DYNAMIC MECHANICAL THERMAL ANALYSIS OF MOSO BAMBOO *(Phyllostachys heterocycla)* AT DIFFERENT MOISTURE CONTENT

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Bamboo is a type of biomass materials that has great potential as a bio-energy resource in China. The thermal-mechanical behavior of bamboo plays an important role in the formation process of pellets. To investigate the effect of moisture content (MC) on thermal-mechanical behavior of bamboo, the storage modulus and loss factor of moso bamboo was determined using dynamic mechanical thermal analysis (DMTA) from -50 to 150 ^{o}C. The experimental results showed that the general feature of bamboo thermal-mechanical properties with temperature is similar to other cellulosic materials, and they are affected by MC. A substantial decrease of storage modulus over the entire temperature range implies that bamboo underwent a glass to rubber transition. Bamboo, at lower MC, has a higher storage modulus, which decreases the mechanical strength of pellets. The loss factor exhibited two major transitions for all samples. There was an α-transition (α_1), attributed to glass transition of lignin, peaking in a higher temperature range. The second major relaxation (α_2), located in a lower temperature range, was attributed to glass transition of hemicelluloses. Activating lignin and hemicelluloses using moisture and temperature in the temperature range of glass transition can be very helpful to achieve durable particle-particle bonding.

Keywords: Biomass; Bamboo; Bamboo pellet; Thermal-mechanical behavior; Glass transition

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INTRODUCTION

Biomass is a main type of carbon-based sustainable energy and is also a potential source of alternative energy that can substitute for fossil fuel in the future. The wide variety of biomass enables it to be utilized by most people around the world (Faizal et al. 2010). Biomass pellets and briquettes are the main types of solid fuel, and they have been widely used for home heating in many countries. Densification into pellets can reduce biomass wastage and improve ease of transportation and storage (Adapa et al. 2006). In recent years, information has become available for pellets derived from various sources such as tea waste (Ayhan 1999), waste paper and wheat straw mixtures (Demirba 1999), agricultural residues (Pallav et al. 2006), forest residues (Pallav et al. 2006), spruce wood sawdust (Ayhan and Ayse 2004), and corn stover (Sudhagar et al. 2006).

Bamboo, like wood, is mainly composed of hemicelluloses, cellulose, and lignin. It has been widely cultivated in the west and south of China. Currently the bamboo resource is very abundant, and the total area of bamboo is about five million hectares.

That of moso bamboo (*Phyllostachys heterocycla*) is about three million hectares in China, and its annual yield is about eighteen million tons (Jiang 2002), which implies that it has great potential as a bio-energy resource of the future in China. In previous research, bamboo pellets were successfully manufactured using a pellet mill in the lab, and the results showed that all properties of the bamboo pellets met the requirement of the Pellets Fuel Institute Standard Specification for Residential/Commercial Densified, and the gross calorific value of bamboo pellets (>18400 J/g) can met the minimum requirement for making commercial pellets of DIN 51731 (>17500J/g) (Faizal et al. 2009). The ash content of bamboo pellets is less than 1.5 %. Bamboo pellets are proposed as a new type of biomass solid fuel that has potential to be development as commercial pellets in China.

The thermal-mechanical behavior of bamboo plays an important role in the formation process of pellets. It affects the mechanical property of bamboo pellets, which is an important factor connected with handling and transporting of pellets. DMTA is a type of thermoanalytical technique, widely used to study thermal-mechanical properties of polymers. Jiang and Lu (2009) studied the dynamic viscoelastic properties of Chinese fir, treated using a high-temperature drying (HTD) method at 115 ^{o}C, a low-temperature drying (LTD) method at 65 ^{o}C, and freeze vacuum drying (FVD), respectively. It was found that the storage modulus (E′) and loss modulus (E″) were the highest for HTD wood and the lowest for FVD wood. Three relaxation processes in HTD and LTD wood are attributed to the micro-Brownian motion of cell wall polymers in the non-crystalline region. Yang et al. (2009) studied thermal and viscoelastic properties of composites with different filler by DMTA. The glass transition and melting temperature did not significantly vary with the filler content, because no chemical bonding occurred at the interface between matrix and filler. Sanchez-Cabezudo et al. (2010) analyzed mechanical properties of poly vinyl acetate (PVAc)/epoxy thermasets as a function of the PVAc content through DMTA. It was found that the storage modulus-temperature curves highly depended on the morphology of samples. The glass transition temperature of PVAc and of epoxy phase in the blends was different from those of the neat polymers. Stelte et al. (2011) investigated thermal transition of the amorphous polymers in wheat straw using DMTA; the key transitions attributable to softening of lignin were found at 53 ^{o}C, 63 ^{o}C, and 91 ^{o}C for moist samples of wheat straw, extracted straw, and spruce, respectively.

Although the previous studies have been very useful and helpful in understanding the thermo-mechanical properties of cellulosic materials, bamboo is a different type of biomass material, and there is a lack of information about thermal-mechanical properties of bamboo materials. In this research, the thermal-mechanical behavior of moso bamboo was therefore investigated using DMTA from -50 to 150 ^{o}C. The study included outside, middle side, and inside of bamboo (OB, MB, and IB) with different moisture content (about 8 % and 14 %). The chemical compositions and structure of OB, MB and IB are different for bamboo material, which affects the properties of bamboo pellets. For example, it is widely known that there is a waxy or silicious layer on the bamboo surface (OB), which results in the poor bonding strength of bamboo composites or pellets. The storage modulus (*E'*) and loss factor (tanδ) were determined to evaluate the thermal-mechanical behavior of bamboo. The aim of this research was to help to design manufacturing process of bamboo pellets and to understand the effect of moisture content on bamboo pellet properties.

MATERIALS AND METHODS

Material

Moso bamboo was used in this study. The initial moisture content of samples was about 6.13%. Bamboo materials were cut off as rectangles with a sample size 17.5±0.2 mm (longitudinal) by 2.2±0.1 mm (radial) by 7.2±0.1 mm (tangential). All samples were dried using a drying oven under rigidly controlled conditions of temperature (105 °C) for 8 h. Then they were removed from drying oven and placed into a desiccator to cool them to room temperature. The next, they were weighed using a precision digital balance (0.0001 resolution). They were returned to the drying oven at 105 °C for 2 h and were cooled and weighed. When mass variance of all samples was less than 0.2 %, the final mass (m_1) was recorded. Samples (two samples of OB, MB and IB, respectively) were placed into the conditioning room with temperature 27 °C and humidity 65% to equilibrate their moisture content to about 8 % or temperature 27 °C and humidity 90% to equilibrate their moisture content to about 14%, respectively. After 14 days, the mass (m_2) was weighed using a precision digital balance, and the moisture content was calculated based on mass change. The information about the samples is shown in Table 1.

Table 1. The Information Moisture Content of Samples

Bamboo part	Sample number	m_1 (g)	m_2 (g)	Moisture content (%)
OB	2	0.6010	0.6503	8.20±0.07
	2	0.3853	0.4172	14.21±0.004
MB	2	0.3440	0.3724	8.40±0.09
	2	0.6321	0.7218	13.53±0.06
IB	2	0.3652	0.4144	8.25±0.10
	2	0.3471	0.3947	13.74±0.05

Test Thermal-mechanical Properties of Moso Bamboo

The thermal-mechanical properties of moso bamboo with different moisture content were tested by means of DMTA instrument (Q800, TA-instruments, New Castle, DE, USA) using a single cantilever grip. The viscoelastic region (strain directly proportional to stress) was determined by performing a strain sweep. Specimens were measured in their exact dimensions, immediately fixed in the grip and cooled to -50 ℃ using liquid nitrogen. Measurements were conducted between -50 ℃ and 150 ℃ with heating rate 5 ℃/min, an amplitude of 5 μm and a frequency of 1 Hz. The storage modulus (E') and loss factor ($\tan\delta$) were used to determine the thermal-mechanical properties of moso bamboo. A minimum of two samples were tested, and data from the first run was used when it was shown to be in accordance with the second run. The average value was not calculated, since small differences in the moisture content occurred that could have affected the transition temperature.

RESULTS AND DISCUSSION

Storage Modulus

Figure 1 shows the storage modulus of moso bamboo with different moisture contents. The general feature of storage modulus variation with temperature was similar to those observed in a previous study of wood materials (Obataya et al. 2003). The substantial decrease of storage modulus over the entire temperature range implied that bamboo materials underwent a glass to rubber transition. The storage modulus decrease was due to the fact that the kinetic energy of material molecules is very low in this temperature range, with motion occurring only in some small units such as side-chains and branched-chains (Jiang and Lu 2009). The substantial decrease of storage modulus could be attributed to crystallization or ordering of the molecules. For OB and MB, the storage modulus gradually increased after 100 ^{o}C. The probable reason is that the moisture content of samples decreases with temperature increase. The test condition is an open system in this research and water starts to evaporate from the samples when they are heated up to 100 ^{o}C. Over the entire temperature range, the bamboo with a lower moisture content had a higher storage modulus. Kelley et al. (2005) also found the glassy modulus to decrease with water content increase. The trend was the most obvious for OB in this research. In general, water is only introduced into the amorphous region of the cell wall for biomass materials, such as wood and bamboo. Because the amorphous region was viscoelastic and its storage modulus is much lower than that of the crystalline region of the cellulose microfibrils, the swelling of bamboo usually involves a reduction of storage modulus, unless a crosslinked structure is formed (Obataya et al. 2003).

Loss factor (tanδ) measurements provided particle information on the glass transition, while storage modulus determined their relevant stiffness (Kim et al. 2005). The maximum and minimum of storage modulus for OB, MB and IB with different moisture content are shown in Table 2. The storage modulus of OB, MB, and IB indicated that the stiffness of OB was the greatest. The storage modulus of bamboo with different moisture contents also indicated that bamboo materials having lower moisture content had a greater stiffness. This confirmed the expected role of water as having a plasticizing effect on the bamboo materials. The stiffness of bamboo particles plays an important role in pellet formation. When bamboo particles are compressed to pellets during the densification process, they undergo elastic deformation and creep. After pellets are formed, some bamboo particles undergo elastic deformation and elastic recovery. The greater is the stiffness of bamboo particles, the bigger the elastic deformation and elastic recovery, which results in easier destruction of the natural binding between bamboo particles. So the mechanical strength of bamboo pellets will be affected by its stiffness.

In preliminary work, the mechanical properties, including durability and fines content, was compared with bamboo pellets manufactured using different moisture content of bamboo particles. Pellet durability increased with increases in moisture content of particle, and the values were 95.07%, 97.95%, and 98.38% at 8%, 12% and 16% levels, respectively. For pellet fines, however, the lowest value (0.27%) was observed at the 16% MC level, the next (0.41 %) was 8%, and the last (0.54 %) was 12 %. This confirmed that bamboo pellets, manufactured using a higher moisture content, achieved a greater mechanical strength. This probably resulted from the lower storage modulus of bamboo particles with a higher moisture content. The results from this research also confirmed that the bamboo pellets manufactured using OB probably had the lowest mechanical strength, because its storage modulus was the greatest compared with MB and IB.

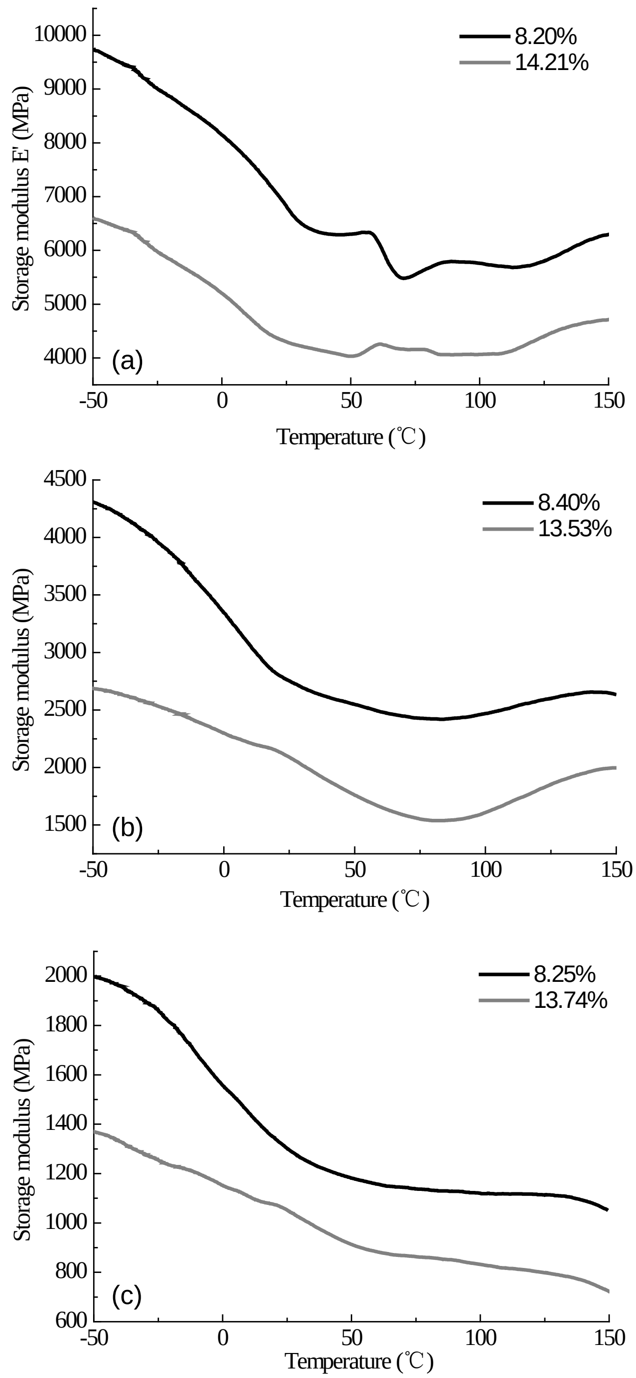

Fig. 1. Storage modulus of moso bamboo with different moisture content: (a) OB, (b) MB, (c) IB

Table 2. Storage Modulus of Moso Bamboo with Different Moisture Content

Bamboo part	MC (%)	Storage modulus (MPa)	
		Minimum	Maximum
OB	8.20	5485	9731
	14.21	4031	6589
MB	8.40	2422	4308
	13.53	1540	2687
IB	8.25	1055	1997
	13.74	727	1369

Loss Factor

Figure 2 shows the loss factor (tanδ) of moso bamboo with different moisture contents. The loss factor (tanδ) showed two major transitions for OB, MB, and IB. The glass transition temperatures of OB, MB and IB with different moisture content are shown in Table 3. There was an α-transition (α_1) peaking at about 65 ^{o}C (OB), 83 ^{o}C (MB), and 75 ^{o}C (IB), respectively. The transition was mostly linked to the glass-rubber transition of lignin. Lignin has a glass transition in the temperature range of 60 ^{o}C to 200 ^{o}C, depending upon the moisture content and measuring technology (Salmen 1984, 1990). Olsson and Salmen (1997) showed that the α_1 transition of moist wood usually occurs between 60 ^{o}C and 95 ^{o}C, due to the glass-rubber transition of lignin. The second major relaxation (α_2) of OB with 8.20% and 14.21% moisture content occurred at 30 ^{o}C and 25 ^{o}C, respectively. For the MB, the α_2 transition temperature was at about 12 ^{o}C and 16 ^{o}C due to different moisture content. That of IB was respectively at about 10 ^{o}C and 18 ^{o}C. This transition was attributed to the glass-rubber transition of hemicelluloses. Hemicelluloses had a glass transition of between -23 ^{o}C and 200 ^{o}C, depending upon the moisture content (Kelley et al. 1987). The results showed that the α_1 and α_2 transition temperatures of OB, MB, and IB were different. The main reason was probably that the chemical compositions and the content of lignin and hemicelluloses were different for OB, MB, and IB. Jiang et al. (2006) found that the contents of hemicelluloses (21.74 %) on the surface of bamboo (OB) were obviously lower than that of lignin (27.24 %), and the hemicelluloses content (21.74 %) in the outer layer (OB) of bamboo was lower than that (24.05 % and 24.29 %) in the inner layer (MB or IB). The experimental results also indicated the effect of water on the loss factor (tanδ). For MB and IB, the α_2 transition temperature increased with increase in moisture content of bamboo. The swelling of bamboo, after absorbing water, usually resulted in an increase of loss factor (tanδ) (Obataya et al. 2003). But for OB, a reversal of the trend occurred, wherein the α_2 transition temperature decreased with increase in moisture content of bamboo. It is possible that natural wax could be responsible for this phenomenon. It has been widely known that there is a waxy layer on the surface of bamboo, as in the case of straw. Stelte et al. (2011) found that the high wax content in wheat straw resulted in a transition at about 40 ^{o}C which was absent in solvent extracted wheat straw samples and spruce. The α_2 transition of wax likely overlapped with the higher temperature of hemicelluloses. Wax is a hydrophobic substance and its glass-rubber transition is unlikely to be affected by the moisture content of bamboo. Therefore it was very possible that the wax transition in the bamboo was partly covered under the intense transition of hemicelluloses (Stelte et al. 2011). The softening and the subsequent flow of the waxes at lower temperature was problematic, since it had been shown to inhibit adhesion between straw particles in fuel pellet production, resulting in the formation of weak boundary layers that were responsible for the low compression strength of straw pellets compared to wood pellets (Stelte et al. 2001).

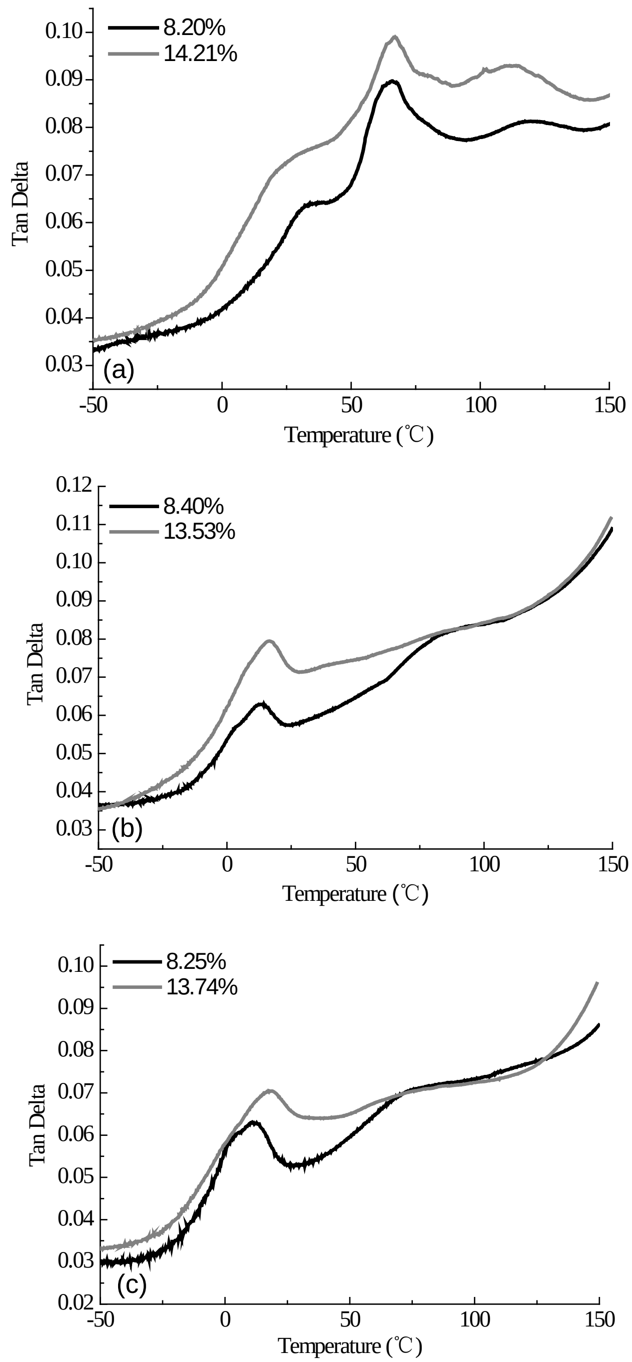

Fig. 2. The loss factor (tan*δ*) of moso bamboo with different moisture content: (a) OB, (b) MB, (c) IB

Compression formation of different materials utilizing natural binder or binding type of particles involves attractive forces between solid particles, interfacial forces, capillary pressure, adhesive and cohesive forces, mechanical interlocking behavior and formation of solid bridges. The bonding between particles was created mainly through solid bridges for corn stover and switchgrass pellets or briquettes. The solid bridges between particles were made by natural binders in the biomass expressed during the densification process (Stelte and Vance 2010). Hemicelluloses and lignin were essentially natural binders in the bamboo components. The glass transition of these amorphous polymers was affected by moisture content of bamboo. Activating (softening) the natural binders using moisture and temperature in the temperature range of glass transition was very important and helpful to make durable particle-particle bonding.

Table 3. Loss Factor (tanδ) of Moso Bamboo with Different Moisture Content

Bamboo part	MC (%)	Temperature of glass transition (^{o}C)	
		α_1	α_2
OB	8.20	65	30
	14.21	65	25
MB	8.40	83	12
	13.53	83	16
IB	8.25	75	10
	13.74	75	18

CONCLUSIONS

The experimental results showed that the general dependency of bamboo thermo-mechanical properties on temperature is similar to other cellulosic materials and that these properties are affected by the moisture in the bamboo. The substantial decrease of storage modulus in the entire temperature range implies that the bamboo materials undergo a glass to rubber transition. Bamboo with a lower moisture content has a higher storage modulus, leading to easier failure of the nature binder of bamboo particles and decreasing the mechanical strength of pellets. The loss factor (tanδ) shows two major transitions for all samples. There is an α-transition (α_1) peak, attributable to glass transition of lignin, at about 65 ^{o}C (OB), 83 ^{o}C (MB), and 75 ^{o}C (IB), respectively. The second major relaxation (α_2) can be attributed to glass transition of hemicelluloses. That of OB with 8.20% and 14.21% moisture content occurs at 30 ^{o}C and 25 ^{o}C. For the MB, the α_2 transition temperature is at 12 ^{o}C and 16 ^{o}C. That of IB is respectively at 10 ^{o}C and 18 ^{o}C. Hemicelluloses and lignin are essentially natural binders in the bamboo components. Activating (softening) the natural binders using moisture and temperature in the temperature range of glass transition is very helpful to enable to formation of durable particle-particle bonding.

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