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Softening Behavior of Black Sweet-Bamboo (*Dendrocalamus asper* Backer) at Various Initial Moisture Contents

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ABSTRACT

Softening behavior of bamboo (*Dendrocalamus asper* Backer) at various initial moisture contents (0 %, 13 %, 37 % and 60 %) was investigated by means of dynamic mechanical thermal analysis (DMTA). The tests were performed in a bending mode over a temperature range of 0 - 300 °C. A heating rate of 3 °C/min with a constant oscillation strain of 0.1 % at a frequency of 1 Hz was employed. It was found that at low temperature the storage modulus of the bamboo decreased with increasing temperature. The glass transition temperature of bamboo with higher initial moisture content was lower than that of bamboo with lower initial moisture content. Moisture content changes at lower levels (<13 %MC) had a greater effect on the glass transition temperature than moisture content changes at higher levels (>13 %MC). Moreover, free water in the cell cavity appeared to have little effect on the glass transition temperature. The maximum and minimum glass transition temperatures of the bamboo were 194±10 °C and 85±10 °C and were obtained from oven dried bamboo and water saturated bamboo, respectively. Relaxation of lignin at various moisture conditions was proposed to be a major mechanism responsible for the softening of the bamboo cell wall. At very high temperatures beyond the temperature of maximum loss tangent, storage modulus increased with increasing temperature which could be a result of the presence of a more crystalline cellulose phase caused by the heating.

Keywords: Black sweet-bamboo, softening, glass transition temperature, moisture content

INTRODUCTION

An increasing demand for timber worldwide together with an environmental concern to protect existing natural forests are major driving forces in the search for alternatives to wood materials to supplement the use of timber in the near future. Bamboo, a fast growing plant, has good potential to be a timber substitute material. Bamboo grows to its mature size in less than one year with an average maturity of 3 - 8 years [1,2]. It is also easy to plant and cultivate at low cost. Bamboo culm, which is cylindrical and hollow, is divided at intervals by nodes. The culm is comprised of an exodermis, parenchyma cells, vascular bundles and an endodermis. The vascular bundle is made up of vessels (for transporting water), sieve tubes (for transporting nutrition) and thick-walled fibers [3]. Mechanical properties of bamboo are very anisotropic. Excellent strength in the longitudinal direction of bamboo mainly arises from the thick-walled fibers, which have comparable mechanical strength to steel [4]. Utilization of bamboo as a solid substitute for timber is restricted due to its tubular shape with transverse diaphragms of bamboo culm. This fact warrants further development of both scientific and technological knowledge of the material properties of bamboo to overcome this constraint. The most important material properties with respect to processing bamboo into materials for timber substitution are those related to softening. Once it is softened, bamboo culm could, in principle, be compressed and fixed into any shape required. Ideally, one should aim to rationalize and quantify the softening behavior by considering the underlying mechanisms and their temperature and moisture dependence at conditions relevant to the manufacturing processes. This is the purpose of this paper.

BACKGROUND

The bamboo cell wall, which contains amorphous phases of hemicellulose, lignin, and non-crystalline cellulose components exhibits viscoelastic behavior when exposed to increasing temperature [5]. At low temperature, amorphous wood constituents are in a “glassy state” exhibiting high strength and modulus. As the temperature increases, the values of strength and modulus drop very sharply within a small temperature range called the glass transition temperature, T_g. Amorphous wood constituents attain another softer state called a “rubbery state”. Glass transition temperatures in wood range from 60 °C to 235 °C, depending on the moisture content, wood chemical composition and method of testing [6]. Lower moisture levels tend to increase the glass transition temperature. Further increasing the temperature causes the amorphous wood constituents to become a viscous fluid. However, this state is not reached in wood because of the total thermal degradation of amorphous wood constituents at high temperature [7].

MATERIALS AND METHODS

Preparation of test specimens

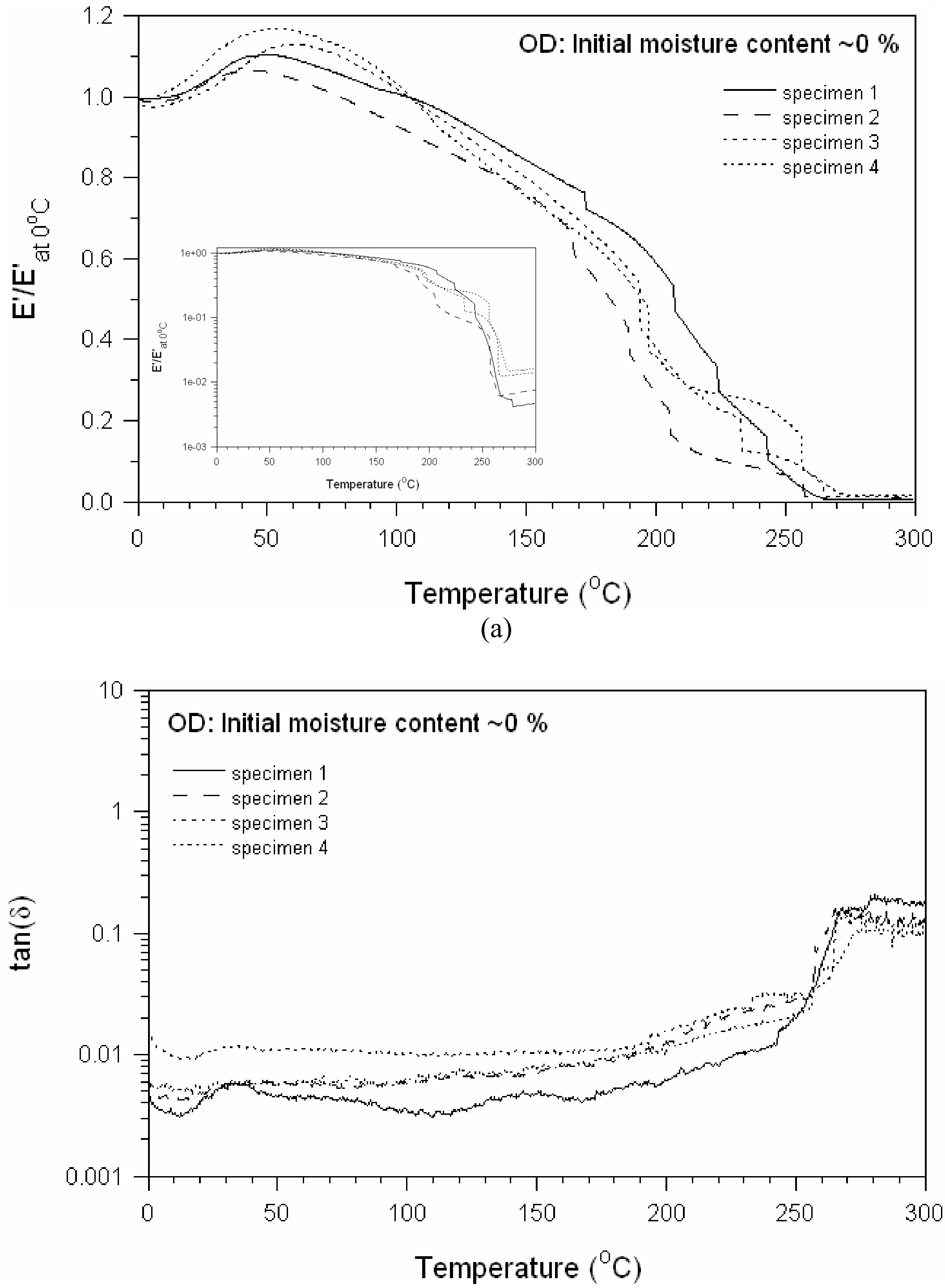
Approximately 3 - 4 years old black sweet-bamboo (*Dendrocalamus asper* Backer) stem segments were cut from a plantation area in Thasala district, Nakhon Si Thammarat province, Thailand. Thirty-two specimens were prepared to give finished dimensions of 3.0 mm (thickness) × 4.5 mm (width) × 50 mm (length), with the lengths cut parallel to the fiber direction. Specimens were allocated randomly among the four test groups. Specimens of the first group (denoted as OD) were oven dried at 103 °C for 24 h to obtain ~0 % moisture content. Specimens of the second group (denoted as EMC) and the third group (denoted as FSP) were conditioned at 20 °C and 65 %RH and 20 °C and 100 %RH, respectively, until equilibrium moisture contents were attained. Specimens of the final group (denoted as SAT) were immersed in water at room temperature at ~29 °C until no further weight changes were observed to give water saturated bamboo. Average moisture contents of the OD, EMC, FSP and SAT groups were determined using four specimens in each group to be 0 %, 13±1 %, 37±2 % and 60±7 %, respectively. Another four samples in each group were sealed in plastic bags ready for dynamic mechanical testing.

Dynamic mechanical testing

A Dynamic Mechanical Thermal Analyzer (Rheometric Scientific DMTA5) at the Scientific Equipment Center, Prince of Songkla University, Songkla, Thailand was used to obtain the flexural storage modulus E′ and tan δ (loss tangent) of the specimens. Specimens were tested in three point bending mode using a constant oscillation strain of 0.1 % at a frequency of 1 Hz. Temperature scans were carried out at a heating rate of 3 °C/min from 0 to 300 °C. The cooling of the system to subambient temperatures was done using a liquid nitrogen apparatus attached to the DMTA. Four specimens for each sample group were tested to ensure the reproducibility of the results.

RESULTS AND DISCUSSION

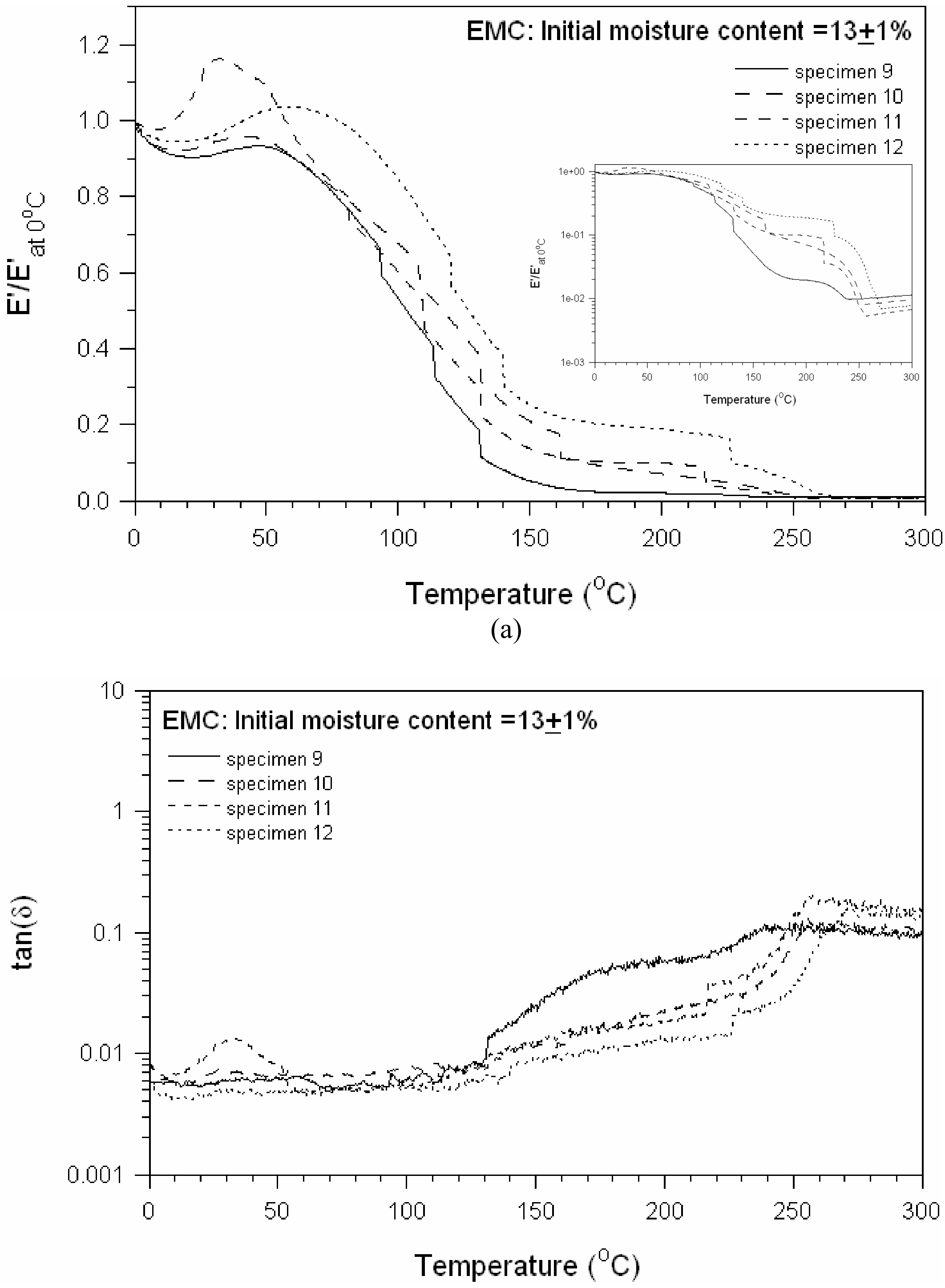
Due to natural variation in the storage modulus of four bamboo replicates, the temperature dependence of the storage modulus at each initial moisture level is best viewed by plotting normalized storage modulus ($E'/E'_{\mathrm{at}\ 0\ ^{\circ}\mathrm{C}}$) against temperature {**Figures 1(a), 2(a), 3(a)** and **4(a)**}. As can be seen, data of all four replicates do indeed almost overlap onto a single master curve for all initial moisture content conditions examined.



(a)

(b)

Figure 1 (a) Normalized storage modulus ($E'/ E'_{\text{at } 0\,°\text{C}}$) and (b) loss tangent (tan δ) responses of oven dried bamboo specimens (OD). The inset is normalized storage modulus plotted on a logarithmic scale.



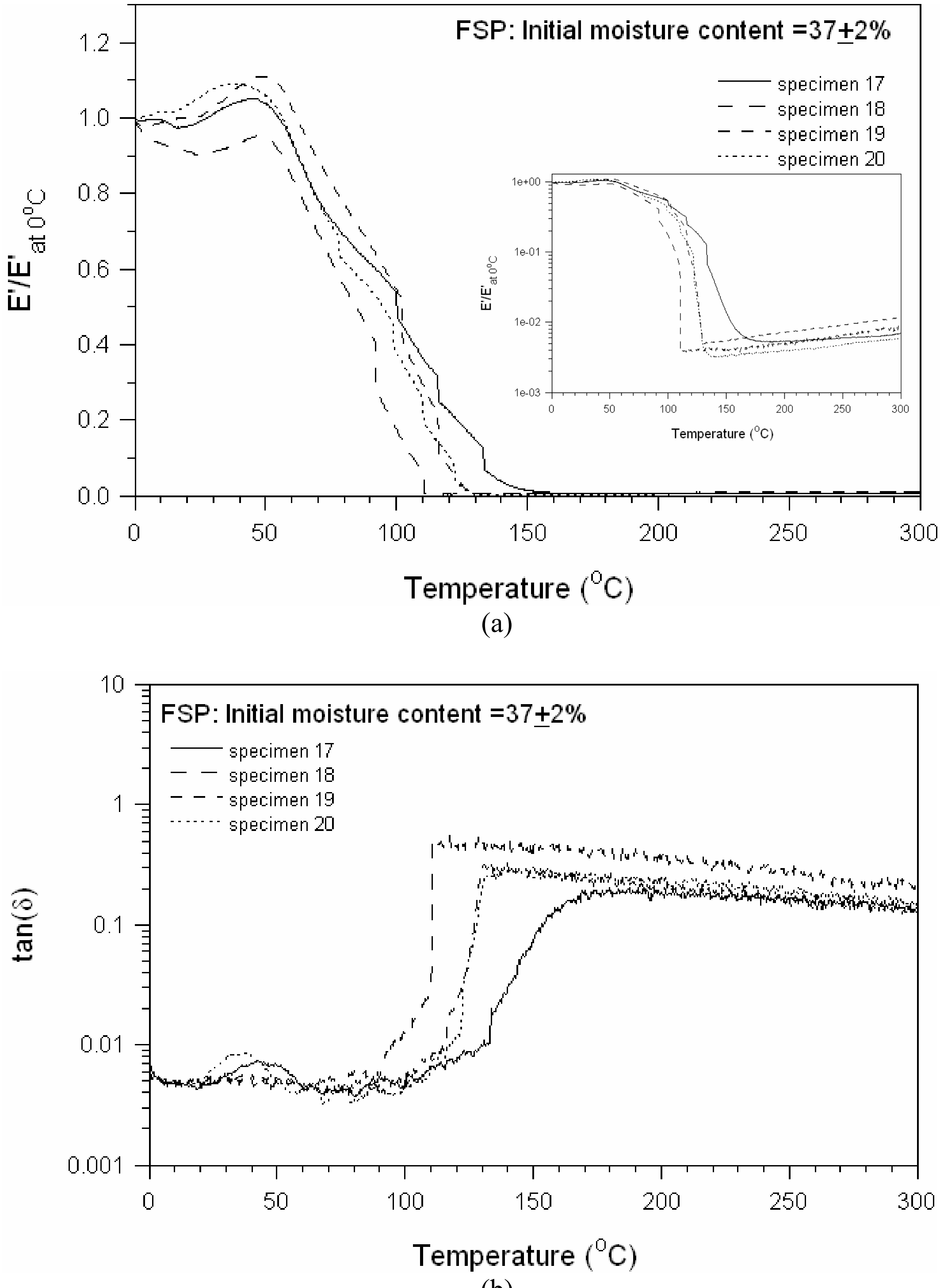
(a)

(b)

Figure 2 (a) Normalized storage modulus (E′/ E′$_{\text{at 0 °C}}$) and (b) loss tangent (tan δ) responses of bamboo specimens (EMC) having an initial moisture content of 13 %. The inset is normalized storage modulus plotted on a logarithmic scale.

Figure 1(a) shows that normalized storage modulus of OD bamboo specimens decreased steadily with increasing temperature from 50 to 270 °C and the glass transition temperature, T_g, (defined as temperature at $E'/E'_{at\ 0\ °C} = 0.5$) was at 194±10 °C. The presence of water (~13 %) in the bamboo cell walls in the EMC bamboo specimens greatly reduced T_g to 114±10 °C with a temperature range at which the modulus decreased from 50 to 150 °C {**Figure 2(a)**}. The plasticizing effect of water on the cell wall components has been reported by other researchers [6,8-10]. It was suggested that disruption of the hydrogen bonds in the cell wall's internal structure by the water molecule to create the new hydrogen bonds with bound water molecule plays a key role in storage modulus reduction [11]. Increasing the amount of bound water in the cell wall to the fiber saturation point of 37 % caused T_g to drop further to 96±8 °C with a temperature range at which the modulus decreased from 50 to 130 °C {**Figure 3(a)**}. An excess of free water in the cell cavity appeared to have an insignificant effect on softening. **Figure 4(a)** shows that temperature dependence of the storage modulus of SAT specimens having a saturated moisture content of 60 % was very similar to that of FSP except that T_g decreases slightly to 85±10 °C. It is concluded that bamboo softening is mainly due to the presence of bound water in the cell wall. The presence of free water in the cell cavity helped to reduce the amount of moisture loss in the cell wall during heating. As a result, it was expected to be more water molecules left in the cell wall of the SAT samples than those left in the FSP samples at any particular temperature during heating.

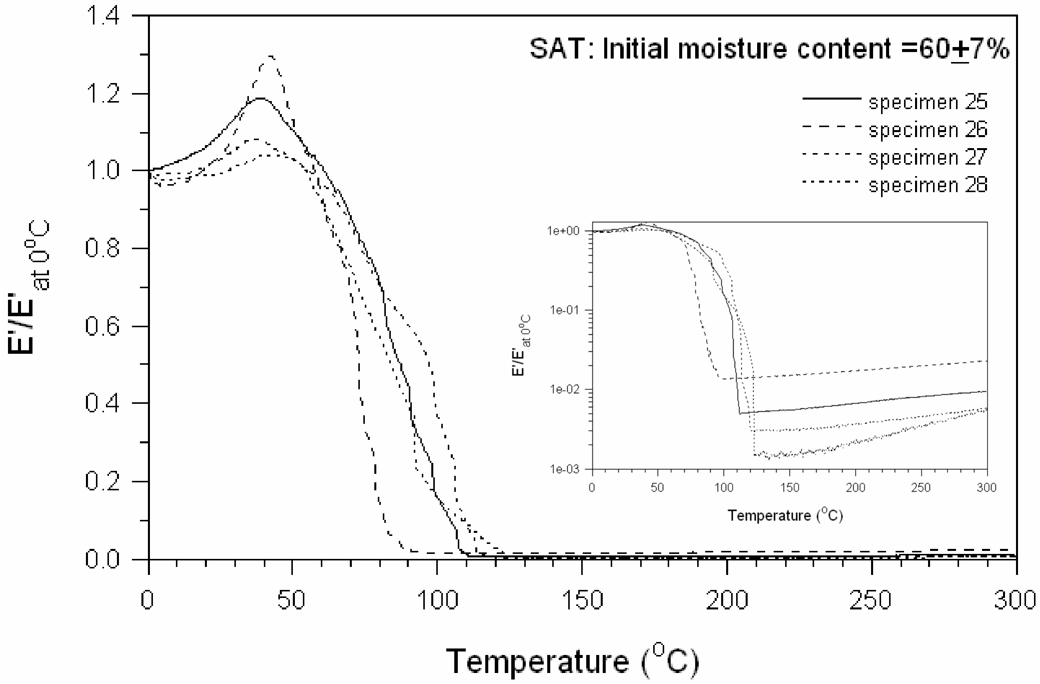
Figure 5 shows the glass transition temperature dependence on the initial moisture levels of bamboo samples. It is evident that the T_g of bamboo reaches a plateau when initial moisture content increases beyond 13 %. Moreover, the results suggest that the plasticization effect of water on the polymer chain segments in bamboo was likely be much greater for the initial layer of water molecules and substantially less for each additional layer as the forces attracting the water molecules to the substrate decrease [6]. The values of T_g obtained from this study were higher than those reported for lignin, hemicellulose [8] and many other wood species [8,9,10] at various moisture levels except in the case of the oven-dried (OD) samples (**Figure 5**). This was partly due to the fact that the moisture content which was reduced as the temperature rises during testing driving the apparent T_g of amorphous polymers e.g. lignin and hemicellulose in bamboo cell wall higher. As a result, for oven-dried samples, less effected by the moisture loss during testing, good agreement in the T_g values were found (**Figure 5**). The T_g of bamboo appeared to lie close to the T_g of lignin reported by Kelley *et al* [8]. It is also possible that softening of lignin might be responsible for the great drop in the storage modulus and therefore the softening of bamboo cell wall. This, however, warrants further study.



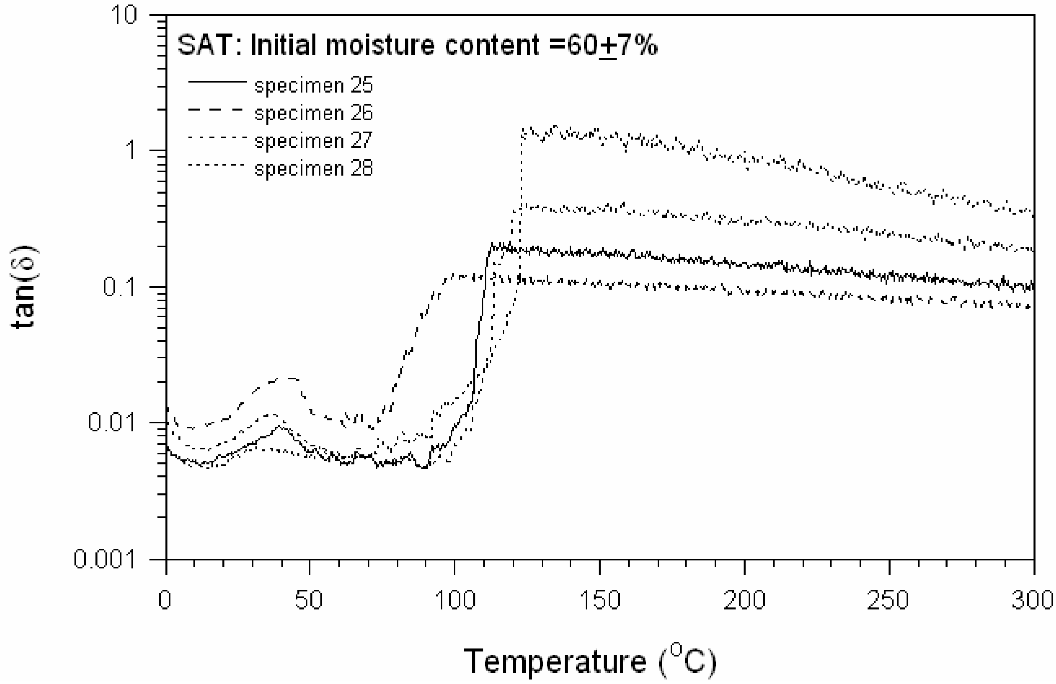
(a)

(b)

Figure 3 (a) Normalized storage modulus ($E'/E'_{\text{at } 0\,°\text{C}}$) and (b) loss tangent (tan δ) responses of bamboo specimens (FSP) having an initial moisture content of 37 %. The inset is normalized storage modulus plotted on a logarithmic scale.



(a)



(b)

Figure 4 (a) Normalized storage modulus ($E'/E'_{\text{at }0\,°C}$) and (b) loss tangent (tan δ) responses of bamboo specimens (SAT) having an initial moisture content of 60 %. The inset is normalized storage modulus plotted on a logarithmic scale.

Figures 1(b), 2(b), 3(b) and **4(b)** show DMTA results of tan δ plotted against temperature at various initial moisture contents. The values of tan δ at room temperature of all specimens lay between 0.005 - 0.01 which were in good agreement with the values reported elsewhere [12]. The variation of tan δ with temperature corresponds well with those against storage modulus (**Figures 1 - 4**). The temperature at maximum tan δ, corresponding to that of minimum storage modulus, greatly reduces from 269±5 °C for the OD specimens to 114±12 °C for the SAT specimens. The amount of maximum tan δ of the SAT and FSP specimens (~0.4) were higher than those of the EMC and OD specimens (~0.1). Small peaks of tan δ between 20 - 60 °C were in the same range as T_g of hemicellulose reported by Kelley *et al* [8]. The level of moisture seemed to have no significant effect on the temperature at which the process occurred. The value of tan δ at this temperature, however, slightly increased with increasing moisture content indicating that the relaxation process of hemicellulose might easily take place with the presence of water in the cell wall structure.

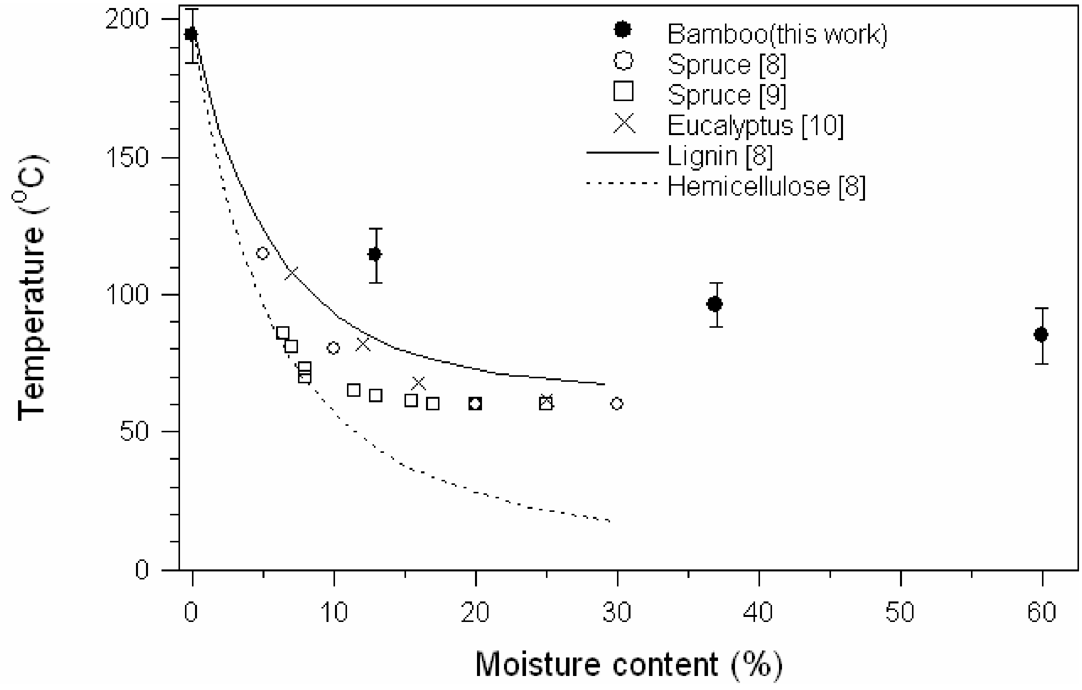


Figure 5 The moisture dependence of the glass transition (T_g) for bamboo, spruce [8,9], eucalyptus [10] and *in situ* lignin and hemicellulose as predicted by the Kwai model [8].

At high temperatures beyond the temperature of maximum tan δ (e.g. >114±12 °C for the SAT, >136±24 °C for the FSP, >255±13 °C for the EMC, and >269±5 °C for the OD), the storage modulus of bamboo specimens slightly increased with temperature up to 300 °C (see inset in **Figures 1 - 4**). Furthermore, the storage modulus increased with almost the same slope regardless of the initial moisture content upon heating. The rubbery state and viscous flow behaviors were not observed in bamboo specimens. Thermal degradation was expected at this temperature. Wolcott *et al* [7], proposed that thermal degradation of the wood cell wall normally occurs prior to the onset of viscous flow. An increase in the storage modulus with temperature at this temperature is expected due to the presence of a more crystalline cellulose phase caused by heating. There is a lot of evidence showing that the crystallinity of wood cellulose increases after heat treatment both under dry and moist conditions [13,14].

CONCLUSIONS

The following conclusions can be drawn from this work:

1. The glass transition temperature of bamboo with higher initial moisture content was lower than that of bamboo with lower initial moisture content. The minimum and maximum glass transition temperatures of bamboo were 85±10 °C and 194±10 °C and were obtained from water saturated bamboo and oven dried bamboo, respectively.
2. When the moisture content was less than 13 % there was a greater effect on the glass transition temperature than when the moisture content was higher. Excess free water in the cell cavity appeared to have little effect on the glass transition temperature.
3. Relaxation of lignin was proposed to be a major mechanism responsible for the softening of the bamboo cell wall.
4. At very high temperature beyond the temperature of maximum loss tangent, the storage modulus increased with increasing temperature which could be a result of the presence of a more crystalline cellulose phase caused by the heating.

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บทคัดย่อ

นิรันดร มาแทน บุญนำ เกี่ยวข้อง และ วันชาติ ปรีชาติวงศ์

พฤติกรรมการอ่อนตัวของไม้ไผ่ตงดำ (*Dendrocalamus asper* Backer) ที่ความชื้นเริ่มต้นต่างๆ

งานวิจัยนี้ศึกษาพฤติกรรมการอ่อนตัวของไม้ไผ่ตงดำ (*Dendrocalamus asper* Backer) ที่ระดับความชื้นต่างๆ (0 %, 13 %, 37 % และ 60 %) โดยใช้เทคนิค dynamic mechanical thermal analysis (DMTA) การทดสอบทำในรูปแบบ bending ในช่วงอุณหภูมิ 0 - 300 องศาเซลเซียส โดยมีอัตราการเพิ่มอุณหภูมิของตัวอย่างที่ 3 องศาเซลเซียสต่อนาที ค่าความเค้นที่ 0.1 % และความถี่ 1 เฮิร์ทซ์ ผลการทดลองพบว่าในช่วงอุณหภูมิต่ำค่าโมดูลัสมีค่าลดลงเมื่ออุณหภูมิเพิ่มขึ้น โดยไม้ไผ่ตงดำที่มีความชื้นสูง มีค่าอุณหภูมิสภาพแก้วต่ำกว่าไม้ไผ่ตงดำที่มีความชื้นต่ำ และการเปลี่ยนแปลงของความชื้นที่ค่าความชื้นต่ำๆ (<13 %MC) มีผลต่อค่าอุณหภูมิสภาพแก้วมากกว่าการเปลี่ยนแปลงของความชื้นที่ค่าความชื้นสูงๆ (>13 %MC) นอกจากนี้การเพิ่มขึ้นของปริมาณน้ำอิสระในช่องว่างของเซลล์มีผลน้อยมากกับค่าอุณหภูมิสภาพแก้ว ค่ามากที่สุดของอุณหภูมิสภาพแก้วซึ่งได้จากไม้ไผ่ตงดำแห้งมีค่าเท่ากับ 194±10 องศาเซลเซียส ในขณะที่ค่าน้อยที่สุดของอุณหภูมิสภาพแก้วซึ่งได้จากไม้ไผ่ตงดำที่อิ่มตัวด้วยน้ำมีค่าเท่ากับ 85±10 องศาเซลเซียส การคลายตัวของลิกนินที่ค่าความชื้นต่างๆคาดว่าเป็นกลไกหลักที่ทำให้ไม้ไผ่ตงดำเกิดการอ่อนตัว ที่อุณหภูมิสูงเกินค่าอุณหภูมิที่ให้ค่า loss tangent สูงสุด ค่าโมดูลัสของไม้ไผ่ตงดำกลับมีค่าเพิ่มขึ้นตามอุณหภูมิซึ่งสันนิษฐานว่าน่าจะเกิดจากการเพิ่มขึ้นของปริมาณผลึกเซลลูโลสในระหว่างการให้ความร้อน

สำนักวิชาวิศวกรรมและทรัพยากร มหาวิทยาลัยวลัยลักษณ์ อำเภอท่าศาลา จังหวัดนครศรีธรรมราช 80161