Static Bending Strength of Heat-Treated and Chromated Copper Arsenate-Treated Plywood

Bruno Santos Ferreira,[a,*] João Vitor Felippe Silva, [b] and Cristiane Inácio de Campos [a]

Plywood can be used in the furniture industry and in civil construction due to its structural strength. However, for long useful life in construction, especially in tropical countries, it needs to undergo treatments against xylophagous organisms. The most common preservative treatment is the chemical chromated copper arsenate (CCA); there are alternatives, such as heat treatment, that do not use chemicals. The objective of this work was to evaluate the mechanical resistance of CCA and heat-treated plywood prepared at three different temperatures (160 °C, 180 °C, and 200 °C). *Pinus taeda* plywood with seven veneers and phenol-formaldehyde adhesive was produced and subjected to the preservative treatments. The results showed that the CCA treatment reduced the mechanical strength of the panels, while the heat treatment did not. Heat treatment also decreased panel hygroscopicity, indicating a better dimensional stability.

Keywords: Wood panel; Mechanical strength; Wood treatment; Phenol-formaldehyde

Contact information: a: Department of Mechanical Engineering, São Paulo State University (UNESP), Avenida Ariberto Pereira da Cunha, 333, Guaratinguetá/SP, Brazil; b: São Paulo State University (UNESP), Campus of Itapeva, Rua Geraldo Alckmin, 519, Itapeva/SP, Brazil;
** Corresponding author: Bruno Santos Ferreira (brunosferreira88@gmail.com)*

INTRODUCTION

Plywood is a manufactured wood product made of wooden sheets bonded in an odd number of layers, where the grain direction is perpendicular between adjacent layers. It can be used both in production of furniture and in construction. Due its structural characteristics, this wood board is used in wood frame construction, mainly for closing wall surfaces. However, for its use in construction in the tropical climate of Brazil, plywood needs to undergo treatments to preserve and stabilize it, as it is more exposed to xylophagous organism attacks and the effects of humidity and temperature.

Thermal treatment is an alternative preservation method that does not use chemical compounds and, therefore, is more ecologically friendly. This treatment uses temperature alone to promote a controlled degradation of wood, particularly the hemicelluloses, which may improve some of its properties (Sandberg *et al*. 2012; Candelier *et al.* 2016). During thermal treatment, hemicelluloses are degraded faster than cellulose, due to their lower thermal stability, which is generated by their amorphous nature (lack of crystallinity) and lower molecular weight (Yildiz *et al.* 2006; González-Peña *et al.* 2009). The degradation of the hemicelluloses is more accentuated at 190 °C, whereas the effect on the cellulose increases above 220 °C, when crystalline cellulose is degraded (Kačíková *et al.* 2013).

Windeisen *et al.* (2007) demonstrated a decrease in the aliphatic hydroxyl groups during thermal treatment, occurring mainly at the highest temperature of 200 °C. At this temperature, the amount of aliphatic hydroxyls was reduced to 60%. This decrease is due to oxidation and dehydration reactions that occurred at higher temperatures. Theoretically, the availability of the OH groups of the hemicelluloses has the most significant effect on the physical properties of the wood. The thermal treatment decreases the water reception, so the cell wall absorbs less water due the decreasing amount of hydroxyl. As a consequence of the reduction of hydroxyl groups, swelling and retraction are decreased (Gündüz *et al.* 2008).

The major consequence of thermal treatment in wood is improved dimensional stability due to hemicellulose degradation, which occurs through dehydration reactions and destruction of hydroxyl groups. The degradation of hemicelluloses, which is the most hydrophilic polymers of wood due to its amorphous structure and large amount of hydroxyl groups, decreases the affinity between wood and water and increases wood dimensional stability (Weiland and Guyonnet 2003). The reduction of hygroscopicity and, consequently, improvement of dimensional stability is also due to a steadier and inelastic lignin macromolecule that experiences crosslinking and condensation reactions after thermal treatment (Tjeerdsma *et al.* 1998). Lignin molecules surround cellulose microfibrils, and as its structure is more rigid, cause the swelling of cellulose microfibrils to decrease and, consequently, their ability to absorb water.

Another property of wood that changes with thermal treatment is surface roughness. In a study by Kamdem *et al.* (2002), the reduction of the surface roughness of thermally treated wood was significant. Unsal and Ayrilmis (2005) show that the surface roughness of *Eucalyptus camaldulensis* wood was reduced with the increase in temperature and time of the thermal treatment, reaching 27.9% decrease in roughness at 180 °C after a treatment of 10 hours. Gunduz *et al.* (2008) and Salca and Hiziroglu (2014) also found the same conclusion for different species; increased temperature and time of thermal treatment decrease the superficial roughness of wood.

The heat treatment also modifies the wood color, making it darker. Such a color change may be due to by-products of the degradation of the hemicelluloses and the formation of oxidation products, such as quinones (Esteves *at al.* 2008; Kocaefe *et al.* 2008). The wood color is also modified by different kinds of thermal treatment as reported by Teacă *et al.* (2013) and Bonifazi *et al*. (2015).

Despite the improvement of physical properties, some mechanical properties of wood are decreased with the increase of time and temperature of treatment (Yildiz *et al.* 2006; Korkut *et al.* 2008a,b; Gunduz *et al.* 2009; Poncsak *et al.* 2011; Kačíková *et al.* 2013; Salca and Hiziroglu 2014).

However, thermal treatment increases the resistance of wood to fungus attack *via* the formation of compounds that act as fungicides. These compounds are derived from thermal decomposition of cellulose, but mainly from hemicelluloses, which are decomposed at lower temperatures (Weiland and Guyonnet 2003). The decomposition of hemicelluloses contributes greatly to the reduction of the fungus attack, as they are the most easily digested wood molecules for fungi (Tjeerdsma *et al.* 1998; Hakkou *et al.* 2006; Boonstra *et al.* 2007; Windeisen *et al.* 2007; Brosse *et al.* 2010).

Due to this improved dimensional stability and resistance to fungal attack, this study considered the thermal treatment of plywood boards to be used in wood frame construction for closing of wall surfaces, ceilings, and floors. Therefore, this study evaluated the effect of thermal treatment on bending strength of *Pinus taeda* plywood panels with or without treatment with chromated copper arsenate (CCA).

EXPERIMENTAL

Materials

The materials used to produce plywood were *Pinus taeda* wood veneers with dimensions of 450 mm × 450 mm × 2.3 mm and phenol formaldehyde adhesive. The wood aged 20 years came from Imbituva in Paraná State, Brazil.

In the produced panels, heat treatment was conducted in three different temperatures and the CCA chemical treatment; plywood without treatment was the control. In total, there were five different conditions, and for each, four panels were produced. The production processes of plywood and treatments are described below.

Plywood Production

Initially, the veneers were dried in a laboratory oven until the moisture content became stabilized at 3%. Subsequently, the phenol-formaldehyde adhesive was applied in the weight of 395 g/m^2 in a double glue line. This adhesive was prepared with a blend of phenol-formaldehyde resin, wheat flour, and water in proportions of 100:10:10, respectively. The resin used had 62% solids content, pH 11, and viscosity of 415 cP.

Seven veneers were superimposed per panel, which, after assembly, were cold pre-pressed in a manual press with a pressure of 1 kgf/cm^2 to remove excess air, avoiding the formation of bubbles in the next process. Afterwards, the slides were hot pressed with a pressure of 10 kgf/cm^2 and a temperature of 180 °C for 10 min, resulting in a plywood with a nominal thickness of 16 mm. The pressing time was divided into three pressing cycles with 3 min each and 30 seconds of pressure relief between cycles.

Heat Treatment

The heat treatment was performed in a laboratory oven without air replacement. The panels were stacked in the oven with the use of partitions, so that all surfaces were in direct contact with the temperature. Thereafter, the heating process was started at a rate of 2.6 °C/min, until the temperature specified for each treatment (160 °C, 180 °C, and 200 °C) was reached. The heating time was approximately 52 min for the temperature of 160 °C, 60 min for the temperature of 180 °C, and 68 min for the temperature of 60 °C. When the required temperature was reached, the heat treatment process was started for 60 min for all conditions. The oven was then turned off, and the panels remained inside for an additional 30 min for cooling.

Preservative Treatment with CCA

The chemical treatment with CCA was performed in an autoclave by the full cell method. CCA type C was composed of 47.5% CrO_3, 18.5% CuO, and 34% As_2O_5, with a solution concentration of 1.6%.

The full cell process consisted of the three stages described below:

1st stage - initial vacuum of 560 mmHg for 30 min to remove air from the wood pores to facilitate penetration of the CCA solution. The autoclave cylinder was filled.

2nd stage - 12 kgf/cm^2 pressure was applied for a period of 60 min to promote the penetration of the solution into the wood.

3rd stage - final vacuum after removal of the solution from the cylinder. At this stage, the material was again subjected to a vacuum of 560 mmHg for 15 min to remove excess solution from the surface of the wood.

After the CCA treatment, the panels were dried outdoors until the moisture stabilized at approximately 12%.

Tests and Results Analysis

Density, moisture content, and static bending tests for the determination of the modulus of rupture (MOR) and modulus of elasticity (MOE) were performed according to NBR 9485 (2011), NBR 9484 (2011), and NBR 9533 (2012), respectively. Ten specimens were used per condition for tests of moisture content and density, and four specimens per condition for static bending. The results were submitted to analysis of variance and the Tukey test at a significance level of 5% using software R version 3.3.1 (2016).

RESULTS AND DISCUSSION

Table 1 shows the mean values of density and moisture content for each condition. The treatments did not influence the density of the panels. However, heat treatment at 180 °C and 200 °C reduced the final moisture content, compared with the control and 160 °C samples, which did not differ from each other. This result reflects that heat treatment reduces the hygroscopicity of the wood, mainly due to the degradation of the hemicelluloses at these higher temperatures, causing it to absorb less water (Tjeerdsma *et al.* 1998; Weiland and Guyonnet 2003; Gunduz *et al.* 2008). The highest moisture content was presented by the panel treated with CCA. This type of treatment, where the panel was immersed in an aqueous solution, caused greater absorption of water and, consequently, a higher moisture content.

Table 1. Mean Values of Density and Moisture Content for Each Condition

Condition	Density (g/cm^3) (mean & coefficient of variation)	Moisture Content (%) (mean & coefficient of variation)
Control	0.65 **a**[1]	12.53 **a**
	4.61%[2]	0.03%
160°C	0.66 **a**	12.12 **a**
	7.57%	7.75%
180°C	0.67 **a**	11.30 **b**
	5.97%	0.35%
200°C	0.68 **a**	10.46 **c**
	11.76%	3.44%
CCA	0.66 **a**	16.08 **d**
	0.03%	0.03%

[1] Means followed by equal letters present no statistical difference (Tukey, $\alpha = 0.05$)
[2] Coefficient of variation of the data

Table 2 presents the results of parallel and perpendicular static bending for all conditions. The MOR values were not significantly different among the treatments tested, only for the parallel MOE, where the CCA presented a lower value. Therefore, the heat treatment up to 200 °C did not decrease the bending strength of the plywood. Thus, this treatment can be used to improve the dimensional stability of the panel without influencing its mechanical properties. In the panel treated with CCA, there was a decrease in the parallel MOE compared with all other treatments, so this treatment decreased the mechanical resistance of the panel. Thus, where resistance against fungal attack is required, the heat treatment can replace the CCA without loss of mechanical resistance.

Table 2. Mean Values of MOE and MOR in Static Bending

Condition	MOR (MPa) Parallel	MOE (MPa) Parallel	MOR (MPa) Perpendicular	MOE (MPa) Perpendicular
Control	59.93 a[1]	8957 a	32.89 a	3624 a
	12.25%[2]	5.95%	3.47%	3.70%
160 °C	61.03 a	8564 a	31.73 a	3417 a
	14.99%	10.63%	15.38%	12.91%
180 °C	56.62 a	8248 a	28.55 a	3155 a
	26.44%	7.89%	12.78%	13.03%
200 °C	44.29 a	8150 a	27.62 a	3094 a
	6.50%	19.06%	12.09%	16.13%
CCA	40.50 a	5837 b	25.75 a	2835 a
	22.79%	21.16%	14.52%	15.55%

[1] Means followed by equal letters present no statistical difference (Tukey, $\alpha = 0.05$)
[2] Coefficient of variation of the data

CONCLUSIONS

1. Heat-treated plywood showed no decrease in mechanical properties but a decrease in panel hygroscopicity, indicating improvements in dimensional stability.
2. The CCA treatment increased the moisture content of the panel and decreased its mechanical resistance. Therefore, it did not present good results in any of the cases.
3. The substitution of the CCA treatment by the heat treatment, especially at 200 °C, where there is a greater resistance to fungal attack, is promising because it does not use chemicals and is less harmful to the environment than CCA.

ACKNOWLEDGMENTS

The authors are grateful for the support of the coordination for the Improvement of Higher Education Personnel (CAPES) – Brazil.

REFERENCES CITED

Bonifazi, G., Calienno, L., Capobianco, G., Lo Monaco, A., Pelosi, C., Picchio, R., and Serranti, S. (2015). “Modelling color and chemical changes on normal and red heart beech wood by reflectance spectrophotometry, Fourier Transform infrared spectroscopy and hyperspectral imaging”, *Polymer Degradation and Stability* 113, 10-21. DOI: 10.1016/j.polymdegradstab.2015.01.001

Boonstra, M. J., Van Acker, J., Kegel, E., and Stevens, M. (2007). "Optimisation of a two-stage heat treatment process: Durability aspects," *Wood Science and Technology* 41(1), 31-57. DOI: 10.1007/s00226-006-0087-4

Brosse, N., El Hage, R., Chaouch, M., Pétrissans, M., Dumarçay, S., and Gérardin, P. (2010). "Investigation of the chemical modifications of beech wood lignin during heat treatment," *Polymer Degradation and Stability* 95(9), 1721-1726. DOI: 10.1016/j.polymdegradstab.2010.05.018

Candelier, K., Thevenon, M.-F., Petrissans, A., Dumarcay, S., Gerardin, P., and Petrissans, M. (2016). "Control of wood thermal treatment and its effects on decay resistance: a review", *Annals of Forest Science* 73(3), 571–583. DOI: 10.1007/s13595-016-0541-x

Esteves, B., Graça, J., and Pereira, H. (2008). "Extractive composition and summative chemical analysis of thermally treated eucalypt wood", *Holzforschung* 62, 344–351. DOI: 10.1515/HF.2008.057

González-peña, M. M., Curling, S. F., and Hale, M. D. C. (2009). "On the effect of heat on the chemical composition and dimensions of thermally-modified wood," *Polymer Degradation and Stability* 94(12), 2184-2193. DOI: 10.1016/j.polymdegradstab.2009.09.003

Gunduz, G., Aydemir, D., and Karakas, G. (2009). "The effects of thermal treatment on the mechanical properties of wild Pear (Pyrus elaeagnifolia Pall.) wood and changes in physical properties," *Materials and Design* 30(10), 4391-4395. DOI:10.1016/j.matdes.2009.04.005

Gunduz, G., Korkut, S., and Korkut, D. S. (2008). "The effects of heat treatment on physical and technological properties and surface roughness of Camiyani Black Pine (*Pinus nigra* Arn. subsp. pallasiana var. pallasiana) wood," *Bioresource Technology* 99(7), 2275-2280. DOI: 10.1016/j.biortech.2007.05.015

Hakkou, M., Pétrissans, M., Gérardin, P., and Zoulalian, A. (2006). "Investigations of the reasons for fungal durability of heat-treated beech wood," *Polymer Degradation and Stability* 91(2), 393-397. DOI: 10.1016/j.polymdegradstab.2005.04.042

Kačíková, D., Kačík, F., Čabalová, I., and Ďurkovič, J. (2013). "Effects of thermal treatment on chemical, mechanical and colour traits in Norway spruce wood," *Bioresource Technology* 144, 669-674. DOI: 10.1016/j.biortech.2013.06.110

Kamdem, D. P., Pizzi, A., and Jermannaud, A. (2002). "Durability of heat-treated wood," *Holz als Roh - und Werkstoff* 60(1), 1-6. DOI: 10.1007/s00107-001-0261-1

Kocaefe, D., Poncsak, S., and Boluk, Y. (2008). "Effect of thermal treatment on the mechanical composition and mechanical properties of birch and aspen," *BioResources* 3(2), 517-537. DOI: 10.15376/biores.3.2.517-537

Korkut, S., Kök, M. S., Korkut, D. S., and Gürleyen, T. (2008a). "The effects of heat treatment on technological properties in Red-bud maple (Acer trautvetteri Medw.) wood," *Bioresource Technology* 99(6), 1538-1543. DOI: 10.1016/j.biortech.2007.03.038

Korkut, S., Akgül, M., and Dündar, T. (2008b). "The effects of heat treatment on some technological properties of Scots pine (Pinus sylvestris L.) wood," *Bioresource Technology* 99(6), 1861-1868. DOI: 10.1016/j.biortech.2007.03.038

NBR 9484. (2011). "Compensado: determinação do teor de umidade," Associação Brasileira de Normas Técnicas (ABNT), Rio de Janeiro, Brazil.

NBR 9485 (2011). "Compensado: determinação da massa específica aparente," Associação Brasileira de Normas Técnicas (ABNT), Rio de Janeiro, Brazil.

NBR 9533 (2012). “Compensado: determinação da resistência à flexão estática,” Associação Brasileira de Normas Técnicas (ABNT), Rio de Janeiro, Brazil.
Poncsak, S., Kocaefe, D., and Younsi, R. (2011). “Improvement of the heat treatment of Jack pine (*Pinus banksiana*) using ThermoWood technology,” *European Journal of Wood and Wood Products* 69(2), 281-286. DOI: 10.1007/s00107-010-0426-x
R Core Team (2016). “R: A language and environment for statistical computing,” *R Foundation for Statistical Computing*, Vienna, Austria, (https://www.R-project.org/).
Salca, E. A., and Hiziroglu, S. (2014). “Evaluation of hardness and surface quality of different wood species as function of heat treatment,” *Materials and Design* 62, 416-423. DOI: 10.1016/j.matdes.2014.05.029
Sandberg, D., Haller, P., and Navi, P. (2012). “Thermo-hydro and thermo-hydro-mechanical wood processing: An opportunity for future environmentally friendly wood products,” *Wood Material Science & Engineering* 8(1). DOI: 10.1080/17480272.2012.751935
Teacă, C.A., Roşu, D., Bodîrlău, R., and Roşu, L. (2013). “Structural changes in wood under artificial UV light irradiation determined by FTIR spectroscopy and color measurements – A brief review,” *BioResources* 8(1),1478-1507. DOI: 10.15376/biores.8.1.1478-1507
Tjeerdsma, B. F., Boonstra, M., Pizzi, A., Tekely, P., and Militz, H. (1998). “Characterisation of thermally modified wood: molecular reasons for wood performance improvement,” *Holz als Roh- und Werkstoff* 56, 149-153. DOI: 10.1007/s001070050287
Unsal, O., and Ayrilmis, N. (2005). “Variations in compression strength and surface roughness of heat-treated Turkish river red gum (*Eucalyptus camaldulensis*) wood,” *Journal of Wood Science* 51(4), 405-409. DOI: 10.1007/s10086-004-0655-x
Weiland, J. J., and Guyonnet, R. (2003). “Study of chemical modifications and fungi degradation of thermally modified wood using DRIFT spectroscopy,” *Holz als Roh- und Werkstoff* . DOI: 10.1007/s00107-003-0364-y
Windeisen, E., Strobel, C., and Wegener, G. (2007). “Chemical changes during the production of thermo-treated beech wood,” *Wood Science and Technology* 41(6), 523-536. DOI: 10.1007/s00226-007-0146-5
Yildiz, S., Gezer, E. D., and Yildiz, U. C. (2006). “Mechanical and chemical behavior of spruce wood modified by heat,” *Building and Environment* 41(12), 1762-1766. DOI: 10.1016/j.buildenv.2005.07.017

Article submitted: May 8, 2017; Peer review completed: June 25, 2017; Revisions accepted: July 6, 2017; Published: July 17, 2017.
DOI: 10.15376/biores.12.3.6276-6282