Immune effects of extractives on bamboo biomass self-plasticization

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Abstract: Bamboo is a fast-growing renewable bioresource. However, bamboo resources are wasted, and bamboo products release toxic gases. Bamboo biomass was therefore extracted and self-plasticized, and the immune effects of bamboo extractives were determined and investigated using nuclear magnetic resonance (NMR) and Fourier-transform infrared (FT-IR) spectroscopies, X-ray diffraction (XRD), and scanning electron microscopy (SEM). The results showed the following. (1) The ^{1}H-NMR signals at ~5.5, 4–8, 7.4–10.2, and 12.22–12.37 ppm were attributed to the chemical shifts of active protons on carbons adjacent to R–OH, RAr–OH, oximes, and –COOH, respectively. This showed that there were highly reactive hydrogen atoms in bamboo benzene/ethanol extractives. The ^{13}C-NMR spectrum gave further confirmation. (2) The extents of the effects of key process parameters were different: temperature > hot pressure > time. The optimal self-plasticizing conditions were temperature 170°C, hot pressure 9 MPa, time 40 min, and extraction of bamboo. (3) SEM, FT-IR, and XRD showed that contact and linkages among bamboo cells were significantly decreased by extractives, so the internal bond strengths of the self-plasticized samples were all higher after bamboo extraction. It was also found that the extractives created a significant barrier to bamboo self-plasticization as a result of their structure and chemical linkage reactions.

Keywords: Bamboo biomass, self-plasticize, bamboo extractives, immune, molecular barrier.

INTRODUCTION

Plasticization is the process by which heated plastics reach the flow state and obtain good plasticity. Plasticization is widely used, and a growing number of raw materials (including biomass materials) are being plasticized to maximize their utilization efficiency and improve their processing performances. In 1947, Haley reported a method of recording plasticizing waves. Ongil Gonzalez (1953) discussed the potential application of plasticized materials in human pathology and related fields. Milch (1968) plasticized the carbohydrate collagen. However, research enabled easy preparation of single plastic components, and the plastics industry developed rapidly, so research on carbohydrate plasticization was not pursued. Researchers worldwide have explored the plasticization mechanism and formation of plastics in depth (Mosén *et al*., 2006; Tsavalas *et al*., 2010). In response to increasing consumption of petroleum resources, scientists began research on plasticizing organic silicon compounds, mainly the self-plasticizing mechanism of silicon carbide (Czosnek *et al*., 2008; Barillet *et al*., 2010). Plasticization of biomass materials has becoming a hot topic in recent years (Gillgren *et al*., 2009).

There are two approaches to the plasticization of wood (including bamboo). In the first approach, based on the plastic properties of resins, the wood or bamboo is plasticized after immersion in resin. Wood shows good plasticization by immersion in resin because of its high porosity, but bamboo, which is dense, is poorly plasticized (Kaufman *et al*., 2010). In the second approach, a plastic and timber (or bamboo) are uniformly mixed, followed by a molding process such as extrusion and injection molding, to give a wood–plastic or bamboo–plastic composite material (Huang *et al*., 2010; 2012). However, the poor interfacial convergence of a bamboo–plastic composite material makes it unsuitable for industrial applications; also, the amount of added plastic is at least 30%, and the price of the plastic is two to five times those of wood or bamboo, resulting in a substantial increase in costs and a decrease in the added value of bamboo–plastic products (Seema *et al.,*1992; Han *et al.,* 2012). In order to improve the plasticization of bamboo and decrease the plasticization costs, it is therefore necessary to investigate self-plasticizing of bamboo cell walls.

Many studies have shown that cellulose can be converted into a new type of thermoplastic polymer material, which can be used alone or blended with other polymers to give specific hydrophobic materials by heat molding; the essence of this conversion is internal plasticization of the cellulose by grafting or chemical methods (Qussi *et al*., 2006; Huang *et al*., 2010). Hemicelluloses, which are the most unstable components of the wood cell wall, are easily destroyed during processing and use. However, hemicelluloses are difficult to separate from processing waste liquids, and plasticization of single hemicelluloses has still not been achieved (Wang *et al*., 1997; Scheller *et al*., 2010). Ethyl acrylate– maleic anhydride copolymer

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**Corresponding author*: e-mails: pengwanxi@163.com; mohkoshi@kpu.ac.jp latex, poly(vinyl chloride), and polystyrene resin have been used to plasticize woody lignin (Liu 2009). Using lignin sulfonate from sulfite pulping byproducts as the raw material, lignin with plasticizing properties was separated and purified (Sun *et al*., 2008; Moura *et al*., 2010). Our latest research showed that wood (or bamboo) extractives were a natural barrier to resisting invasion by foreign objects, and would perform two functions during the plasticization process: a barrier function and a bridging role (Peng *et al*., 2012). These studies examined the theoretical foundations of self-plasticizing of bamboo cell walls, and also investigated the plasticization of pure cellulose and lignin; however, there is still no research on cell wall self-binding. Bamboo biomass was therefore extracted and self-plasticized, and the small interferential characteristics of bamboo extractives were investigated using nuclear magnetic resonance (NMR) and Fourier-transform infrared (FT-IR) spectroscopies, X-ray diffraction (XRD), and scanning electron microscopy (SEM).

MATERIALS AND METHODS

Materials

Five-year-old *Phyllostachys heterocycla*, which was grown in Xiangtan city, Hunan province, China, was provided by the Hengdun Co., Ltd. (Hunan). The bamboo samples were dried to absolute dryness at 105°C. A 40–60 mesh powder was sieved out using an AS200 sieve (USA). Cotton bags and cotton thread were extracted with benzene/ethanol solution for 12 h. Ethanol, benzene, and acetic ether (chromatographic grade) were used for the subsequent experiments. The volume ratio of the benzene/ethanol solution was benzene:ethanol 1:2.

Analysis of bamboo extractives

Extractives preparation: Bamboo powder (50 g) was placed in a cotton bag and the bag was tied using cotton thread. Extractions were carried out using a large-caliber Soxhlet with 300 mL of benzene/ethanol solution. The extractions were performed at 85°C for 8 h. After

Table 1: Test results for self-plasticized bamboo samples

No.	Level of test factors			Extracted samples		Unextracted samples	
	Temperature/A [°C]	Hot pressure/B [MPa]	Time/C [min]	Density [g/cm^{-3}]	IB [MPa]	Density [g/cm^{-3}]	IB [MPa]
QX1	1 (170)	1 (11)	1 (10)	1.31	1.32	1.25	1.25
QX2	1	2	2	1.17	1.03	1.32	0.44
QX3	1	3	3	1.04	1.07	1.19	0.57
QX4	1	4	4	1.22	1.12	1.59	0.52
QX5	2 (160)	1	2 (40)	1.22	1.23	1.29	0.56
QX6	2	2 (7)	1	1.12	0.9	1.16	0.53
QX7	2	3	4	1.04	0.98	0.78	0.52
QX8	2	4	3	1.20	1.18	1.06	0.53
QX9	3 (150)	1	3 (20)	1.29	0.64	0.96	0.30
QX10	3	2	4	1.16	0.76	0.94	0.28
QX11	3	3 (5)	1	1.02	0.41	0.90	0.25
QX12	3	4	2	1.19	0.89	1.16	0.33
QX13	4 (140)	1	4 (30)	1.23	0.72	1.07	0.37
QX14	4	2	3	1.08	0.83	1.04	0.30
QX15	4	3	2	1.11	0.81	0.92	0.27
QX16	4	4 (9)	1	1.11	0.75	1.04	0.19

Table 2: Results of range analysis on self-plasticized bamboo samples

Factors	Unextracted bamboo						Extracted bamboo					
	IB [MPa]			Density [g/cm^{-3}]			IB [MPa]			Density [g/cm^{-3}]		
	A	B	C	A	B	C	A	B	C	A	B	C
$\overline{K_1}$	0.70	0.62	0.56	1.34	1.14	1.09	1.14	0.98	0.85	1.18	1.26	1.14
$\overline{K_2}$	0.54	0.39	0.40	1.07	1.12	1.17	1.07	0.88	0.99	1.15	1.13	1.17
$\overline{K_3}$	0.30	0.40	0.43	0.99	0.95	1.07	0.68	0.82	0.93	1.16	1.05	1.15
$\overline{K_4}$	0.28	0.39	0.42	1.02	1.21	1.10	0.78	0.99	0.90	1.13	1.18	1.16
R	0.42	0.23	0.16	0.35	0.26	0.11	0.46	0.17	0.15	0.05	0.21	0.03
Effect order	A > B > C			A > B > C			A > B > C			A > B > C		

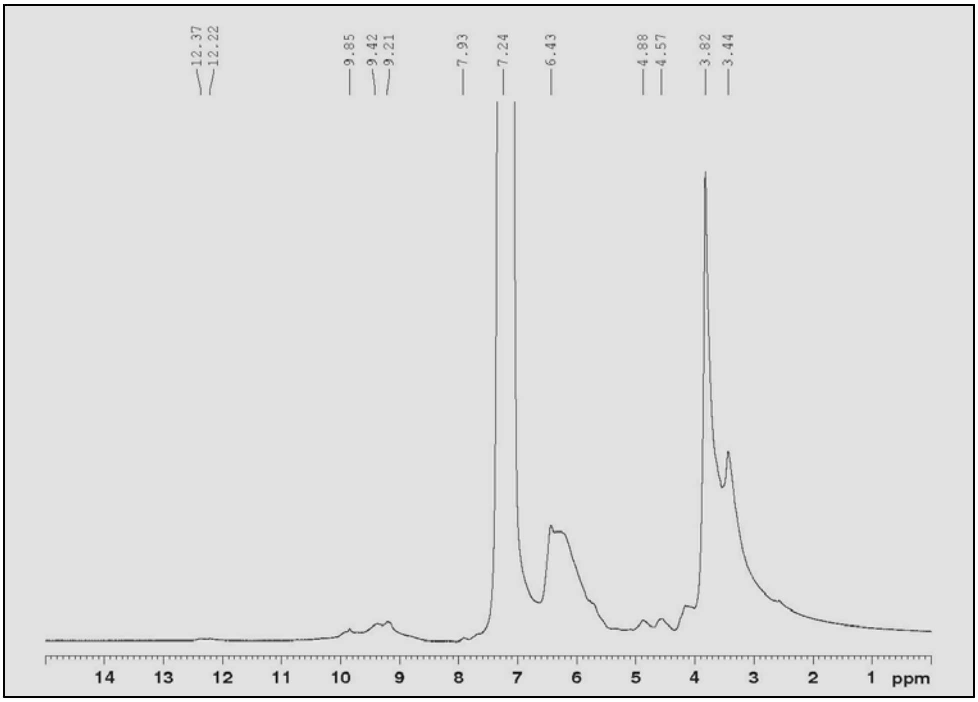

Fig. 1: ^{1}H-NMR spectrum of bamboo benzene/ethanol extractives.

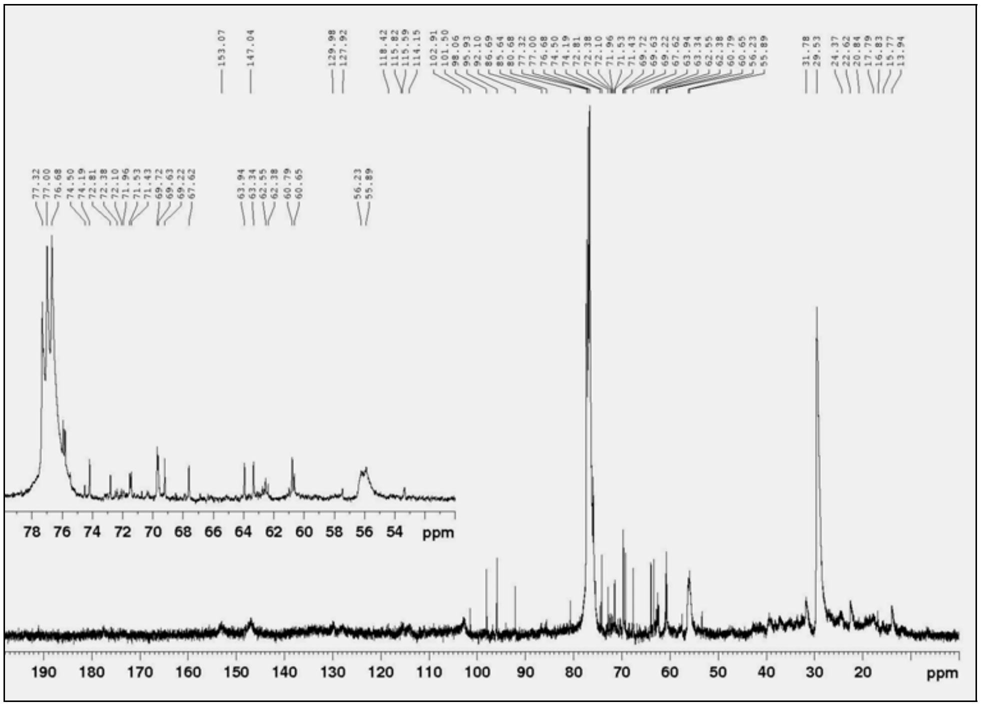

Fig. 2: ^{13}C-NMR spectrum of bamboo benzene/ethanol extractives

extraction, the bamboo benzene/ethanol extractives were obtained by evaporating the solvent very slowly at 45°C and 0.07 MPa.

^{1}H-NMR analysis: The ^{1}H-NMRspectra were recorded with a Bruker AV III NMR spectrometer at 400.13 M Hz using 5 mg of bamboo extractives dissolved in 0.5 mL of $CDCl_3$. The chemical shifts were calibrated relative to the signal from $CDCl_3$, used as an internal standard, at 7.24 ppm. The acquisition time was 3.9 s and the relaxation time was 1.0 s. The number of scans was 128.

^{13}C-NMR analysis: ^{13}C-NMR spectra were obtained using a Bruker spectrometer at 100.6 MHz. The sample (40 mg)

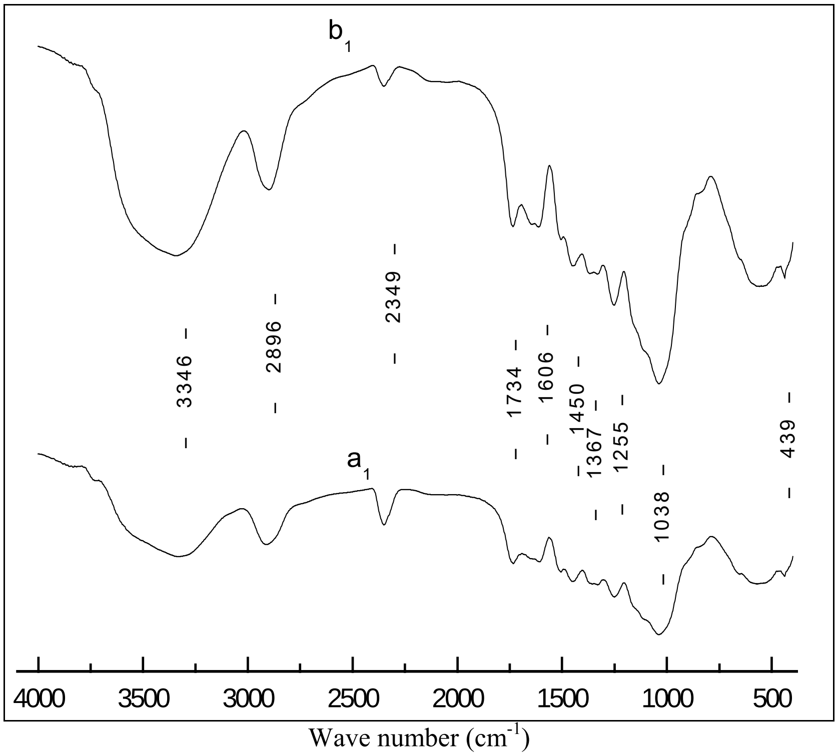

Fig. 3: FT-IR spectra of bamboo self-plasticized samples with maximum Ibs

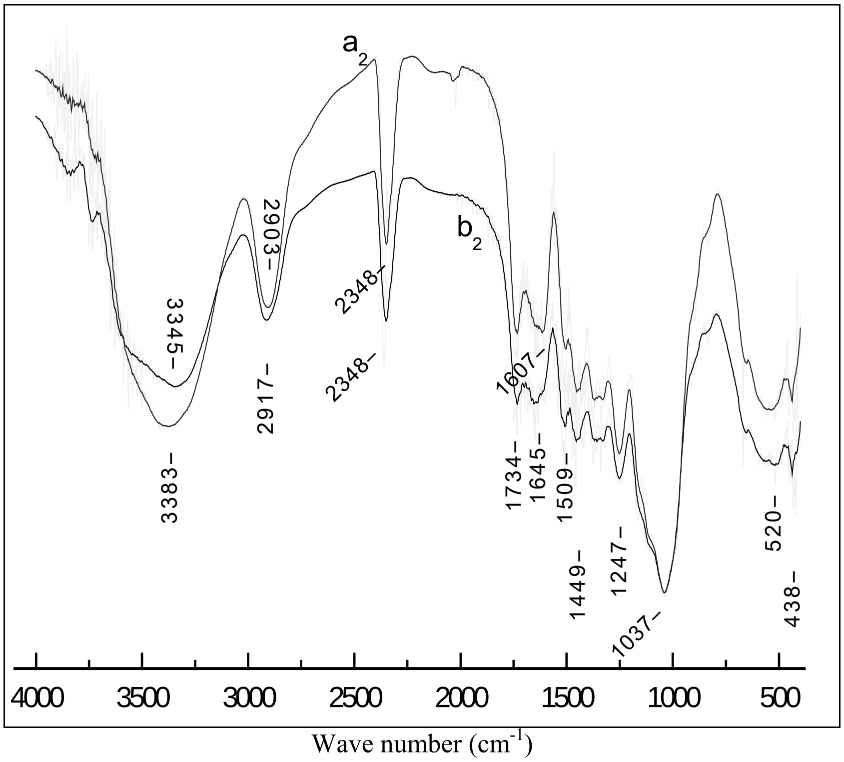

Fig. 4: FT-IR spectra of bamboo self-plasticized samples with minimum Ibs.

was dissolved in 1.0 mL of $CDCl_3$. The chemical shifts were calibrated relative to the signals from chloroform, used as an internal standard, at 77 ppm. The spectra were recorded at 25°C after 30 000 scans. A 30 pulse flipping angle, a 9.2 s pulse width, a 1.89 s delay time, and a 1.36 s acquisition time between scans were used. The number of scans was 15 000.

Bamboo self-plasticizing process

Bamboo powder extraction pretreatment: Bamboo powder (100 g) was placed in a cotton bag and the bag was tied with cotton thread. Extraction was carried out with a large-caliber Soxhlet using ethanol, acetic ether, and benzene/ethanol, in different orders, at 85°C. The times for ethanol extraction, acetic ether extraction, and benzene/ethanol extraction were 8 h, 8 h, and 6h, respectively. After extraction, the samples were baked to absolute dryness at 55°C and 0.01 MPa.

Bamboo self-plasticizing: Treated or untreated bamboo powder was weighed and placed in a mold. According to the orthogonal table L16(4^3), the bamboo biomass was self-plasticized using an HX100 pressing machine (Wuhan Huazhong Science and Technology Hot Processing Engineering Research Institute). The experimental factors and levels are listed in table 1. The number of parallel samples in each test was two.

Analysis of self-plasticized bamboo samples

FT-IR analysis: FT-IR spectra were obtained with an FT-IR spectrometer (Tensor 27) using a KBr disk containing 1% of finely ground sample. Thirty-two scans were taken of each sample, recorded from 400 to 4000 cm^{-1} at a resolution of 2 cm^{-1} in transmission mode.

XRD analysis: After sample preparation, the samples were examined using an XD-2 diffractometer (General Analysis of Beijing General Instrument Co., Ltd.). The X-ray tube was Cu (λ 1.5406 nm), the voltage was 36 kV, and the current was 20 mA. The range 2θ–θ was scanned continuously with a linkage scanning system, rotary half-cone angle 2θ, from 5°to 42°, at a scanning velocity of 2°/min, with a scan step angle of 0.01°. A graphite crystal monochromator was used, slit device DS = 1°, SS = 1°, RS = 0.3 mm. The cellulose crystallinity was calculated as follows:

$$Cr = (I_{002} - I_{am})/I_{002} \times 100\% \qquad (1)$$

where Cr is the relative crystallinity, I_{002} is the intensity of the peak at 002 in the crystal region, and I_{am} is the diffracted intensity of the peak at 2θ = 18° in the amorphous region.

SEM observations: The sample surfaces were coated in a vacuum evaporator with a thin film of Au and observed using an SM6490LV microscope.

RESULTS

Based on the above test method, the internal bond strengths (IB) and densities of self-plasticized bamboo samples were measured. The test results are shown in table 1. The results of range analysis are listed in table 2.

To obtain further information on bonds to hydrogen atoms in the bamboo extractives, ^1H-NMR spectroscopy was performed. Fig. 1 shows the ^1H-NMR spectrum of the benzene/ethanol extractives of bamboo. Fig. 2 shows the ^{13}C-NMR spectrum of bamboo benzene/ethanol extractives.

FT-IR spectra of self-plasticized bamboo samples QX1, QX11, and QX16, chosen on the basis of their IBs, were obtained, and are shown in figs. 3 and 4.

Crystallinity is an important index and indicates the degree of crystallization of high polymers in biomass. The XRD patterns of some self-plasticized samples were obtained, and are shown in figs. 5 and 6.

In order to observe the combination interface of self-plasticized bamboo samples, SEM images of their linkage surface were obtained, and are shown in Figures 7–10. And the self-plasticized samples with the maximum IBs were used for cracking tests, and SEM images of their fracture surfaces are shown in figs. 11 and 12.

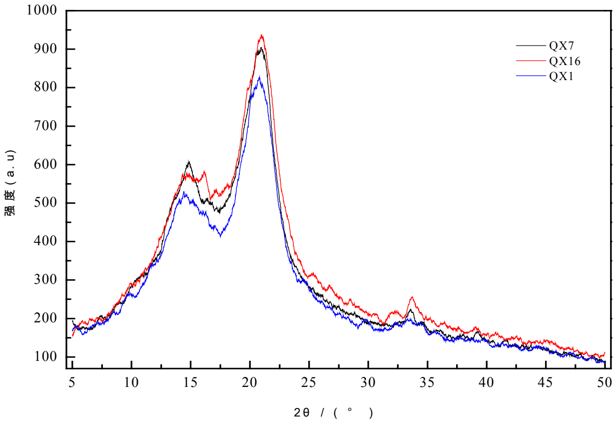

Fig. 5: XRD patterns of self-plasticized unextracted bamboo samples.

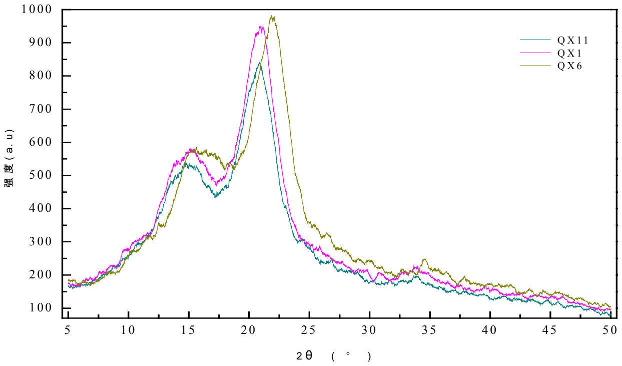

Fig. 6: XRD patterns of self-plasticized extracted bamboo samples.

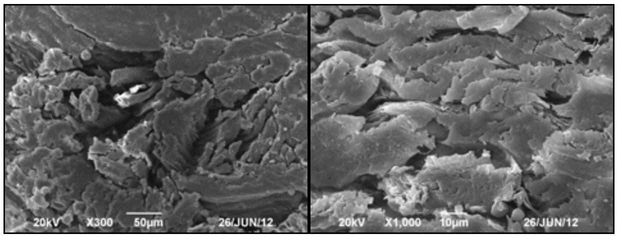

Fig. 7: SEM images of linkage surface of unextracted bamboo sample QX1.

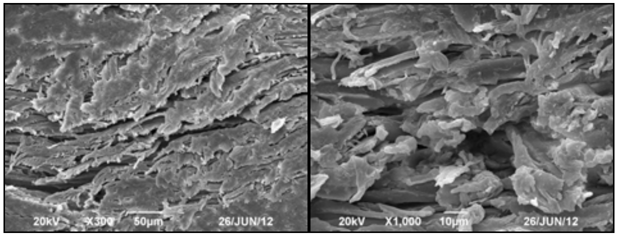

Fig. 8: SEM images of linkage surface of unextracted bamboo sample QX11.

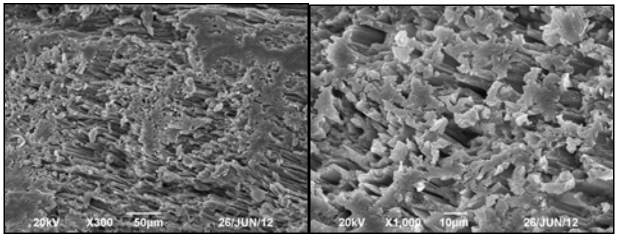

Fig. 9: SEM images of linkage surface of extracted bamboo sample QX1.

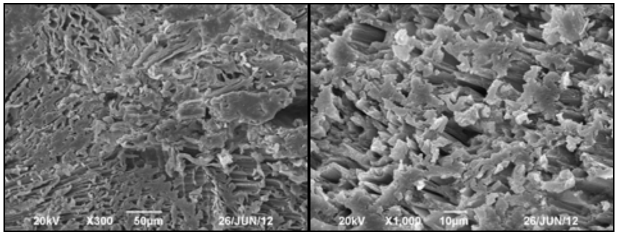

Fig. 10: SEM images of linkage surface of extracted bamboo sample QX16.

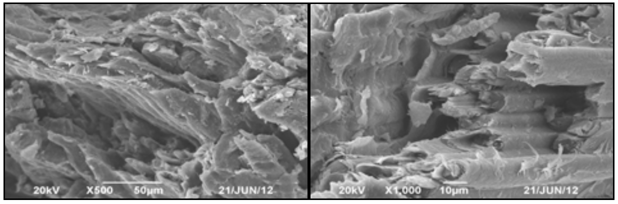

Fig. 11: SEM images of fracture surface of extracted bamboo sample QX1.

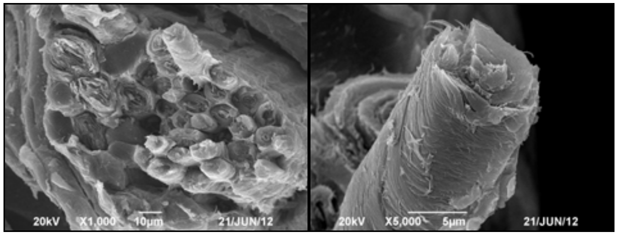

Fig. 12: SEM images of fracture surface of unextracted bamboo sample QX1.

ANALYSIS

^{1}H-NMR analysis

As can be seen from fig. 1, the bamboo benzene/ethanol extractives contained many active hydrogen atoms. Protons on carbons adjacent to alcohols (CHOH) or ether (CH–O–C) occurred at 3.4–4.5 ppm. The protons on carbons adjacent to alkene groups exhibited peaks at 5.1–5.5 ppm. The signal at about 4.17–9.99 ppm represented the chemical shifts for protons on carbons adjacent to pyridine and its derivatives. The spectrum had a peak at 7.24 ppm from residual chloroform present in CDCl$_3$. The peaks at ~5.5, 4–8, 7.4–10.2, and 12.22–12.37 ppm represent the chemical shifts for active protons on carbons adjacent to R–OH, RAr–OH, oximes, and carboxylic acids (–COOH), respectively. The spectrum shows that there were highly reactive hydrogen atoms in the bamboo benzene/ethanol extractives.

^{13}C-NMR analysis

The peaks at 110–160 ppm represent carbon atoms from unsaturated compounds such as alkenes or coextracted phenolic compounds. The peaks at 140.7–147.5, 130.0–134.5, and 120.3–129.7 ppm are unsaturated carbon double bonds (–CH=CH–) in heteroaryl rings, alkenes, fatty acids, and fatty acid esters. The peaks at 114.2–118.9 ppm represent C-3/C-5 and C-β of coextracted phenolic substances; the strongest peaks are at 152.9–155.5 ppm. The characteristic signals observed in the spectra were the strong resonances (147, 129, 127 ppm) from C-α and C-1 of coextracted phenolic compounds. The peaks at 103.0–109.1 ppm are from substituted alkenes. All the signals at 50.0 to 87.0 ppm are assigned to C=C in a single bond of alkynes. All the signals at 0.0 to 50.0 ppm are attributed to carbon atoms in single bonds in alkanes. The spectrum further confirmed that there were many active ingredients in the bamboo benzene/ethanol extractives.

Analysis of physical and mechanical properties of self-plasticized bamboo samples

Effect of temperature on bamboo self-plasticization

The data in table 2 show that the temperature significantly affected the densities and IBs of the self-plasticized bamboo samples. The density and IB of a self-plasticized bamboo sample gradually increased with increasing temperature. The IBs of the self-plasticized samples reached maximum values of 1.14 MPa (extracted bamboo) and 0.70 MPa (unextracted bamboo) at 170°C. The densities of the self-plasticized samples reached maximum values of 1.18 g/cm^3 (extracted bamboo) and 1.34 g/cm^3 (unextracted bamboo) at 170 °C. Bamboo biomass is mainly composed of cellulose, hemicelluloses, and lignin, which are all thermoplastic. When the temperature was increased, the bamboo cell walls began to soften gradually, producing flow deformation as a result of the plasticities of the cellulose, hemicelluloses, and lignin, leading to close contacts among the bamboo cell walls. This caused increases in the densities and IBs of the self-plasticized samples. The best temperature for the process was 170°C.

Effect of hot pressing on bamboo self-plasticization

The data in table 2 show that hot pressing of self-plasticized samples clearly affected the densities and IBs of the self-plasticized bamboo samples. With increasing hot pressure, the IBs of the extracted bamboo and the densities of the unextracted bamboo self-plasticized samples first increased and then decreased; however, the IB of the unextracted bamboo and the density of the extracted bamboo self-plasticized samples gradually increased. When the hot pressure was 9 MPa, the IB of the self-plasticized samples reached a maximum of 0.99 MPa after bamboo extraction. When the hot pressure was 11 MPa, the IB of the self-plasticized samples reached a maximum of 0.62 MPa if the bamboo was not extracted. The standard IB of wood-based panels should be not less than 0.70 MPa. So, bamboo biomass should be extracted before self-plasticization. The best hot pressure for the process was 9 MPa.

Effect of time on bamboo self-plasticization

The data in table 2 show that the effect of time on the densities and IBs of self-plasticized bamboo samples was less obvious than those of temperature and hot pressing. With increasing time, the IBs of self-plasticized samples of extracted bamboo gradually increased, but the IBs of self-plasticized samples of unextracted bamboo gradually decreased, and the densities of the self-plasticized bamboo samples gradually increased. When the time was 40 min, the IB of the self-plasticized samples reached a maximum of 0.99 MPa for extracted bamboo samples. When the time was 10 min, the IB of the self-plasticized samples reached a maximum of 0.56 MPa for unextracted bamboo samples. The standard IB of wood-based panels should be not less than 0.70 MPa. So, bamboo biomass should be extracted before self-plasticization. The best time for the process was 40 min.

The data in table 1 show that the IBs of self-plasticized samples of extracted bamboo were all greater than those of unextracted bamboo, and the IBs of self-plasticized samples were less than 0.7 MPa, except for the unextracted self-plasticized bamboo sample QX1. The data in table 2 indicate that under self-plasticizing conditions of 140–170 °C, 5–11 MPa, and 10–40 min, the IBs of nearly all the self-plasticized samples of extracted bamboo were greater than 0.7 MPa, except one sample, which had a value of 0.68 MPa; however, the IBs of nearly all the self-plasticized samples of unextracted bamboo were less than 0.70 MPa, except one sample, which had a value of 0.70 MPa. The densities of the self-plasticized samples of extracted bamboo were not very different from those of unextracted bamboo. The above results show that the extractives interfered with bamboo biomass self-plasticization. Further work was needed to clarify the role of the bamboo extractives.

FT-IR Analysis of Bamboo Self-plasticized Samples

Fig. 3 shows the FT-IR spectra of the self-plasticized samples with the maximum IBs; a_1 is the extracted bamboo self-plasticized sample QX1, and b_1 is the unextracted bamboo self-plasticized sample QX11. Fig. 4 shows the FT-IR spectra of the self-plasticized samples with the minimum IBs; a_2 is the extracted bamboo self-plasticized sample QX1, and b_2 is the unextracted bamboo self-plasticized sample QX16. The FT-IR spectra in figs. 3 and 4 show peaks at 3375–3340, 2920, 1740, 1244, and 1110 cm^{-1}, which are the stretching vibrations of –OH, $-CH_2-$, C=O of carbonyl or carboxyl groups, C–O–C of alcohols and phenols, and C–O, respectively. The two sharp bands at 1328 cm^{-1} represent the methyl bending vibration. The peak at 1104 cm^{-1} is Ar–OH and C–O of secondary alcohol stretching vibrations. The three sharp bands at 1600, 1500, and 1425 cm^{-1} are the characteristic peaks of lignin.

There were many differences among the FT-IR spectra of the self-plasticized samples. Fig. 3 shows that the main characteristic peaks all appeared, and the absorbances of the peaks from self-plasticized unextracted bamboo samples were more intense than those of the self-plasticized extracted bamboo samples. Fig. 4 shows that there were small changes in the main characteristic peaks, and the intensity of the absorbance of the –OH peak decreased, but the intensities of the others increased, when the bamboo was extracted and then self-plasticized. This indicates thermal degradation of the cellulose, hemicelluloses, and lignin in the bamboo biomass at high temperature and pressure to produce many active groups, and then more stable bonds were formed by a bridging effect, to give the bamboo cells bonding strength. The bamboo extractives contained a number of active compounds such as 2,3-butanediol, and sixteen acids, such as linoleic acid, oleic acid, and γ-sitosterol (Zhang *et al.*, 2013). Furthermore, the compounds were rich in highly active hydrogen bonds, carbonyls, carboxyls, and others, and these easily reacted with the main ingredients of bamboo, producing chain reactions among bamboo cells. The bamboo cells were therefore bonded more fully during self-plasticization after extraction.

XRD analysis of bamboo self-plasticized samples

Fig. 5 shows the XRD patterns of self-plasticized unextracted bamboo samples QX1, QX7, and QX16; their IBs gradually decreased. Figure 6 shows the XRD patterns of self-plasticized extracted bamboo samples QX1, QX6 and QX11; their IBs also gradually decreased.

The crystallinities were calculated based on the XRD patterns in Figures 5 and 6. When the bamboo was unextracted, the crystallinities of self-plasticized samples QX1, QX7, and QX16 were 74.15%, 68.77%, and 63.42%, respectively. When the bamboo was extracted, the crystallinities of the self-plasticized samples QX1, QX6, and QX11 were 90.91%, 88.46%, and 73.45%, respectively. This demonstrated that the crystallinities of self-plasticized samples increased as the IB increased. The crystallinities of the self-plasticized samples of extracted bamboo were higher than those of unextracted bamboo, and increased by 16.76%, 19.69%, and 10.02%, respectively. The results of variance analysis showed that the extraction pretreatment significantly influenced the crystallinity of self-plasticized bamboo at the level of 0.1 ($F_{0.05} = 7.7 > F = 6.1 > F_{0.1} = 4.54$). Bamboo extractives are deposited in cell cavities, pits of cell walls, and cell gaps, as well as in the amorphous regions of cellulose. Alcohols, phenols, aldehydes, ketones, acids, and other active components in bamboo extractives could be involved in dehydration, etherification, and esterification reactions with –OH and –COOH in the amorphous regions in cellulose, preventing further crystallization of cellulose. İt was concluded that the extractives could block greater crystallization of cellulose or produce chain reactions among celluloses during bamboo self-plasticization.

SEM analysis of bamboo self-plasticized samples

The bamboo cell wall consists mainly of cellulose, hemicelluloses, and lignin, which are all macromolecular compounds. Also, the cells have hollow structures. Bamboo cell walls deform under extreme pressure, and the forms and volumes of cellulose, hemicelluloses, and lignin are also changed; in addition, their plasticities and mobilities increase under high temperatures and pressures. The spaces between cellulose, hemicelluloses, and lignin therefore became small enough to produce chain reactions to give linking strength. Extractives could also affect bamboo self-plasticization. The extractives in the luminal and pit cavity surface were dissolved out after extraction, increasing the probability of contact among cellulose, hemicelluloses, and lignin. Figures 7–10 show that the bonding interfaces of self-plasticized samples of extracted bamboo became uniformly fine and had complete structures, cells were closely combined, and the volumes and numbers of cell gaps decreased significantly. The bonding interfaces of the self-plasticized extracted bamboo samples were therefore better than those of the unextracted samples. Comparisons of figs. 7 and 8, and figs. 9 and 10 show that when the IBs of the self-plasticized samples increased, their inner structures became denser and more uniform, and stress concentration phenomena could also be reduced or even eliminated. Of course, the self-plasticized samples were cracked and fractured. Fig. 11 shows that there was no cavitation in the self-plasticized extracted sample; the bamboo fibers were first stretched and then fractured, and pulled out a short. The fracture was a ductile fracture. This showed that the bamboo fibers were sufficiently self-plasticized for them to bond and integrate. Fig. 12 shows that there were prominent self-plasticized fibers on the fracture surface of unextracted bamboo sample QX1. This indicated that the self-plasticized bamboo cell walls did not combine tightly, as a result of structural barriers formed by the extractives. So, the extractives in the luminal and pit cavity surfaces prevented the bamboo cell walls from forming tight bonds among cellulose, hemicelluloses, and lignin.

CONCLUSION

In the ^{1}H-NMR spectra, the peaks at ~5.5, 4–8, 7.4–10.2, and 12.22–12.37 ppm represented the chemical shifts for active protons on carbons adjacent to R–OH, RAr–OH, oximes, and carboxylic acids (–COOH), respectively, showing that highly reactive hydrogen atoms were present in bamboo benzene/ethanol extractives. The ^{13}C-NMR spectra confirmed that there were highly reactive compounds such as phenolic compounds, fatty acids, alkenes, alkynes, and alkanes in the bamboo benzene/ethanol extractives. It was therefore deduced that the bamboo extractives contained many highly active chemical groups.

The effects of temperature and hot pressing on the densities and IBs of self-plasticized bamboo samples were clear. Extraction pretreatment significantly influenced bamboo self-plasticization, at the 0.1 level. More importantly, the IBs of self-plasticized extracted bamboo samples were all greater than those of unextracted bamboo samples; however, the densities of the self-plasticized extracted bamboo samples were not very different from those of the unextracted bamboo samples. These results show that the extractives interfered with bamboo biomass self-plasticization. The optimal self-plasticizing parameters were temperature 170°C, hot pressure 9 MPa, time 40 min, and extraction of bamboo.

The extractives, which were attached to the surfaces of the cell lumen, pit cavities, and cell gaps, not only prevented bamboo cells from touching each other, but also hindered bonding among cellulose, hemicelluloses, and lignin. SEM, FT-IR, and XRD analyses further confirmed that contact and linkages among bamboo cells increased significantly in self-plasticization if the extractives were dissolved out. As a result, the extractives formed a significant barrier to bamboo self-plasticization in terms of structure and chemical linkage reactions.

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