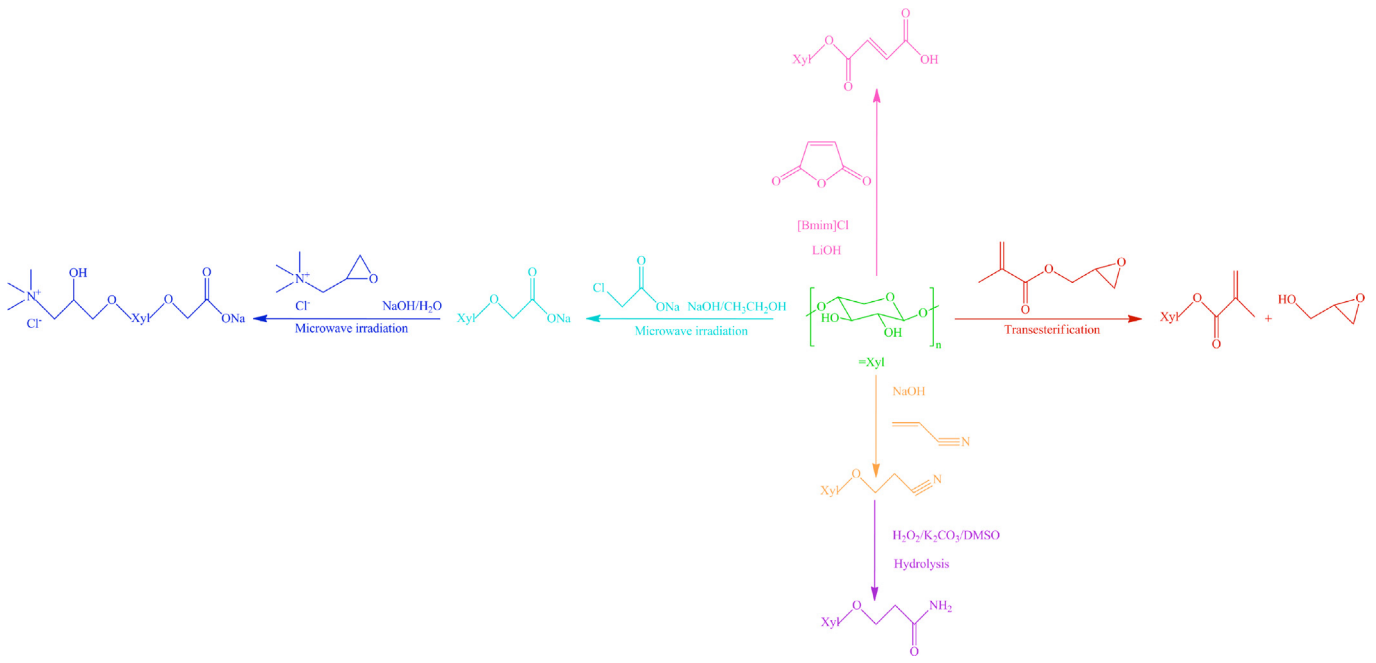

Fig. 5. Reaction pathways for the modification of hemicelluloses from bamboo.

carbamoylethyl hemicelluloses were prepared by hydrolysis of CEH with H_2O_2/K_2CO_3/DMSO at room temperature. The obtained cyanoethyl and carbamoylethyl hemicelluloses can be used as versatile polymers.

4.2. Biomaterials

Biomaterials from renewable resources are receiving great attention due to their good biocompatibility and biodegradability. Nowadays, the research on biomaterials based on bamboo hemicelluloses is mainly focused on the preparation of hydrogels, films, antioxidant agent, and stabilizer. Hydrogels, which give the necessary three-dimensional, hydrophilic and polymeric networks capable of imbibing large amounts of water or biological fluids, have increasingly found wide applications in tissue engineering, drug delivery, and environmental protection. Peng, Ren, Zhong, Peng, and Sun (2011) reported the preparation of ionic hydrogels (Fig. 6A) by free radical graft copolymerization of acrylic acid and bamboo hemicelluloses using *N,N*-methylene-bis-(acrylamide) as cross-linker and ammonium persulfate/*N,N,N′,N′*-tetramethylethylenediamine as initiator system. The obtained hemicelluloses-*g*-AA hydrogels showed sensitive behavior to chemical environment such as pH, ionic strength and composition of the media, and organic solvents. It was found that the network of hydrogels became more expanded in the solutions at higher pH, whereas shrinkage occurred at lower pH or in salt solutions as well as in organic solvents. In this case, the highest swelling ratio of 822 could be achieved in distilled water, which is much higher than those of xylan/chitosan hydrogel (<100) (Gabrielii & Gatenholm, 1998), nonionic galactoglucomannan hydrogels (<80) (Liu, Hu, & Zhuo, 2004; Voepel, Edlund, & Albertsson, 2009), and methacryloylated hemicelluloses hydrogels (<190) (Söderqvist Lindblad, Albertsson, Ranucci, Laus, & Giani, 2005). Interestingly, the hemicelluloses-*g*-AA hydrogels also exhibited the reversible on-off switching behavior in acidic-basic solutions or water–ethanol or acetone solutions. Subsequently, this type of hydrogel was developed to provide a way for adsorption of heavy metal ions Pd^{2+}, Cd^{2+}, and Zn^{2+} from aqueous solutions by Peng, Zhong, Ren, and Sun (2012). The results demonstrated that as the pH of metal ion solutions increased, the adsorption capacities of Pd^{2+}, Cd^{2+}, and Zn^{2+} increased and the maximum values were 859, 495, and 274 mg/g during about 60 min, respectively, in which the metal ion adsorption on hemicelluloses-*g*-AA hydrogel was proved to follow the Langmuir isotherm model ($R^2 > 0.99$). In addition, the experiment of repeated adsorption/desorption revealed the recovery rates were yet above 96% after cycle 8, suggesting the hydrogel has high efficiency of regeneration and metal ion recovery. Generally, the above-described hydrogels belongs to the hydrogels of interpenetrating polymer networks (IPNs), in which the polymer networks cannot be separated unless chemical bonds are broken. Unlike IPNs, semi-IPNs hydrogels, which are composed of one linear polymer entrapped within the networks of another polymer, have received increasing attention because the constituents of linear polymers can be separated from the networks without breaking chemical bonds. As recently reported by Peng et al. (2014), a series of semi-IPNs hydrogels were prepared by radical polymerization of bamboo (*Phyllostachys pubescens*) hemicelluloses, acrylic acid, and the phosphorylated poly(vinyl alcohol) using potassium persulphate as initiator and *N,N*-methylenebisacrylamide as crosslink agent. The maximum equilibrium swelling ratios of the hydrgels in distilled water and 0.9 wt% NaCl solutions were up to 1085 g/g and 87 g/g, respectively. Apart from chemical method, physical method was also applied to prepare hemicelluloses based hydrogels. For example, Guan, Bian, Peng, Zhang, and Sun (2014) described that the novel hydrogels with high strength were prepared from bamboo (*Phyllostachys pubescens*) hemicelluloses, polyvinyl alcohol, and chitin nanowhiskers by freeze/thaw technique with 0, 1, 3, 5, 7, and 9 times. The results showed that the highest compressive strength of these hydrogels was 10.5 MPa after 9 times of freeze/thaw cycles. This work provided a remarkable way for preparation of hydrogels with good mechanical properties, which have a potential application in tissue engineering.

The hemicelluloses based films are other important biomaterials and exhibit excellent oxygen barrier property, which makes them good potential candidates for food-packaging applications. Up to now, a number of native or modified hemicelluloses (konjac glucomannan, galactoglucomannan, arabinoxylan, and xylans) films were developed by either single-use or blend-use with various

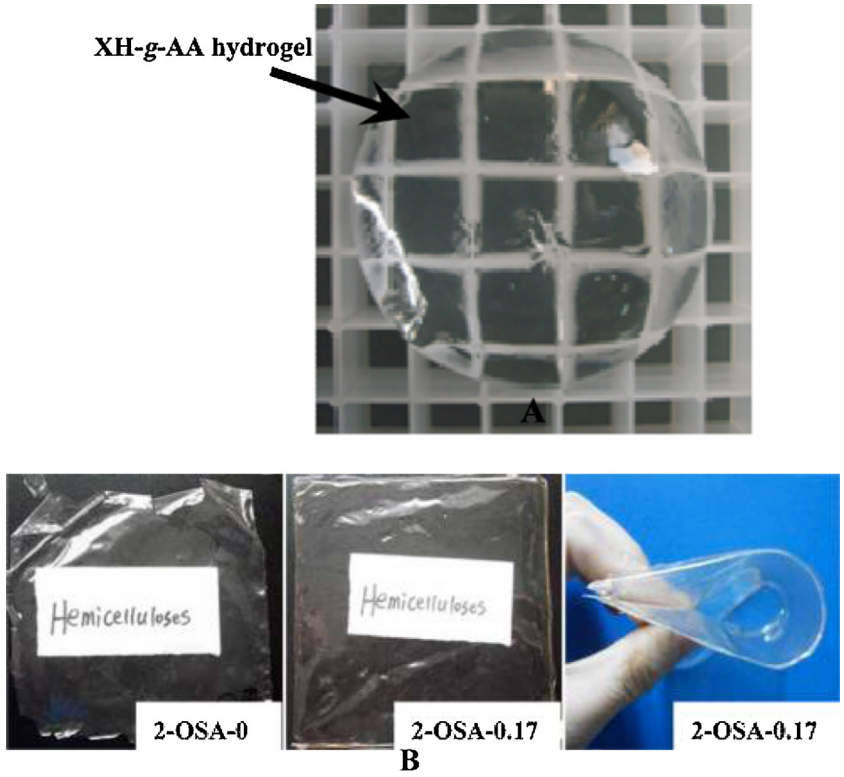

Fig. 6. Hydrogel (A) and film (B) based on hemicelluloses from bamboo *Dendrocalamus membranaceus* Munro (Peng, Ren, Zhong, Peng, et al., 2011; Zhong et al., 2013).

natural polymers, such as starch, chitosan, lignin, alginate, etc., in the presence of plasticizers (e.g., sorbitol, glycerol, and xylitol) (Edlund, Ryberg, & Albertsson, 2010; Goksu, Karamanlioglu, Bakir, Yilmaz, & Yilmazer, 2007; Hansen & Plackett, 2008; Hartman, Albertsson, & Sjöberg, 2006; Höije, Sternemalm, Heikkinen, Tenkanen, & Gatenholm, 2008). Apart from oxygen permeability and water vapor transmission, mechanical strength and flexibility are key target properties for packaging films. For this reason, an effective approach was described to improve mechanical properties of the films by Peng, Ren, Zhong, and Sun (2011). In this work, the incorporation of cellulose nanofibers (CNF, 0–20 wt%) into bamboo hemicelluloses (64–75 wt%) was carried out to prepare nanocomposite films in the presence of sorbitol (16–25 wt%) at 23 °C and 50% relative humidity. As expected, incorporation of CNF could lead to a significant improvement in the tensile strength of the nanocomposite films. Compared to native hemicelluloses film, the addition of 20 wt% CNF increased the tensile stress and Young's modulus of the nanocomposite film by 232 and 363%, respectively. Meanwhile, the thermal stability of the nanocomposite film was also improved. In addition, the hydrophilic nature of hemicelluloses restricts the application of their films at high humidity conditions. To improve the film performance, Zhong, Peng, Yang, Cao, and Sun (2013) described a new and effective strategy to prepare bamboo xylan films (Fig. 6B) with less moisture sensitive and high mechanical strength properties by grafting of the xylan with 2-octenylsuccinic anhydride (2-OSA, C8) and 2-dodecenyl-1-succinic anhydride (2-DSA, C12), respectively. The measurement of equilibrium moisture content showed that the externally plasticized xylan film contained high moisture content (13.92 wt%), whereas 2-OSA-xylan and 2-DSA-xylan films had lower moisture contents (5.90–11.67 wt%). Meanwhile, the contact angle of xylan film was 31.0°, while the chemical modification with 2-OSA led in films with higher contact angles (39.5–71.9°). Those results indicated that the grafting of hydrophobic long alkenyl chains into xylan backbone made film less moisture sensitive. Moreover, tensile strength testing displayed that the tensile strength and tensile strain of 2-OSA-xylan film (DS = 0.064) were improved by 111 and 132% than those of xylan film, respectively. In comparison, 2-OSA-xylan had better film-forming properties than those of 2-DSA-xylan. Probably the reason of this feature is related to the 2-OSA half-ester groups, which act as built-in internal plasticizers for interfering with the association of hydroxyls and disturbing the regular arrangement of xylan chains in the film-forming process.

On the other hand, the potential application of bamboo hemicelluloses as antioxidant agents seems to be possible as well in the field of food storage. Li, Shi, Jin, Ding, and Du (2013) prepared controllable antioxidative products by Maillard reaction of bamboo hemicelluloses (1%, w/v) with chitosan (1%, w/v) at 100 °C for different time periods (0, 60, 120, and 180 min). Those Maillard reaction products (MRPs) were used for lipid food storage in lecithin model system and refrigerated pork meat. Their antioxidant activity was tested against lecithin liposome peroxidation induced by 2,2′-azobis(2-methylpropionamidine) dihydrochloride. The results revealed that the inhibition percentage of MRPs heated for 120 (91.0%) and 180 (95.0%) min were much higher than that for 60 min (39.4%). Moreover, in the experiment of fresh pork protection, it was found that the MRPs heated for 60 and 120 min retarded the growth of spoilage organisms more effectively. Furthermore, bamboo hemicelluloses as stabilizers were used to prepare silver nanoparticles under microwave treatment by Peng, Yang, and Xiong (2013).

4.3. Biofuel and food

The increasing environmental concerns and decline in fossil fuel reserves have triggered the search for renewable energy. Using biomass as an alternative feedstock for biofuel production is a viable option to replace wherever possible the present dominating and non-renewable fossil fuels in recent years. Currently, the simultaneous saccharification and fermentation (SSF) and simultaneous

Table 4
Composition and total yield of XOS released by enzyme from bamboo hemicellulosic subfractions (Peng, Peng, Bian, Xu, & Sun, 2011).

Fraction	Molar composition (mol%)[a]						Total yield[b]
	Xylose	Xylobiose	Xylotriose	Xylotetraose	Xylopentose	Xylohexose	
HA	2.3	49.4	28.9	17.4	1.7	0.3	23.1
H_{15}	2.4	49.8	28.7	17.3	1.5	0.3	21.5
H_{30}	2.1	50.6	27.7	17.6	1.7	0.3	32.5
H_{45}	2.1	51.0	27.6	17.2	1.8	0.3	26.3
H_{60}	2.5	55.3	27.4	14.1	0.7	n.d.[c]	38.9
H_{75}	4.5	74.5	15.9	5.1	n.d.	n.d.	40.6

[a] Expressed in relative molar percentages.
[b] Based on the original xylose (w/w%).
[c] Not detectable.

saccharification and co-fermentation (SSCF) are two ubiquitous approaches for converting hemicelluloses into bioethanol (Peng, Peng, Xu, & Sun, 2012). SSF is a combination of the enzymatic hydrolysis of hemicelluloses and fermentation in one step, while SSCF is considered to be an improvement to SSF and refers to the fermentation of both hexoses and pentoses into bioethanol. In study on saccharification of bamboo carbohydrates (starch, cellulose, and hemicelluloses) for the production of bioethanol, carbohydrates obtained from cooking of bamboo (*Bambusa vulgaris* Schrad) were hydrolyzed with commercial amylases and a mixture of fungal culture broths containing cellulolytic and hemicellulolytic enzymes (De Menezes, Dos Santos, & Azzini, 1983). It was shown that glucose, xylose, and cellobiose were present in the hydrolysates. However, only 50% of the total carbohydrates were digested, and 78.9% of them were converted to reducing sugars after 48 h saccharification. Subsequently, after 24 h fermentation with *Saccharomyces cerevisiae*, the alcohol efficiency was about 85%.

XOS from xylan-rich hemicelluloses or raw materials can be potentially applied in the fields of functional food and pharmaceutical industries, since they possess properties beneficial to health such as non-cariogenicity, low caloric value, and promoting the growth of intestinal bifidobacteria in the colon. In particular, study pointed out that XOS obtained by autohydrolysis of bamboo had a cytotoxic effect on human leukemia cells (Ando et al., 2004). In addition, XOS show some specific characteristics such as resistance to heat, stability in acidic media, and significant biological effects at low daily intakes, which are driving research a great deal of effort to investigate the production of XOS. Various methods involved acid hydrolysis (Reis, Domingues, Ferrer-Correia, & Coimbra, 2003), enzymatic hydrolysis (Peng, Peng, Bian, Xu, & Sun, 2011), and autohydrolysis (Ando et al., 2003; Xiao et al., 2013) of xylan-rich raw materials or hemicelluloses have been suggested depending upon the different requirements. In comparison, acid hydrolysis creates corrosive and environmental problems as well as the production of undesired degradation products (furfural, phenolic acids, etc). Enzymatic hydrolysis requires long conversion time and costly enzymes, whereas autohydrolysis needs to be carried out under severe conditions. Peng, Peng, Bian, Xu, and Sun (2011) investigated the effect of the structural features of xylans on the enzymatic hydrolysis. The hemicelluloses (4 mg) fractionated by graded ethanol precipitation from bamboo was incubated with *endo*-(1,4)-β-D-xylanase (10 U/ml) in 50 mM sodium acetate buffer pH 5 (1 ml) at 50 °C for 24 h. After inactivation of the enzyme (100 °C, 10 min) the XOS were subjected to HPAEC-PAD. The total yield of XOS (DP 1–6) was shown to range from 21.5% to 40.6% based on the original xylose (Table 4). Meanwhile, a difficult hydrolysis of the low substituted GAX by an endoxylanase was observed. It was concluded that the effect of enzyme-resistance on hydrolysis was mainly caused by the aggregation among molecules rather than the substitution of backbone in case of more linear xylans. In fact, the hemicelluloses might be protected from enzymatic attack due to reduced accessibility of xylanases to their backbone when they are aggregation. In addition to mineral acids, enzymes, and autohydrolysis, solid catalysts within the green chemistry community have shown a trend emerged for hemicelluloses conversion. The benefit of using solid catalysts is their easy separation, good catalytic activity, and high recyclability. Although there are only few reports of using solid catalysts for hydrolyzing hemicelluloses, Ogaki et al. (2009) presented a investigation for selective production of xylose and XOS from bamboo (*Phyllostachys pubescens*) by sulfonated allophone solid acid catalyst during the reaction at 130–160 °C. After the reaction at 150 °C for 6 h, peaks of XOS in HPLC chromatograms were almost disappeared, which suggested that XOS were thought to be completely decomposed to xylose or other compounds at more than 6 h.

Finally, xylitol, which is produced via catalytic hydrogenation or microbial conversion of xylose, is already on the market and has received great attention in the food industries due to its several beneficial features, such as anticaries, antiinflammatory, and sweetening properties (Mäki-Arvela, Salmi, Holmbom, Willför, & Murzin, 2011). Bamboos are viewed as ideal candidates for the production of xylitol because their hemicelluloses are mainly composed of arabinoglucuronoxylan. Miura et al. (2013) reported the microbial conversion of hemicelluloses hydrolysate prepared from *Phyllostachys pubescens* culm to xylitol by the yeast *Candida magnoliae* using two-phase aeration process. In this study, a hemicelluloses hydrolysate containing 19 g/l xylose was obtained from culm of bamboo by hydrolysis with 3% sulphuric acid with a liquor to solid ration of 10 ml/g at 121 °C for 1 h. After detoxification of the hydrolysate with activated char followed by neutralization with calcium carbonate, the resulting sugar solution was subjected to fermentation. The maximum xylitol production (10.5 g/l) and the maximum xylitol volumetric productivity (0.42 g/(l h)) were attained under agitation set at 400 min^{-1} and aeration rate of 0.67 vvm (Miura et al., 2013).

5. Conclusions and challenges

Over the last decades, considerable efforts have been devoted to developing research on hemicelluloses from bamboo. The main focus of those works was on extraction, compositional analysis, and structural characterization of bamboo hemicelluloses. Then, strategies of chemical modification and degradation were applied to widen the range of utilization of bamboo hemicelluloses. Such achievements could allow bamboo as a valuable feedstock to be ready for current biorefinery concept, which can open an efficient way to convert bamboo into high value-added products such as fuels, chemicals, and biomaterials. In some processes, available approaches or techniques including pretreatment, 2D-HSQC NMR, IL as media, and so on have been proposed. However, there are many obstacles and challenges to be overcome during the valorization of hemicelluloses, which are vital for bamboo or even for any biomass. To our knowledge, various obstacles and challenges are: (i) Breakthrough in the molecular theories and biological roles of

hemicelluloses in plant cell wall is required to provide directions for their subsequent fractionation prior to valorization. Moreover, it would be beneficial to carry out genetic modulation of plants and render biomass more amenable to processing; (ii) Valorization of hemicelluloses would eventually have to face practical difficulties involving the collection of raw materials. Some factors should be taken into account. For example, natural woods are not allowed to be cut down in China, while agricultural wastes are limited by the conditions of growth, climate, and harvest, etc. More importantly, the requirement of large amounts of agricultural wastes and long distance transportation undoubtedly increase the production cost due to their low mass density; (iii) A major challenge is the lack of competitiveness in cost for hemicelluloses based products contrast to petroleum based products. The primary reason for this is that several extraction, fractionation, and purification steps for hemicelluloses from bamboo or even any biomass are not yet developed on an industrial scale with more economical ways; (iv) Some improvements in the present technologies for the bulk conversion of hemicelluloses into higher value products could be achieved with new routes and (v) As a general rule, sustainable policies and economic subsidies by government can promote the valorization of hemicelluloses. Nevertheless, hemicelluloses are already available for commercial applications or are potential intermediates for several applications areas.

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