PHYSICAL AND CHEMICAL PERFORMANCE OF EUCALYPTUS WOOD WITH IMPREGNATED CHEMICALS

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Methylolurea and carbamide were used to impregnate eucalyptus wood to improve its physical and chemical properties. The physical properties and dimensional stability were examined. TGA was used to evaluate the thermal stability of the wood. FTIR was used to state the changes of functional groups. The changes of wood structure were observed by SEM. The results showed the bending strength and compressive strength parallel to the grain increased by 15.10% and 16.78%, respectively. The basic density of modified wood was improved by 14.29%. The shrinkage of volume and swelling of volume were significantly decreased compared to the untreated wood. The TGA results indicated that the mass loss was around 8% during the second stage, from 120°C up to 280°C, while the mass loss of treated wood was around 4%. The treated wood exhibited LOI (limited oxygen index) values of about 42%, while the natural wood exhibited a LOI value of 22%. The FTIR analysis successfully showed that chemical bond was produced between wood and methylolurea as a result of chemical reaction between wood and methylolurea. The SEM results indicated that the transverse and tangential sections of the treated specimens were filled with the reaction products, which can prevent the absorption of moisture.

Keywords: Chemical modification; Eucalyptus; Methylolurea; Physical and Chemical performance

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INTRODUCTION

Eucalyptus species are widely planted all over the world, and the area of eucalypttus planting area reaches about 19.5 billion m^2 (Huang 2011). The majority of this resource has been used as wood chips. Chips can be considered as lower added-value products at present because solid wood products suffer from critical drying problems and low physical strength, such as deformation and cracks (Wu et al. 2006). Therefore, it is urgently important to overcome barriers to the development of higher added-value solid eucalypts wood products such as furniture, construction, flooring, decoration, and so on.

In order to prevent cracking of eucalyptus species during drying treatment and enhance the physical properties of natural eucalyptus wood, the species have been impregnated with water-based solutions of chemicals (Stamm 1977; Håfors 1990). The mechanism of stabilization mechanism involves the presence of the chemical molecules in the cell wall, where they reduce the extent of cell wall swelling and shrinkage due to variations in the moisture content in the drying. Hudson (1951) also discusses beneficial effects from chemical impregnation of wood in the green state, and points out that the surface appears flat and failure appears to be dominated by brittle fracture. Cracks may fail in individual cell wall layers, but they often grow between two layers. The weaker, non-impregnated dried specimens show a more brittle fracture surface appearance. For wood impregnated in the green state, the impregnating chemical in the cell wall substitutes for some of the moisture and therefore limits the drying stresses. As a consequence, damages are limited and more of the cell wall ultrastructure in green wood is preserved.

A method has been presented where green wood is impregnated using a solution of water and a bulking compound such as glycerol (Thuvander et al. 2001). Data demonstrate significantly higher strength for wood impregnated in the green state. Damage development during drying is also limited. This is because the impregnating chemical (glycerol in the present case) in the cell wall substitutes for some of the moisture and therefore limits the drying stresses. As green specimens were impregnated with glycerate and silver nitrate, silver was found to be evenly distributed throughout cross-sections of the cell wall. It was also found that the applied chemical treatment improves the wood properties such as resistance to dimensional stability (Karlsson et al. 2011). Various possible modification reactions are available. Chemicals used to modify wood include: anhydrides, acid chlorides, isocyanates, alkyl chlorides, lactones, nitryles, and epoxides (Kumar 1994; Rowell 1983; Hon 1996). In wood particles, chemical modification is mainly achieved through the reaction of the hydroxyl groups in the materials (Flaque 1991).

Santos (2000) argued that the chemical modification with PEG 1000 is accompanied by an increase of dimensional stability and liquid water repellence, at the expenses of some chemical composition degradation and strength properties; namely it is hardness and abrasion resistance that are reduced. Wood color becomes darker with the hydrolysis of hemicelluloses subjected to heat treatment (Ishiguri et al. 2005). The reaction takes place in the cell wall. The chemical modification of beech wood increased crystal conversion; however, in the case of pine wood the same process decreased the crystal conversion. Zhang (2006) showed that impregnation of methacrylates into sugar maple resulted in vessel and lumen filling. Brinell hardness and hardness modulus were generally enhanced through impregnation and in-situ polymerization. However, Gao and Li (2007) pointed out that the dimension stability and mechanical properties of wood treated by only acetone would be reduced because the acetone would disrupt the crystallinity of celluloses and the interface between cellulose and lignin.

In the present work we have carried out chemical modification of eucalyptus wood by methylolurea and carbamide. The impregnated wood was dried in a conventional drying kiln. The aim of this study was to evaluate the physical and chemical performance, including the physical properties and dimensional stability, thermal stability, the reactivity of the functional groups changes, and microstructure of natural and modified wood. These approaches have potential to become common in the wood industry, as it can not only increase competitiveness and cut cost, but also it can increase the added-value of the eucalyptus wood.

EXPERIMENTAL

Materials

The study was performed with eucalyptus (*E. grandis* × *E. urophylla*) wood obtained from Zhang Zhou, China, which were green logs. They had initial moisture contents that ranged from 60 to 70% before they were impregnated. The urea, formaldehyde, and ammonia were purchased from Shantou Xilong Chemical Plant as analytical pure compounds. The carbamide was purchased from Petrochina NingXia Petrochemical Company as an industrial pure grade.

Synthesis of Methylolurea

A three-necked flask was charged with urea, formaldehyde, and ammonia at a certain molar ratio (Pu et al. 2009a). The reaction mixture was stirred and heated to 30°C for 3 hours. Then, sodium hydroxide or hydrochloric acid was used to adjust the methylolurea in the range of pH 4 to 7. Finally, the reaction mixture was transferred into a container and sealed.

Pulse-dipping and Drying

The pulse-dipping machine can treat one wood species at a time. Six logs were impregnated in the experiment. The dimensions of the wood samples for impregnation were 22 cm in diameter and 100 cm in length. The modifier, carbamide (25 % w/w) and the methylolurea (15 % w/w), was impregnated into the fresh eucalyptus wood with the pulse - dipping machine at a pressure of 0.7 - 0.8 MPa for 30 min (Pu et al. 2009b). The retention value was more than 15 days under atmospheric conditions. After impregnation, the logs were sawn into blocks with dimension of 7cm (T) × 14cm (R) × 100cm (L) for a conventional drying kiln. It takes about 16 days for drying and the pressure on the timber is 0.4 MPa (Pu et al. 2009c; Wu et al. 2010). The impregnated samples were dried according to the drying schedule shown in Fig. 1. The figure shows the relative humidity and temperature of dry medium, temperature, and moisture content of wood. The natural samples were dried according to the drying schedules as reported in the literature (Wu et al. 2007).

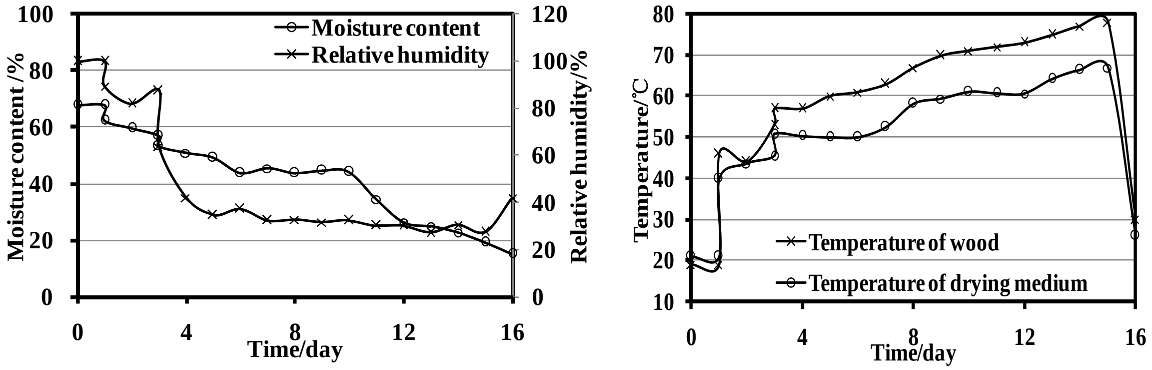

Fig. 1. The drying schedules for the impregnated specimens

Physical Properties and Dimensional Stability

Ten specimens of untreated and treated were analyzed with a universal mechanical testing machine (MWW-50). Tests were carried out according to GB/T 1936.1 - 91 (Method of testing in bending strength of wood, China), GB1936.2 - 91 (method for determination of the modulus of elasticity in static bending of wood, China), GB/T 1935 - 91 (Method of testing in compressive strength parallel to grain of wood, China), and GB/T 1933 – 91 (Method for determination of the density of wood, China). The dimensional stability was determined by GB1932-91 (Method for determination of the shrinkage of wood, China), GB1934.2-91 (Method for determination of the swelling of wood, China), GB1934.1-91 (Method for determination of the water absorption of wood, China). 15 specimens were measured for bending strength, the modulus of elasticity in static bending and compressive strength parallel to grain. 10 specimens were measured for the density of wood. 30 specimens were measured for shrinkage, water absorption, and swelling of wood.

Thermal and Flame Retardant Properties

The thermal stability was assessed with thermogravimetric analysis (TGA) carried out on a SHIMADZU TGA-60 instrument. The temperature range was from room temperature to 600°C at a heating rate of 20°C /min. These tests were carried out under nitrogen atmosphere (20 ml/min) in order to prevent thermoxidative degradations. α-Al_2O_3 was taken as the reference material. Limited oxygen index (LOI) of 15 samples was tested on an oxygen index instrument at room temperature on an oxygen index instrument (JF-3, Jiangning, China). The flame retardant property was measured according to the GB/T2406-93 (Plastics determination of flammability by oxygen index).

FTIR Characterization

FTIR spectra were measured directly from untreated and treated wood using a Tensor 27 (Bruker, Germany) device in the range of 4,000 to 400 cm^{-1}. Pellets were prepared from the mixtures of the samples and KBr (1:100 in weight). 32 scans were accumulated at a resolution of 2 cm^{-1}.

Scanning Electron Microscope

A JSM 5900 model scanning electron microscope (SEM) was used to observe the untreated and treated wood. Samples to be observed under the SEM were mounted on conductive adhesive tape, sputter coated with gold, and observed in the SEM using a voltage of 15 kV.

RESULTS AND DISCUSSION

Physical Properties and Dimensional Stability

The Mechanical and physical properties of specimens are shown in Table 1 and Table 2. Although there was significant scatter in the results, indicated by the standard deviations, it may be observed that the specimens treated with methylolurea exhibited high properties. Table 1 shows that the treated wood exhibited significantly higher bending strength and compressive strength parallel to the grain in comparison to the untreated wood samples. The bending strength, the modulus of elasticity in static bending, and compressive strength parallel to the grain increased by 30.20%, 15.10%, and 16.78% compared with the untreated wood samples.

Table 1. Mechanical Properties of Untreated and Treated Wood Specimens

Properties	Treated	Untreated	Improvement
Bending strength(MPa) (SD)	78.50 (6.31)	68.20 (7.72)	15.10
Modulus of elasticity in static bending (MPa) (SD)	13064 (134.23)	10034 (165.56)	30.20
Compressive strength parallel to the grain (MPa) (SD)	49.40 (1.52)	42.30 (1.93)	16.78

It can also be observed from Table 2 that the basic density of treated wood increased 14.29% compared with the untreated wood samples. And the oven-dried density of treated wood increased by 27.91%. The shrinkage of volume and swelling of volume values of less than 29.28% and 14.57% were obtained by treatment with methylolurea. This suggests that the methylolurea was deposited extensively into the wood cell wall and thus were effective in reducing the swelling of wood specimens during water immersion or drying in the kiln.

Table 2. Physical Properties of Untreated and Treated Wood Specimens

Properties	Treated	Untreated	Improvement
Basic density ($g{\cdot}cm^{-3}$) (SD)	0.48 (0.04)	0.42 (0.06)	14.29
Oven-dried density ($g{\cdot}cm^{-3}$) (SD)	0.55 (0.06)	0.43 (0.08)	27.91
Shrinkage of volume (%) (SD)	3.23 (0.19)	4.57 (0.28)	29.28
Swelling of volume (%) (SD)	9.87 (0.87)	11.56 (0.98)	14.57

The good dimensional stability is considered to be due to a bulking effect. Bulking agents can be used in order to limit dimensional changes of wood due to changes in the wood moisture content. The idea is to replace moisture in the cell wall with the bulking agent (Thuvander et al. 2001). The stabilization mechanism is that methylolurea is present in the cell wall in order to reduce the extent of cell wall swelling and shrinkage. Cross-linking reaction occurs between methylolurea and wood.

Water absorbance of the untreated and treated wood specimens is shown in Figs. 2 and 3. Results are shown for cold water immersion during 72 hrs. The water repellency was improved by the impregnation treatment. The water absorbance decreased from 77.7% to 73.09% according to statistical analysis. The dimensions of radial, tangential, and volume also dropped from 5.83%, 7.16%, and 13.12% to 5.37%, 6.34%, and 11.59%. The number of accessible hydroxyl groups in the wood increased the water absorption. However, the chemical modification reduced the hydroxyl groups and reduced the water absorption because of the crosslinking reaction between methylolurea and the wood (Wu et al. 2010).

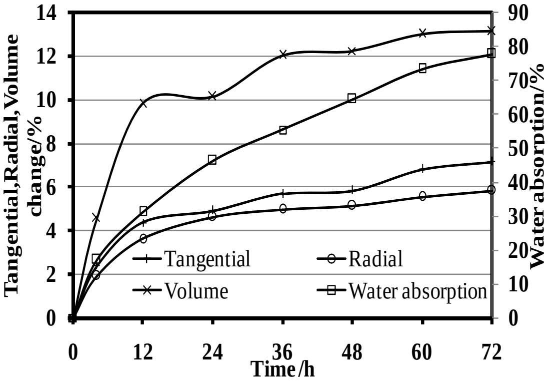

Fig. 2. Water absorption of untreated wood specimens

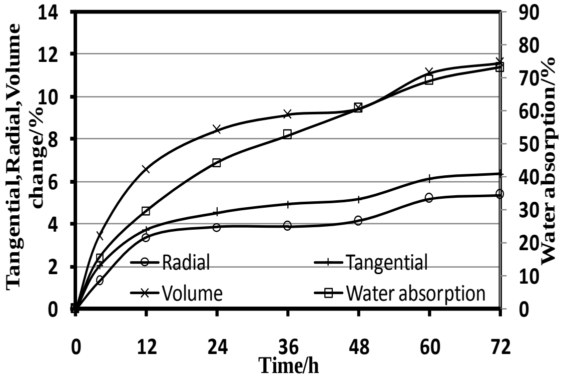

Fig. 3. Water absorption of treated wood specimens

The hygroscopicity was determined in an incubator with 65% relative humidity and 20°C according to GB1934.2-91 (Method for determination of the swelling of wood, China). Rectangular specimens were prepared having dimensions of 20 mm (L) × 20 mm (T) × 20 mm (R). The dimensions of radical, volume, tangential, and weight were taken. Figures 4 and 5 show the hygroscopicity and the radial, tangential, and volume swelling of untreated and treated wood specimens with initial moisture content of nearly 7%. The radial, tangential, and volume swelling of the treated samples were lower than those of the control samples. The values of untreated specimens were 3.33%, 3.87%, and 7.13%, respectively, at the end of 25 days, while the treated specimens were 3.26%, 3.43%, and 6.66%. The hygroscopicity decreased from 14.17% to 10.85%, which indicated that the specimens impregnated with methylolurea were less hydrophilic than the untreated specimens.

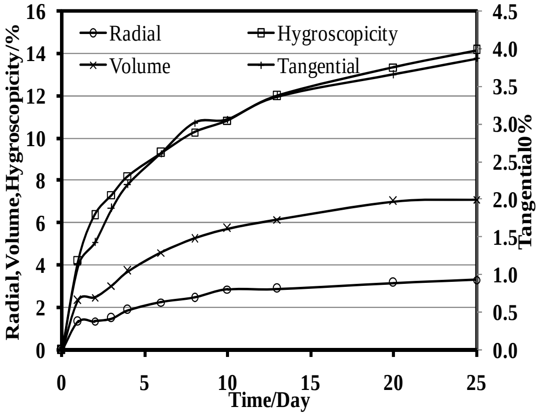

Fig. 4. Hygroscopicity of untreated wood specimens

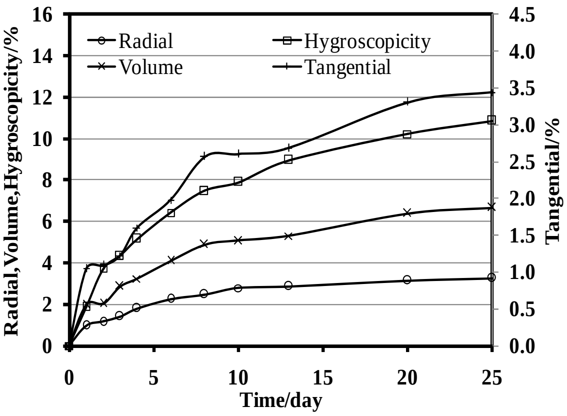

Fig. 5. Hygroscopicity of treated wood specimens

Thermal and Flame Retardant Properties

Representative TGA and DTA curves of the untreated wood and methylolurea treated samples with the initial moisture content of nearly 3% are shown in Fig. 6. The related experiments were carried out in flowing nitrogen from ambient temperature to 600°C. The TGA curves contained four stages. In Fig. 6 (b), the first step from the room temperature up to 120°C is a dehydration process. The mass losses during this process were in the range of 2 to 3%. After that, thermal decomposition of a wood sample depends very much on the oxygen partial pressure in the gas phase (Gao et al. 2006). Under a nitrogen atmosphere the mass loss was around 8% during the second stage, from 120°C up to 280°C. Mass loss was around 60% in a temperature range between 280°C and 380°C, and an additional 30% from 380°C to 600°C. The former is mainly ascribed to thermal degradation of hemicellulose and cellulose fibers, and corresponds mainly to hemicelluse and cellulose decomposing into char residues and CO_2, CO, CH_4, CH_3OH, and CH_3COOH. Lignin degradation occurred when the temperature rose to 380°C.

According to Fig. 6 (a), the thermal stability of treated specimens improved compared to the control specimens. The mass loss of treated wood was around 4% in the second stage. In particular, the mass loss and the maximum rate of mass loss at this stage were decreased obviously. Nearly 60% of mass also exhibited degradation in the temperature range between 280°C and 380°C. The mass loss of the treated was slower than the untreated specimens, which showed that the treatment can enhance the thermal stability within the temperature range of 280°C to 380°C. Figure 6 also shows that the temperature of the maximum rate of mass loss of the treated wood was lower than the untreated wood. In particular, the mass loss and the maximum rate of mass were decreased a little.

The flame retardant properties of the wood were further examined by measuring their limited oxygen index (LOI). The treated wood exhibited LOI values of about 42%, while the natural wood exhibits a LOI value of 22%. The LOI values of these cured carbamide and methylolurea are high enough to be considered flame retardant systems. The impregnated chemicals not only can improve the physical properties and dimensional stability, but also can enhance the thermal stability and flame retardant.

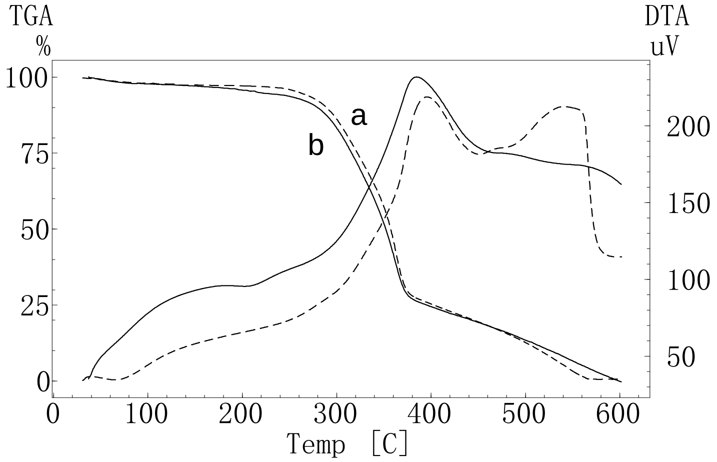

Fig. 6. TGA and DTA curves of wood specimens
(a-The treated specimens b-The untreated specimens)

FTIR Characterization

Figure 7 shows the infra-red spectra of treated and untreated wood. The FTIR spectrum of untreated specimens shows the presence of bands at 3400 cm^{-1} for -OH stretching, 2927 cm^{-1} and 2852 cm^{-1} for -C-H stretching of modifying hydrocarbon, 1619 cm^{-1} for -OH bending, 1738 cm^{-1} (C=O stretching), and 1261 cm^{-1} (C-O stretching) (Devi and Maji 2011). The FTIR spectrum of treated specimens showed a significant reduction in the -OH absorbance at 3400 cm^{-1}, and the -OH stretching peak of treated wood shifted slightly to a lower wavenumber, which indicated that reaction occurred between the -OH of wood and the CO-NH_2 of methylolurea.

Further evidence of such reaction consists of an observed enhancement of dimensional stability. The interaction between wood and methylolurea was also confirmed, as indicated by an enhanced peak at 1738 cm$^{–1}$ in the carbonyl region after the reaction with methylolurea.

The peak (around 1457 cm$^{–1}$) which may be due to C-H deformation (methyl and methylene) was found to increase in the case of methylolurea-treated samples compared to untreated samples. The peak around 1610 cm$^{–1}$, which is due to aromatic skeletal vibration and carbonyl stretching, was found to be more pronounced in the case of methylolurea treated samples compared to that of untreated ones. The absorption peak at 1665 cm $^{-1}$ is amide (N-C=O), which is due to the bond between the function groups of -$NHCH_2OH$ of methylolurea and the wood carboxyl C=O.

As wood temperature increases in the drying process, chemical bonding is produced between wood and methylation as a result of chemical reaction between wood and methylolurea. On the other hand, polymerization occurs easily among the methylolurea entities along with higher temperature and lower moisture content of timber. A stereo reticulation structure was built within the wood's internal void structure and filled in the amorphous regions, which can shield hydroxyl groups located within the timber. The dimension stability improved with the decreasing hydroxyl content.

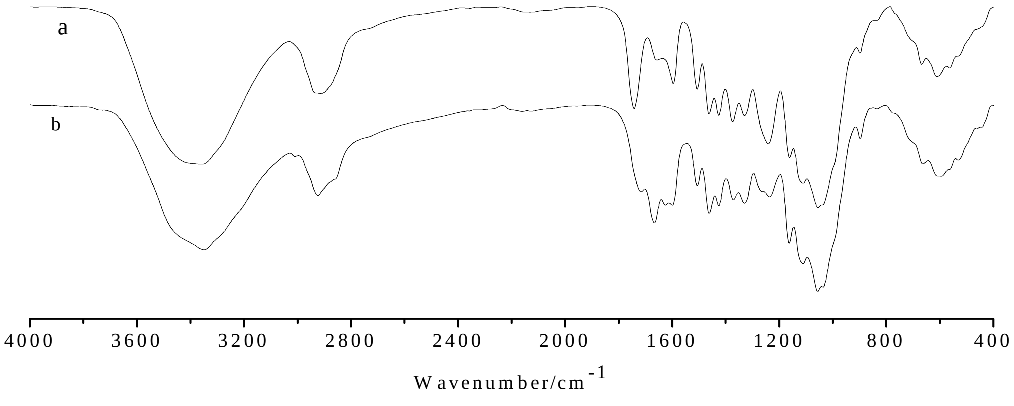

Fig. 7. FTIR curves of untreated wood specimens
(a-Treated wood specimens b-Untreaed wood specimens)

Scanning Electron Microscopy

Figure 8 shows the SEM micrographs of untreated and treated wood specimens. For the transverse and tangential sections of the untreated specimens, the empty cell lumen, the pit, and parenchyma are seen. In the treated wood, these empty spaces were occupied by the reaction product. The chemical reaction products between the wood and the methylolurea penetrated into the cell wall and were large in quantity, indicating an important contribution to the dimensional stability. The surface of treated wood was smoother than that of untreated wood. The reason may be that the monomer mixture was penetrated into the cell wall and vessels of wood. The small particles in vessels of treated wood may be the carbamide and methylolurea precipitated during the wood drying process.

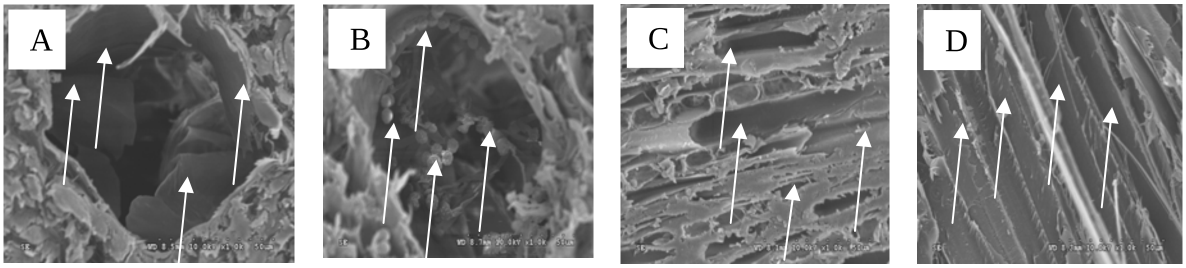

Fig. 8. SEM micrographs of natural and modified wood: A -Transection of untreated; B - Transection of treated; C - Tangential section of untreated; D - Tangential section treated

CONCLUSIONS

The physical properties of eucalyptus wood were improved. The basic density, oven-dried density, bending strength, and compressive strength parallel to the grain increased by 14.29%, 27.91%, 15.10%, and 16.78% as result of impregnation with methylolurea and carbamide.

The shrinkage of volume and swelling of volume values were decreased by 29.28% and 14.57%. The water absorbance and hygroscopicity were also improved by the impregnation.

The TGA results indicated that the mass loss was around 8% from 120°C up to 280°C, while the mass loss of treated wood was around 4%. TGA results also showed that the treatment can enhance the thermal stability above a temperature of 380°C. The treated wood exhibited LOI values of about 42%, while the natural wood exhibited a LOI value of 22%. The thermal stability of treated specimens improved compared to the control specimens because the carbamide and methylolurea played an important role in flame retardant.

The FTIR analysis successfully showed that a chemical bond was produced between wood and methylolurea as a result of chemical reaction between wood and methylolurea. The SEM results indicated that the transverse and tangential sections of the treated specimens were filled with the reaction products, which can prevent the absorption of moisture. A stereo reticulation structure was built in the wood internal and filled in the amorphous regions.

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