WOOD RESEARCH
64 (6): 2019
1045-1054

EFFECTS OF HEAT-TREATMENT ON BONDING PERFORMANCE OF *BETULA ALNOIDES*

Zhigang Wu, Sicheng Chen, Meifen Tian, Lifen Li, Liping Yu
Guizhou University
Guizhou, P.R. China

Xuedong Xi
University of Lorraine
Epinal, France

Jiankun Liang
Kaili University
Guizhou, P.R. China

Bengang Zhang, Hong Lei, Jun Zhang, Taian Chen
Southwest Forestry University
Kunming, Yunnan, P.R. China

(Received March 2019)

ABSTRACT

Heat-treatment woods of *Betula alnoides* were prepared by using vapor as the heat-conducting medium. Effects of heat-treatment time and heat-treatment temperature on equilibrium moisture content, density, pH value, contact angle and bonding performance of *Betula alnoides* were discussed in this paper. The results indicated that: (1) With the increase of heat-treatment temperature, the equilibrium moisture content, density and pH value of *Betula alnoides* decreased gradually. (2) With the increase of heat-treatment temperature, the contact angle of *Betula alnoides* increased from 70.08° to about 100°, resulting in the reduction of bonding strength gradually. Bonding strength of *Betula alnoides* after heat-treatment was related with the used adhesive. Bonding strength of different adhesives decreased to different extents. The bonding strength of *Betula alnoides* wood with polyvinyl acetate (PVAC) resin was generally higher than that of melamine-urea-formaldehyde (MUF) resin. The former were 6.35-4.56 MPa, and the latter were 5.60-3.00 MPa. (3) Heat-treatment time influenced equilibrium moisture content, density, contact angle, pH value and bonding strength of *Betula alnoides* less than heat-treatment temperature. (4) Heat-treatment could affect strength and surface performance of *Betula alnoides* greatly and the processing medium should be extended.

KEYWORDS: Vapor, heat-treatment, surface characteristics, bonding performance, *Betula alnoides*.

INTRODUCTION

Wood is a kind of renewable green material and it is highly appreciated by the good visual characteristics, touching characteristics, temperature and humidity regulating functions and relatively high ratio of strength to weight. Recently, there's a shortage of natural timber resources around the whole world and the major timber resources turn to artificial forest. Due to the short rotation of artificial forest, the proportion of juvenile wood is relatively high, which is characteristic of hemicelluloses and lignin contents, low quality and density as well as poor size stability and durability (Boonstra et al. 2007, Sernek et al. 2008, Tjeerdsma et al. 1998, Kaygin et al. 2009). These disadvantages restrict applications of juvenile woods. Therefore, it is urgent to develop a method of reasonable utilization of timber resources. Moreover, people propose increasingly higher requirements on environment with the improving of people's living standard in the world.

Heat processing technique of wood not only can improve size stability, corrosion resistance and weather resistance and realize high-efficiency utilization of timber materials, but also can increase categories and improve quality of products (Esteve and Pereira 2009, Olek et al. 2013, Bal 2014, Cao et al. 2012, Dilik and Hiziroglu 2012). Heat-treatment of wood is an effective physical mean to improve utilization of wood materials. It can improve size stability, corrosion resistance and weather resistance of woods. Furthermore, heat processing of wood materials adds no chemical components and thereby has high significance of environmental protection. Different colors of heat-treatment woods could be gained, and even precious wood materials can be simulated by adjusting carbonization temperature and time of heat process. This is able to realize diversity of products and increase its added value (Ferrari et al. 2013, Ozcan et al. 2012, Fang et al. 2012, Olek et al. 2013, Jalaludin et al. 2010).

Vapor was applied as the heat-conducting medium to prepare heat-treatment *Betula alnoides* in this study. Key attentions were paid to influences of heat-treatment on density, equilibrium moisture content, pH value, contact angle and bonding strength of *Betula alnoides*.

MATERIALS AND METHODS

Materials

Betula alnodies with a size of 130 × 50 × 20 mm and moisture content 8-10% were purchased for the preparation of glued wood. Polyvinyl acetate (PVAC) resin was obtained from Haoyao material Co., Ltd, China, whose molecular weight was about 50,000 and solid content was 50%. Melamine-urea-formaldehyde (MUF) resin with solid content 54% and viscosity 126 mPa·s was prepared in the lab. Chemical reagents used in this work were all in analysis grade.

Preparation of heat-treatment wood samples

Betula alnoides without cracks, corrosions and allochromatic defects were chosen and cut into the experiment required sizes. These wood samples were dried in a drying oven under 95°C for 4 days before the heat processing test.

Three-stage heat processing technique was used: the dry-bulb temperature was heated to 85°C and kept by 1 h to assure uniform heating of the wood. Next, the temperature was increased to the processing temperatures (160, 180, 200 and 220°C) at a rate of 10°C/h and then kept for a certain time (1 h and 2 h), followed by cooling and humidity adjustment. The wet-bulb temperature was adjusted to 70°C firstly and then it was adjusted to and kept at 95°C when the dry-bulb temperature exceeded 100°C. Samples were removed when the temperature was lower than 40°C. Samples were repeated by 10 times.

Test of heat-treatment wood samples

The *Betula alnoides* wood after heat processing was cut according to following requirements (Fig. 1). ① and ② were used to test the bonding strength according to the China National Standard GB/T 14074-2006 and samples were cut in 30 × 25 × 10 mm. ③ was applied for pH test, and the samples were pulverized into powder and then mixed with water at a mass ratio of 1:9 standing for 24 hours. ④ was used to density test according to the China National Standard GBT1933-2009, with a specification of 25 × 25 × 20 mm. ⑤ was used to test the equilibrium moisture content according to the China National Standard 1933-2009. ⑥ was applied to test a contact angle with a specification of 20 × 10 × 10 mm. Water was taken on the clean *Betula alnoides*, after stabilization, image of droplet was obtained by the microscope lens and camera of JC2000A static drop contact angle measuring instrument, and then the contact angle was measured by newjce2000 software.

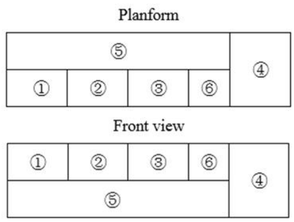

Fig. 1: Cutting diagram of heat-treatment wood.

Preparation of glued wood and the test of shear strength

The PVAC and MUF adhesives were used for the preparation of two-layer glued *Betula alnoides* with a dimension of 30 × 25 × 10 mm. The wood with double sides adhesive loading was 120 $g \cdot m^{-2}$ rested at room temperature for 15-20 min. The assembled samples were then sent into a single-layer hot press (XLB, Shanghai Rubber Machinery Plant) and pressed under a pressure of 1.5 MPa at 120°C for 10 min. A WDS-50KN mechanical testing machine from Shimadzu was used to shear strength of the glued specimens. The bonding strength was calculated from Eq. 1:

$$\sigma = P/S \quad \text{(MPa)} \tag{1}$$

where: P the glued area (kN),
S - bond area 625 (mm^2).

Fourier transform infrared spectroscopy (FT-IR)

0.001g *Betula alnoides* wood powder was mixed well with 1g KBr to prepare a pill. And then the pill was tested in an infrared spectrophotometer (Varian 1000, USA) within the range of 400-4 000 cm^{-1} with a 4 cm^{-1} resolution using 32 scans.

RESULTS AND DISCUSION

Effects of heat-treatment on equilibrium moisture content of wood

Effects of heat-treatment on equilibrium moisture content of *Betula alnoides* are shown in Fig. 2.

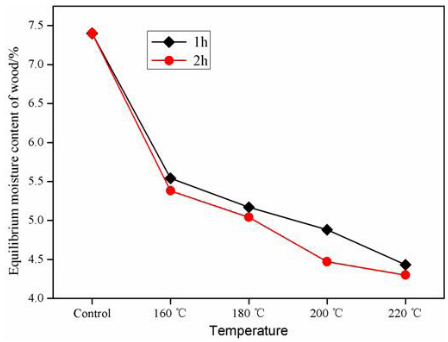

Fig. 2: Effects of heat-treatment on equilibrium moisture content of Betula alnoides.

The equilibrium moisture content of *Betula alnoides* was decreased significantly after the heat processing. Water in wood materials can be divided into chemically combined water, free water and absorbed water according to the bonding form and position with wood (Gunduz et al. 2008, Engelund et al. 2013). After heat processing, free water was volatilized completely, whereas some absorbed water and chemically combined water were eliminated. With the increase of heat processing temperature, more adsorbed water and chemically combined water were removed, thus decreasing moisture content in wood. Moisture content at different positions of wood materials might be different, thus resulting in different water loss after heat processing of wood.

Equilibrium moisture content of *Betula alnoides* at 2h and under 160, 180, 200 and 220°C were 5.38%, 5.04%, 4.47%, and 4.30%, respectively. They were 27.30%, 31.89%, 39.59% and 41.89 % lower than that of the control group (7.40%), indicating that heat processing decreased equilibrium moisture content of wood significantly.

It can be seen from Fig. 2 that given the same processing temperature, the equilibrium moisture content was similar as the processing time varies. The processing temperature had influence on equilibrium moisture content of *Betula alnoides* more significantly compared with processing time. This was because heat processing temperature was positively related with vapor pressure.

Effects of heat-treatment on wood density

Mechanical properties of wood materials are significantly related with density. During heat processing, temperature determines the pyrolysis degree during the heat processing, and carbonization time reflects the degree of pyrolysis. Hence, density of samples under different heat processing temperatures and time was different It can be seen from Fig. 3 that density of wood materials decreased gradually with the increase of heat-treatment temperature and heat-treatment time.

Wood densities under 160, 180, 200 and 220°C at 1 h were 5.16%, 7.12%, 7.81% and 9.71% lower than that of the control group, indicating the strong pyrolysis of wood in the temperature range of 160-180°C. Under the same heat processing temperature, wood density was almost the same the processing continues. In a word, heat-treatment temperature influences wood density more significantly than heat-treatment time.

Wood is a kind of high polymer materials composed mainly of hemicelluloses, celluloses and lignin. Hemicelluloses are the substance with the poorest thermostability among wood components. Few acetyl groups in hemicelluloses are pyrolyzed firstly during the heat processing, which the major cause of reduction of wood density. When heat-treatment temperature increased, most acetyl groups were split into acetic acids. The acetic acid concentration was increased with the increase of heat-treatment temperature and time, which further catalyzed structural changes or decomposition of lignin and celluloses. As a result, decomposition of chemical components in wood was strong and density was decreased gradually (Yao and Cai 2018, Hartley et al. 1992, Ding et al. 2015, Song et al. 2018). In addition, volatilization of volatile components like extract in wood was one of reasons of density reduction.

To sum up, there were complicated chemical changes in wood materials during the heat processing. The content of "real substances" in wood were decreased as a result of the degradation of hemicelluloses, few cellulose and lignin as well as volatilization of extracts, finally resulting in reduction of wood density.

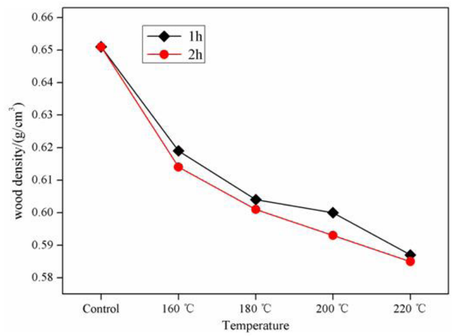

Fig. 3: Effects of heat-treatment on the wood density.

Effects of heat-treatment on pH value of wood

Effects of heat-treatment on pH value of *Betula alnoides* are shown in Fig. 4. pH value of wood was decreased gradually after the heat processing. In other words, acidity of wood materials increased after the heat processing. In the heat processing, extract and wood components were oxidized or decomposed into acetic acid and formic acid. The increase of non-volatile acid substances decreased pH value of *Betula alnoides*.

Heat processing time influenced pH value of wood more than heat processing temperature. This is because more acid substances were produced under high temperature. Under the same heat-treatment, decomposition of wood components was influenced slightly by heat-treatment time.

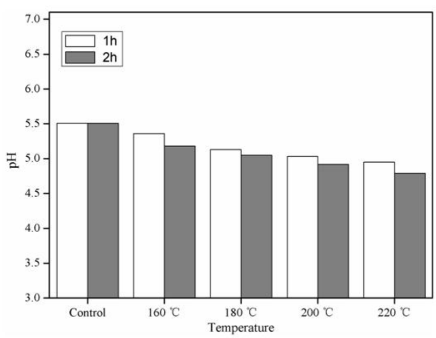

Fig. 4: Effects of heat-treatment on pH of wood.

Effects of heat-treatment on wettability of wood

Wood is a kind of wettable material. There are many free radicals on the surface, especially hydroxide radicals. Free radicals play a very important role in wetting of wood, thus influencing the contact angle indirectly. Effects of heat processing on contact angle of *Betula alnoides* were shown in Fig. 5.

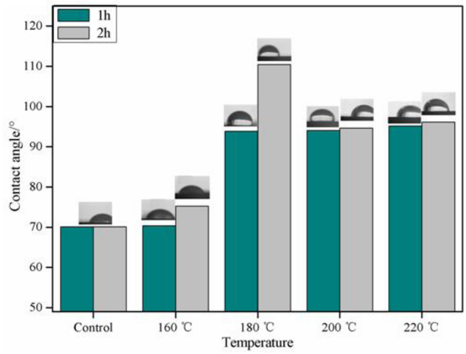

Fig. 5: Effects of heat-treatment on wettability of surface of Betula alnoides.

The contact angle of wood generally increased with the increase of heat-treatment temperature. Since the number of free radicals on wood surface decreased with the increase of temperature, surface wettability declined. Therefore, the higher temperature was, the larger contact angle would be. Contact angle of all woods after heat processing were higher than that of the control group. Moreover, the effects of heat processing time on contact angle of wood were smaller than heat processing temperature.

The liquid can be spread out completely on wood surface only when the surface tension of the liquid is equal to or lower than surface free energy of wood, which is manifested by a small contact angle. Wood is a kind of anisotropic material and its surface wettability is influenced by many factors. A series of physical and chemical changes were taken place in wood during the heat processing, which reduced the quantity of polar groups on wood surface and thereby decreased polarity of wood surface. Consequently, surface free energy of wood materials was decreased. In addition, moisture content, porosity, surface roughness and microscopic arrangement all may influence surface wettability of wood (Liu 2018, Yamauchi et al. 2005).

Effects of heat-treatment on bonding strength of wood

Effects of heat-treatment on bonding strength of *Betula alnoides* were shown in Fig. 6. Shear strength of both PVAC and MUF was decreased to different extents. The shear strengths of PVAC at heat processing 2 h under 160, 180, 200 and 220°C were 6.35 MPa, 6.14 MPa, 6.00 MPa and 4.56 MPa, which were 13.49 %, 16.35% 18.26% and 37.87% lower than that of the control group (7.34 MPa). Similarly, the shear strengths of MUF under 160, 180, 200 and 220°C were decreased by 13.85%, 24.77%, 35.85% and 53.85% compared with that of the control group.

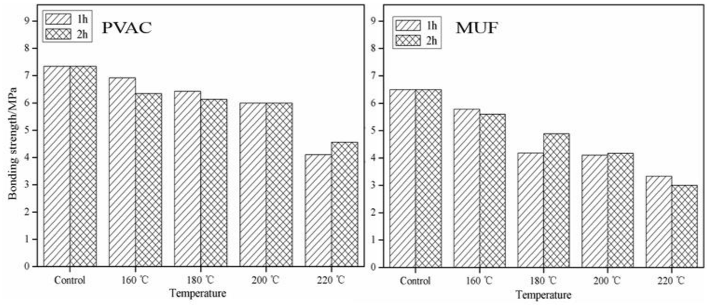

Fig. 6: Effects of heat-treatment on bonding strength of wood.

The reduction of bonding strength caused by heat processing might be attributed to following three reasons: (1) Bonding strength is closely related with strength of wood materials. After heat processing, the amorphous region composed of hemicelluloses and celluloses of wood materials was degraded after heat processing, so that wood density and strength decreased accordingly. Furthermore, translocation of lignin in processing increased brittleness of wood and thereby decreased bonding strength of wood. (2) Moisture content of wood materials influences bonding strength greatly. When the moisture content of wood was high, adhesives on wood surface was diluted and viscosity was decreased. Adhesives infiltrated into wood tissues excessively, this resulting in pure joints and decreasing the bonding strength. Long-time drying for wood under high temperature may cause excessive low moisture content, weaken wettability of adhesive and decrease bonding strength. PVAC and MUF are both water soluble adhesives. The reduction of equilibrium moisture content of *Betula alnoides* after heat processing can affect the wettability and permeability of PVAC and MUF on wood surface, which will further influence bonding performance of *Betula alnoides*. (3) pH value of wood materials influences curing degree of adhesives. PVAC was easy to be cured, while MUF resin could be cured completely under appropriate pH. After heat processing, acids were produced on wood surface, which might disturb curing of MUF. The bonding strength of MUF decreased with the deepening of heat processing.

FT-IR analysis

FT-IR results of non-processed wood (a) and processed *Betula alnoides* under 200°C (b) were compared in Fig. 7.

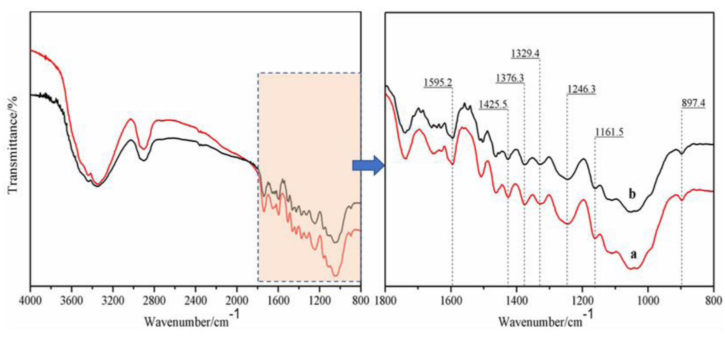

Fig. 7: FT-IR curves of Betula alnoides.(a) Betula alnoides wood (b) Betula alnoides wood with heat-treatment.

The absorption peak at about 1,425.5 cm^{-1} belonged to the stretching vibration of aromatic ring of lignin and the bending vibration of CH_3 in -OCH_3. This absorption peak decreased slightly after heat processing, which might be attributed to condensation reaction of lignin during the heat processing (Yin et al. 2017, Liu et al. 2019). The absorption peak at about 1,376.3 cm^{-1} was caused by bending vibration of CH in hemicelluloses and cellulose. This peak intensity was decreased after heat processing, indicating the degradation of polysaccharides in wood materials during the heat process. The absorption peak at about 1,329.4 cm^{-1} was caused by bending vibration of O-H of aliphatic series. This absorption peak was enhanced slightly after heat processing, which could be interpreted by depolymerization of lignin upon the condensation reaction of wood materials. Some β-aryl oxide bonds in lignin was depolymerized into carbocations in the heat processing and these carbocations further made condensation reaction under the catalysis of acetic acids produced from degradation of hemicelluloses under high temperature (Sivonen et al. 2002). The absorption peak at about 1,246.3 cm^{-1} belonged to hydroxyls and methoxy groups which connected with phenyl groups. This peak intensity decreased after heat processing, indicating that lignin experienced demethoxy reactions during the heat processing and it was also verified by the conclusions of Wikberg (Wikberg and Maunu 2004).

CONCLUSIONS

Heat-treatment woods of *Betula alnoides* were prepared by using vapor as the heat-conducting medium. Effects of heat-treatment time and heat-treatment temperature on equilibrium moisture content, density, pH value, contact angle and bonding performance of *Betula alnoides* were discussed in this paper. The results indicated that:

(1) With the increase of heat-treatment temperature, the equilibrium moisture content, density and pH value of *Betula alnoides* decreased gradually.

(2) With the increase of heat-treatment temperature, the contact angle of *Betula alnoides* increased from 70.08° to about 100°, resulting in the reduction of bonding strength gradually. Bonding strength of *Betula alnoides* after heat-treatment was related with the used adhesive. Bonding strength of different adhesives decreased to different extents. The bonding strength of *Betula alnoides* wood with PVAC resin was generally higher than that of MUF resin. The former were 6.35-4.56 MPa, and the latter were 5.60-3.00 MPa.

(3) Heat-treatment time influenced equilibrium moisture content, density, contact angle, pH value and bonding strength of *Betula alnoides* less than heat-treatment temperature.

(4) Heat-treatment could affect strength and surface performance of *Betula alnoides* greatly and the processing medium should be extended.

ACKNOWLEDGMENTS

This work was supported by First-class Discipline Construction Project in Guizhou Province (GNYL[2017]007), Science-technology Support Foundation of Guizhou Province of China ([2019]2308 and [2019]2325), National Natural Science Foundation of China (31800481), Forestry Department Foundation of Guizhou Province of China ([2017]14 and [2018]13).

REFERENCES

1. Bal, B.C., 2014: Some physical and mechanical properties of thermally modified juvenile and mature black pine wood. European Journal of Wood and Wood Products 72(1): 61-66.
2. Boonstra, M., Acker, J., Kegel, E., Sttevens, M., 2007: Optimisation of the two-stage heat treatment process: durability aspects. Wood science and technology 41(1): 31-57.
3. Cao, Y., Lu, J., Huang, R., Jiang, J., 2012: Increased dimensional stability of Chinese fir through steam-heat treatment. European Journal of Wood and Wood Products 70(4): 441-444.
4. Dilik, T., Hiziroglu, S., 2012: Bonding strength of heat treated compressed Eastern redcedar wood. Materials & Design 42: 317-320.
5. Ding, T., Gu, L.B., Cai, J.B., 2015: Effects of heat treatment on the moisture adsorption characteristic and dimensional stability of wood. Journal of Nanjing Forestry University 39(2): 143-147.
6. Engelund, E.T., Thygesen, L.G., Svensson, S., Hill, C.A., 2013: A critical discussion of the physics of wood-water interactions. Wood Science and Technology 47(1): 141-161.
7. Esteve, B.M., Pereira, H.M., 2009: Wood modification by heat treatment: a review. BioResources 4(1): 370-404.
8. Fang, C.H., Mariotti, N., Cloutier, A., Koubaa, A., Blanchet, P., 2012: Densification of wood veneers by compression combined with heat and steam. European Journal of Wood and Wood Products 70(1-3): 155-163.
9. Ferrari, S., Cuccui, I., Allegretti, O., 2013: Thermo-vacuum modification of some European softwood and hardwood species treated at different conditions. BioResources 8(1): 1100-1109.
10. Gunduz, G., Niemz, P., Aydemir, D., 2008: Changes in specific gravity and equilibrium moisture content in heat-treated fir (*Abies nordmanniana subsp. bornmulleriana* Mattf.) wood. Drying Technology 26(9): 1135-1139.
11. Hartley, I.D., Kamke, F.A., Peemoeller, H.,1992: Cluster theory for water sorption in wood. Wood Science and Technology 26(2): 83-99.
12. Jalaludin, Z., Hill, C.A., Xie, Y.J., Aamsi, H.W., Husain, H., Awang, K., Curling, S.F., 2010: Analysis of the water vapour sorption isotherms of thermally modified acacia and sesendok. Wood Material Science & Engineering 5(3-4): 194-203.
13. Liu, X.H., 2018: The main factors affecting temperature change of mat during the manufacturing process of thermoplastic resin plywood. Journal of Forestry Engineering 3(2): 35-39.
14. Kaygin, B., Gunduz, G., Aydemir, D., 2009: The effect of mass loss on mechanic properties of heat-treated paulownia wood. Wood Research 54(2): 101-108.
15. Olek, W., Majka, J., Czajkowski, L., 2013: Sorption isotherms of thermally modified wood. Holzforschung 67(2): 183-191.
16. Liu, M.L., Li C.F., Liu, Y.L., 2019: Physical and mechanical properties of modified poplar wood by heat treatment and impregnation of sodium silicate solution. Wood Research 64(1): 145-154.
17. Ozcan, S., Ozcifci, A., Hiziroglu, S., Toker, H., 2012: Effects of heat treatment and surface roughness on bonding strength. Construction and Building Materials 33: 7-13.
18. Sernek, M., Boonstra, M., Pizzi, A., Despres, A., Gérardin, P., 2008: Bonding performance of heat treated wood with structural adhesives. Holz als Roh-und Werkstoff 66(3): 173-180.
19. Sivonen, H., Maunu, S. L., Sundholm, F., Jämsä, S., Viitaniemi, P., 2002: Magnetic resonance studies of thermally modified wood. Holzforschung 56(6): 648-654.

20. Song, L.L., Ren, H.Q., Wang, X.Z., Ma, J.M., Li, Y.C., Li, Y.J., Xu, B., 2018: Effect of high temperature saturated steam treatment on bamboo properties. Journal of Forestry Engineering 3(2): 23-28.
21. Tjeerdsma, B.F., Boonstra, M., Pizzi, A., Tekely, P., Militz, H., 1998: Characterisation of thermally modified wood: Molecular reasons for wood performance improvement. Holz als Roh-und Werkstoff 56(3): 149-153.
22. Wikberg, H., Maunu, S.L., 2004: Characterisation of thermally modified hard-and softwoods by 13C CPMAS NMR. Carbohydrate Polymers 58(4): 461-466.
23. Yamauchi, S., Iijima, Y., Doi, S., 2005: Spectrochemical characterization by FT-Raman spectroscopy of wood heat-treated at low temperatures: Japanese larch and beech. Journal of Wood Science 51(5): 498-506.
24. Yao, Q., Cai, J.B., 2018: Determination and analysis of moisture adsorption and desorption isotherms of heat-treated *Radiata pine*. Journal of Forestry Engineering 3(3): 35-41.
25. Yin, J.P., Yuan, T.Q., Lu, Y., Song, K.L., Li, H.Y., Zhao, G.J., Yin, Y.F., 2017: Effect of compression combined with steam treatment on the porosity, chemical composition and cellulose crystalline structure of wood cell walls. Carbohydrate Polymers 155: 163-172.

Zhigang Wu, Sicheng Chen, Meifen Tian, Lifen Li, Liping Yu
Guizhou University,
College of Forestry
Guiyang 550025
Guizhou
P.R. China

Xuedong Xi
University of Lorraine,
Enstib-Lermab 88051
Epinal
France

Jiankun Liang*
Kaili University
Qiandongnan 556011
Guizhou
P.R. China

Bengang Zhang, Hong Lei*, Jun Zhang, Taian Chen
Southwest Forestry University
Yunnan Provincial Key Laboratory of Wood Adhesives and Glued Products
Kunming 650224
Yunnan
P.R. China
*Corresponding author: 1002469654@qq.com, fxgirl@163.com and dushimensheng@126.com