

THE EFFECTS OF THERMAL MODIFICATION ON THE PROPERTIES OF TWO VIETNAMESE BAMBOO SPECIES, PART I: EFFECTS ON PHYSICAL PROPERTIES

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Bamboo is a very interesting bioresource for use as a building material because of its properties of strength in combination with low density. However, its susceptibility to fungi and insects is problematic for its usage. Thermal modification is used in Vietnam to improve the durability and dimensional stability of bamboo. The thermal modification causes many changes related to the physical properties of bamboo, e.g., mass, color, and equilibrium moisture content (EMC). All these changes are dependent on the modification conditions (modification temperature and duration). The mass loss (ML), the color difference (ΔE^*_{ab}), and the reduction of EMC (ΔEMC) were due to the thermal modification increase with higher temperature and/or longer duration. Therefore the temperature had greater influence than the modification duration. The changes were slight at 130 °C (ML: 0,3...0,6 %; ΔE^*_{ab} : 3...5; ΔEMC : 0,5...0,8 %), moderate at 180 °C (ML: 1,5...4 %; ΔE^*_{ab} : 21...37; ΔEMC : 3,6...4,4 %), but very strong at 220 °C (ML: 14...16 %; ΔE^*_{ab} : 46...51; ΔEMC : 5,6...5,7%). There are close correlations between the changes mentioned above.

Keywords: Bamboo; Thermal modification; *Dendrocalamus barbatus*; *Dendrocalamus asper*; Changes in physical properties; Color difference; Mass loss; Equilibrium moisture content

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INTRODUCTION

Bamboo is a multipurpose material in Vietnam that has countless applications. It can be used as a building material, as a raw material for handicrafts, for the production of chopsticks and toothpicks, and recently, for the production of pulp, paper, and wood-based panels (Vu *et al.* 2002; Do 2006). Bamboo is a natural material that is susceptible to fungi and insects. Therefore, its utilization is in many cases problematic (Liese and Kumar 2003; Liese 2007). In order to increase its durability and dimensional stability and to extend its service life, bamboo needs to be modified. For this reason, the thermal modification of bamboo is a promising and environmentally friendly approach (Kamdem *et al.* 2002; Militz 2002; Leithoff and Peek 2001; Sulaiman *et al.* 2006).

The thermal modification technique used in Vietnam today is based only on empirical knowledge. There have been no fundamental examinations of the relationships between thermal treatment and changes in properties until now. Therefore, no reproducible processes have been established in Vietnam. However, in recent years many studies on thermal modification of different wood species have been carried out in

Europe, North America, and Asia to analyze the changes in physical properties (Kamdern *et al.* 2002; Militz 2002; Alen *et al.* 2002; Esteves *et al.* 2008; Schnabel *et al.* 2007; Borrega and Kärenlampi 2007, Pfriem *et al.* 2009, 2010; Todorovic *et al.* 2012) and chemical composition (Tjeerdsma *et al.* 1998, Boonstra and Tjeerma (2006), Windeisen *et al.* 2009) and to improve the dimensional stability and biological durability of wood (Burmester 1975; Edvardsen and Sandland 1999; Militz 2002; Kamden *et al.* 2002; Hill 2006; Dubey *et al.* 2011). But for bamboo there exist few results in this field. The thermal modification of bamboo has been mainly carried out with hot oil (Leithoff and Peek 2001; Manalo and Acda 2009; Rafidah Salim *et al.* 2010). The objective of our research is to analyze the changes in the physical properties of two common Vietnamese bamboo species and determine how these changes are affected by the parameters of the thermal treatment in nitrogen atmosphere, especially modification temperature and duration. Results of such research may help in the development of thermal modification processes for the preparation of bamboo having defined properties. Furthermore, knowledge of the correlations between the changes in the different physical properties would allow for the identification of a simple detectable parameter that could be used to test the quality of the thermal treatment.

EXPERIMENTAL

Materials and Methods

Two of the main bamboo species growing in Vietnam were chosen for this investigation. These are:

- *Dendrocalamus barbatus* Hsueh et D. Z. Li (*D. barbatus*) and
- *Dendrocalamus asper* Backer ex Heyne (*D. asper*)

The culms were harvested in the area of Tan Lac, Province Hoa Binh. They were about 3 years old and 15 m high. The first 10 m from the bottom were used for the investigation. These 10 m culms were cut into two equally sized pieces, the bottom half and the top half. The bamboo culms used in this investigation were fresh and contained high moisture content. In order to avoid crack formation during drying and/or thermal modification process, the fresh bamboo culms were dried (before thermal modification) in three steps: first at 40 °C for 2 days, then 2 days at 60 °C, afterward at 80 °C until weight constancy (mass change < 0.1% after 24 hour).

For this investigation, only the internodes were used. Each internode was cut into five slices. Each slice was split into two parts, one part to be used for the modification and the other part to be the twin sample (untreated control sample).

Bamboo belongs to the grass family and differs from wood in chemical composition and structure. Its components seem to be less stable in high temperature than wood. Therefore the conditions for thermal modification of bamboo in these investigations were moderate (temperature of 130 or 180 °C and duration of 2 or 5 hours) in order to avoid massive loss of mechanical properties. Nevertheless, the bamboo samples were also treated at 220 °C and 5 hours to analyse the changes in physical properties corresponding to an extreme modification condition.

The thermal modification was carried out in a closable treatment chamber (Fig. 1). At first, the chamber (with samples) was evacuated to 200 mbar, and then it was filled with nitrogen (inert gas). After that, the samples were modified under the above-mentioned conditions. The treatment conditions are shown in Fig. 2.

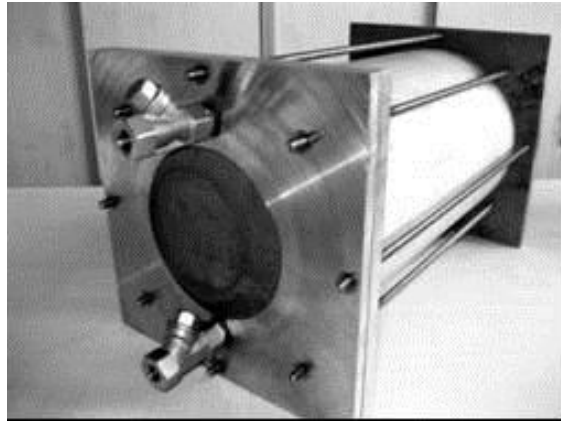


Fig. 1. Treatment chamber for the thermal modification of bamboo

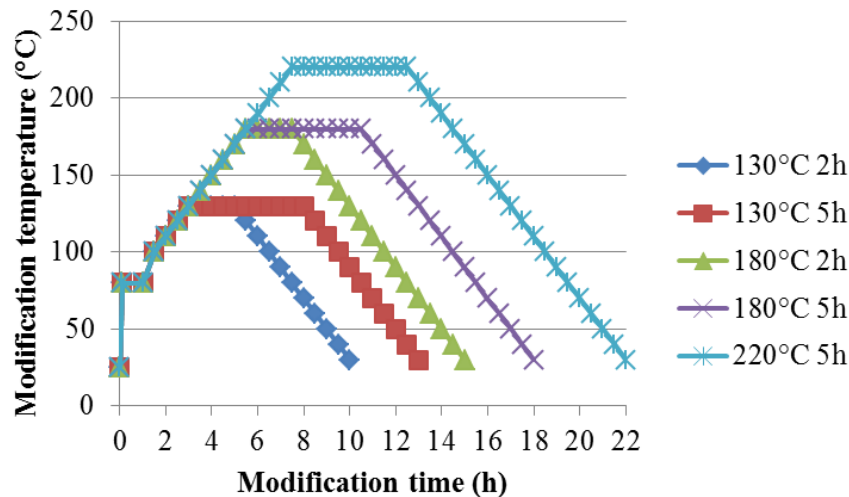


Fig. 2. Treatment charts for the modification at 130, 180, and 220 °C

The modified samples and the twin samples (untreated, control) were stored under standard conditions (20 °C; 65 % rh) for 2 weeks before being cut into various specimens for different analyses and tests.

The color was determined according to the CIELAB color space, which is characterized by the lightness L^* and the two chromatic coordinates a^* (green-red) and b^* (blue-yellow) (DIN 5033 2009). The color of the bamboo (outer layer) was measured with a spectrophotometer (SpectroEye X-rite) under a D65 light source with an observer angle of 10°. For every bamboo sample, 20 measurements at different places were carried out. Some samples of untreated bamboo showed two zones (a bright and a dark zone) that differed strongly in color, and for these samples the zones were investigated separately (40 measurements per sample). The color difference ΔE^*_{ab} was calculated from the mean color values (L^* , a^* , and b^*) of the modified and control samples according to Equation (1),

$$\Delta E^*_{ab} = ((\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2)^{1/2} \quad (1)$$

where,

$$\Delta L^* = L^*_t - L^*_0 \quad (2)$$

$$\Delta a^* = a^*_t - a^*_0 \quad (3)$$

$$\Delta b^* = b^*_t - b^*_0 \quad (4)$$

and t means after treatment, whereas 0 means before treatment.

To determine the mass loss that was due to thermal modification, the weights of the oven-dried bamboo sample were measured before and after the modification. The mass loss was calculated according to Equation (5),

$$ML (\%) = 100 * (m_0 - m_t)/m_0 \quad (5)$$

where, m_0 is the the mass of the oven-dried sample before the thermal modification, and m_t is the mass of the oven-dried sample after the thermal modification.

For the estimation of the equilibrium moisture content, the mass of the oven-dried sample (30 mm x 15 mm x wand thickness) and the mass of the same sample at 20 °C and 65 % rh were measured (20 measurements per variant). The EMC was determined according to Equation (6),

$$EMC = 100 * (m_f - m_0)/m_0 \quad (6)$$

where, m_0 is the the mass of the oven-dried sample before the thermal modification, and m_f is the the mass of the sample at 20°C and 65 % rh. ΔEMC is the reduction of EMC caused by thermal modification and was determined according to Equation (7),

$$\Delta EMC = EMC_0 - EMC_t \quad (7)$$

where, EMC_t is the EMC of the modified sample, and EMC_0 is the EMC of the untreated control sample (twin sample).

RESULTS AND DISCUSSION

Thermal modification causes a lot of changes to the physical properties of the bamboo such as the color, the mass, and the equilibrium moisture content (EMC), all of which are indicative of changes in chemical composition (Part II, Bremer *et al.* 2012 submitted).

Mass Loss

One remarkable change in the bamboo due to thermal modification was a change in mass. Like wood, bamboo consists of three main components (cellulose, hemicelluloses, and lignin) as well as extractives (Liese 1985, 1998; Fengel 1989; Kollmann 1982). These components differ in their thermal stability. The loss of mass that was observed for the bamboo depended on the modification conditions. The mass loss

increased with the increase in treatment temperature and/or duration. Similar results for wood have been obtained in different studies by Esteves *et al.* (2008), Zaman *et al.* (2000), Todorovic *et al.* (2012), Alén *et al.* (2002), Dubey *et al.* (2011), Hill (2006), and Vu and Li (2010).

The mass loss of bamboo at 130 °C was very low (0.34...0.55 %), and at 180 °C it was lower than 5% (1.49...4 %). However, at 220 °C it was shown capable of reaching more than 14 % (Fig. 3). At lower temperature (130 °C) only some volatile compounds were degraded, whereas additionally hemicelluloses were decomposed at higher temperatures, particularly at 220 °C. Windeisen *et al.* (2009) and Tjeerdsma *et al.* (1998) reported similar results for wood. Furthermore, the mass loss depended on both the bamboo species and the culm zones. When the bamboo age and modification conditions were the same, *D. asper* lost a little bit more weight than did *D. barbatus*, and the mass loss of the bamboo at the bottom zone was higher than at the top (Figs. 3 and 4).

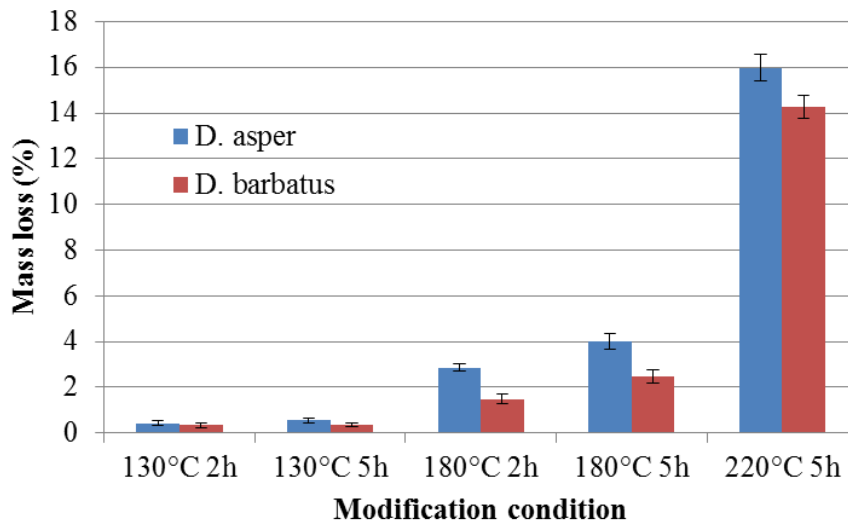


Fig. 3. Influence of thermal modification conditions on the mass loss of the two bamboo species

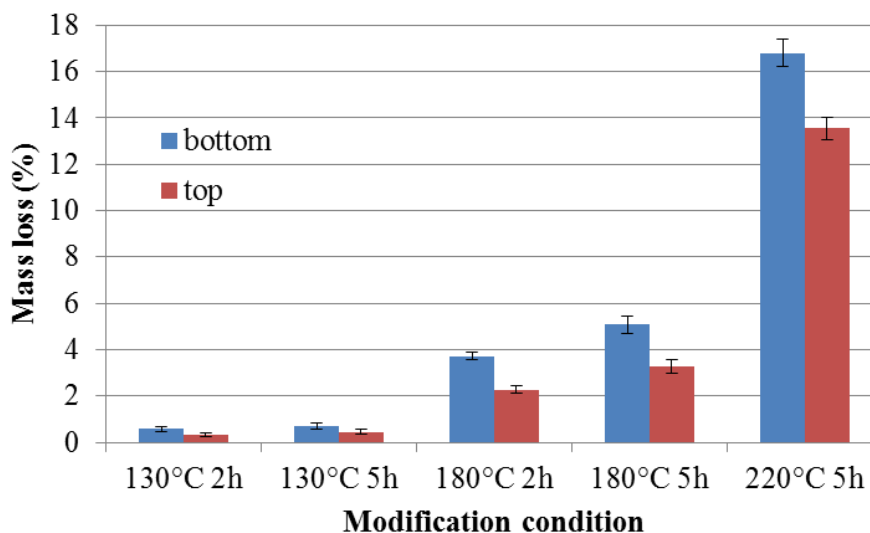


Fig. 4. Influence of different culm zones on the mass loss of *D. asper* during thermal modification

Color

The most remarkable change in the bamboo that occurred due to thermal modification was the color. In this investigation, the color of the outer layer (the epidermis) was measured. As for many wood species, the characteristic parameters L^* , a^* , and b^* of bamboo were also significantly changed by the thermal modification (in comparison to the untreated control samples), and these changes also depended on the modification conditions (Bekhta and Niemz 2003; Schnabel *et al.* 2007; Esteves *et al.* 2008; Manalo and Acta 2009; Vu and Li 2010). However, Figs. 5 and 6 show that with more severe modification conditions (higher temperature and/or longer duration), the L^* -value decreased (ΔL^* : negative), whereas the a^* -value increased (Δa^* : positive). The change in the b^* -value was different from the other changes: it increased (Δb^* : positive) at lower temperature (130 °C) and decreased (Δb^* : negative) at higher temperatures (180 °C and 220 °C). The color of the two investigated bamboo species shifted to a darker color (brown or dark brown). The color also became more homogeneous with the rise in modification temperature and duration.

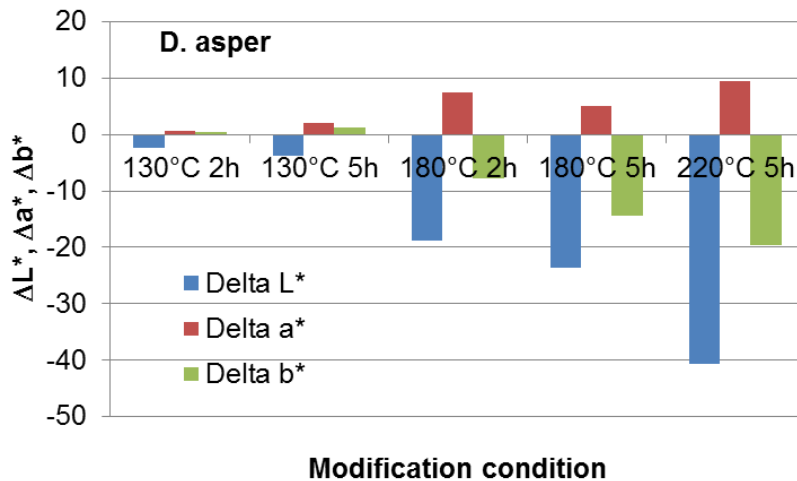


Fig. 5. ΔL^* , Δa^* , and Δb^* of *D. asper* vs. modification

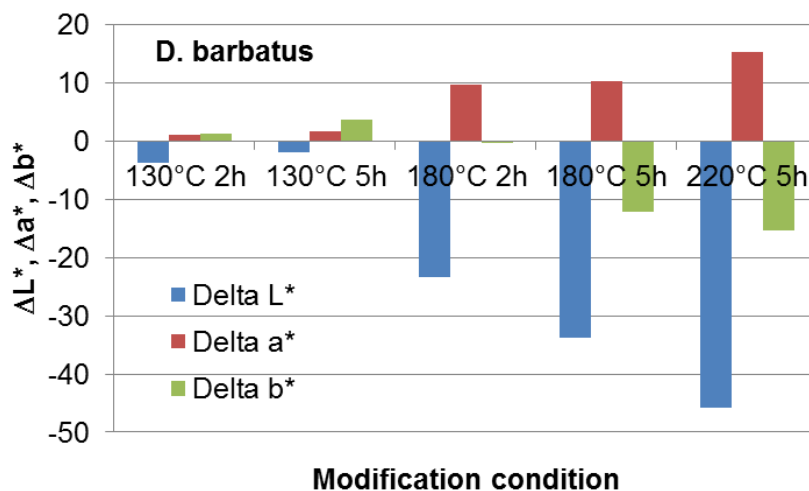


Fig. 6. ΔL^* , Δa^* , and Δb^* of *D. barbatus* vs. modification condition

The key parameter for the evaluation of the color change is the color difference ΔE^*_{ab} . This was also dependent on the modification conditions. The color difference ΔE^*_{ab} increased with the increase in modification temperature and/or duration (Fig. 7), but the influence of the modification temperature was greater than that of the modification duration. The color difference ΔE^*_{ab} of bamboo at 130 °C was low (3 to 5), whereas it was high at 180 °C (21 to 37) and even higher at 220 °C (46...51). The change in color was caused by colored products formed from extractives and hemicelluloses degradation (Sehistedt-Persson 2003; Sundqvist 2004; Esteves *et al.* 2008). Moreover, the content of the lignin was another factor involved in the color change (Part II, Bremer *et al.* 2012 submitted).

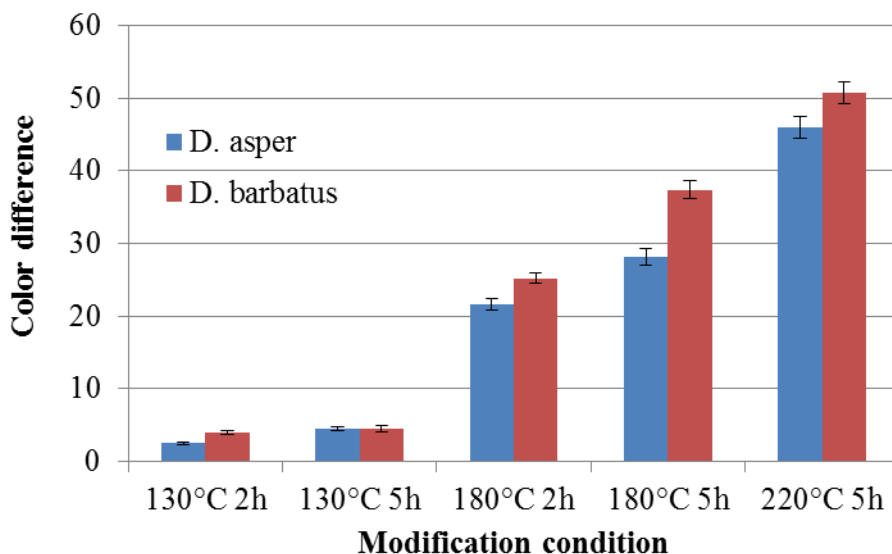


Fig. 7. Color difference ΔE^*_{ab} due to thermal modification vs. modification conditions

Equilibrium Moisture Content (EMC)

Like wood, bamboo is hygroscopic; it absorbs moisture from the environment or releases it into the environment, adjusting its equilibrium moisture content for the particular climate (Kollmann 1982; Liese 1985). The number of free OH-groups in hemicellulose is mainly responsible for the EMC of wood or bamboo. Thermal modification causes the hemicelluloses decomposition, and its content decreases (Part II, Bremer *et al.* 2012 submitted). Consequently, the number of free OH-groups in the hemicelluloses declines as well. Similar results were achieved for different wood species (Windeisen *et al.* 2009; Tjeerdsma *et al.* 1998).

As was expected, the EMC of the modified bamboo was reduced in comparison to unmodified control samples. This is also reported by Borrega and Kärenlampi (2007) and Johansson (2008) for wood and by Salim *et al.* (2010) for the bamboo species *Gigantochloa scortechinii* when considering samples that had been thermally modified in hot oil. The EMC (20 °C and 65% rh) of thermally treated bamboo decreases with increasing modification temperature and duration. The reduction of EMC (Δ EMC) due to the thermal modification was very slight at 130 °C (0.54 to 0.76%), much stronger at 180 °C (3.60 to 4.44%), and at 220 °C and 5 hours it was even higher (5.6 to 5.7 %). The EMC of treated bamboo at 220 °C and 5 hours was about 4 %, also more than 50% lower as their control sample (9.7 to 9.9%).

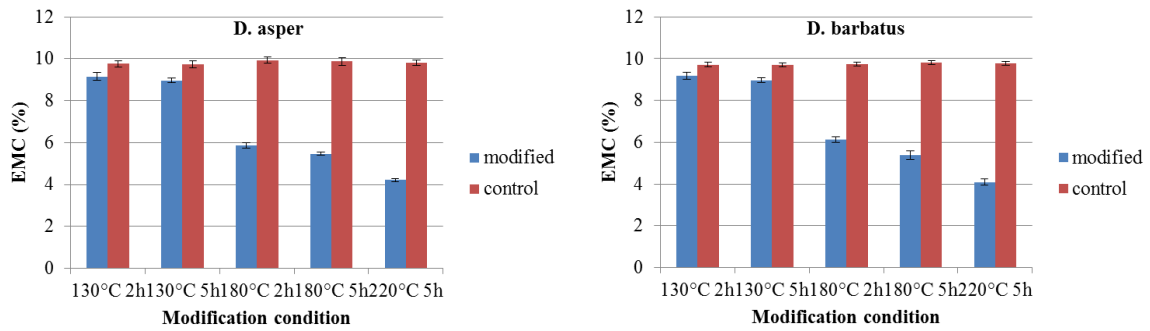


Fig. 8. The EMC of bamboo vs. modification conditions

Figures 3, 7, and 8 show further that the influence of the modification temperature on the mass loss, color, and EMC was significantly higher than that of the modification duration.

Furthermore, it was found that there were strong correlations between the color difference, mass loss, and EMC (Figs. 9 to 11).

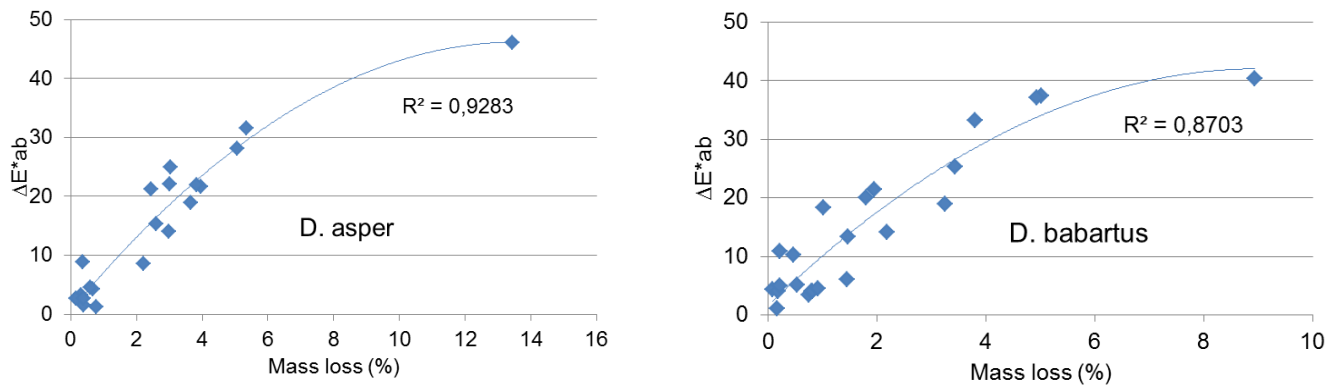


Fig. 9. Correlation between the color difference ΔE^*_{ab} and the mass loss

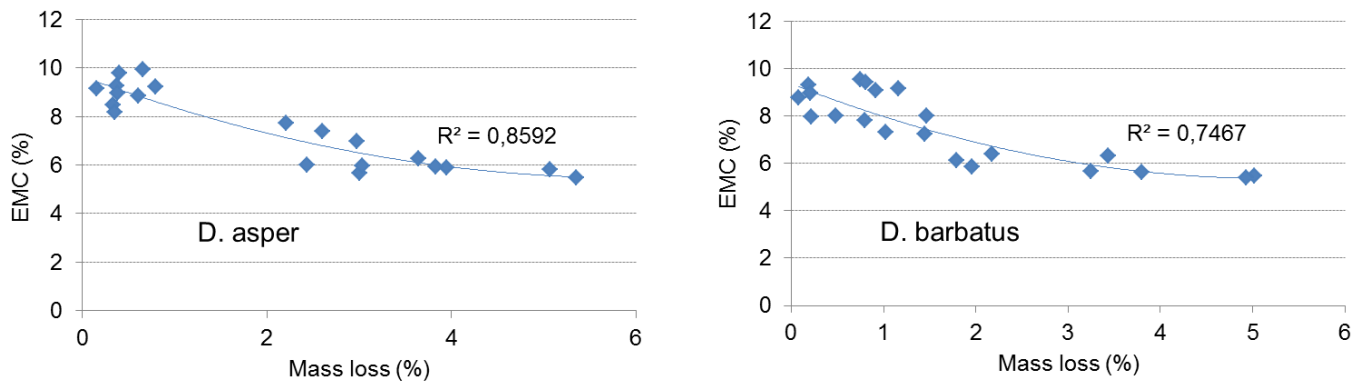


Fig. 10. Correlation between the EMC and the mass loss

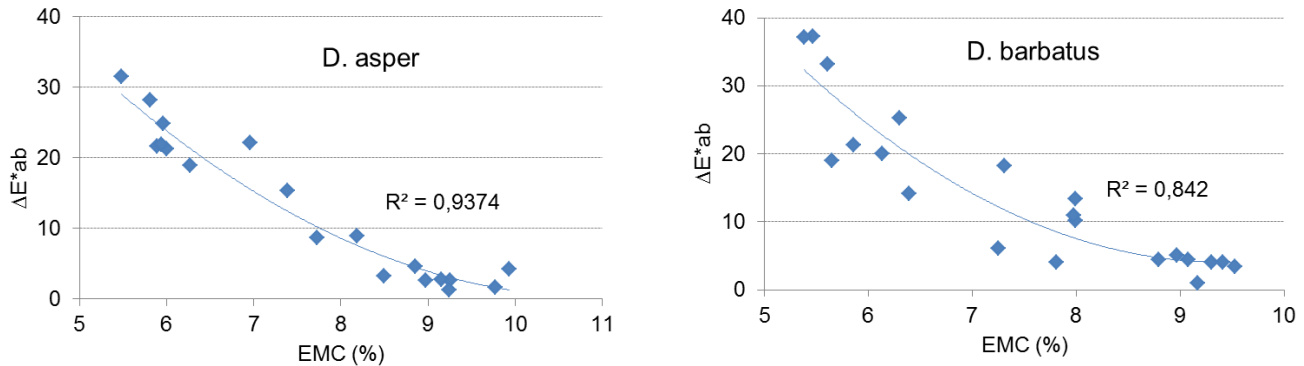


Fig. 11. Correlation between the EMC and the color difference

The changes in color as well as in EMC were mainly caused by the decomposition of the hemicelluloses. The reason for the mass loss during thermal modification was partly the evaporation of volatile compounds, though the decomposition of hemicelluloses (mainly at higher temperatures) also played a role (Part II, Bremer *et al.* 2012 submitted; Windeisen *et al.* 2009; Boonstra *et al.* 2006; Tjeerdsma *et al.* 1998). Therefore, the changes in the properties of mass, color, and the EMC should be strongly correlated.

Because of these correlations, the possibility of using color measurements for quality tests of thermal modification has to be assessed. For this reason, the correlations between color and strength properties are of special interest. This will be the next step of the investigation.

CONCLUSION

1. Thermal modification leads to various changes in the properties of bamboo from Vietnam. All these changes are dependent on the modification conditions; however, temperature clearly has a greater influence than duration. The changes increase with the severity of the modification conditions. The changes are very slight at 130 °C, moderate at 180 °C, but very strong at 220 °C.
2. The most remarkable and most easily recognizable change is that of color. The color of bamboo turns brown or dark brown during the modification.
3. The change in the EMC is very important because the EMC of the modified bamboo was lower than that of its control sample.
4. There are close correlations between the changes in properties, in particular between the mass loss, the color difference, and the EMC. This is why color difference could be seen as a key parameter for the evaluation of the thermal modification of bamboo.
5. Because of its lower EMC, the dimensional stability and the durability of the modified bamboo are expected to be better than those of the unmodified bamboo. Further investigations are planned that will seek to quantify these improvements.

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