

## EFFECT OF THERMAL TREATMENT WITH METHYLOLUREA IMPREGNATED ON POPLAR WOOD

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The aim of this research was to study the physical and chemical performance of poplar wood treated by chemi-thermal modification. A thermal treatment was used to catalyze the effect of the methylolurea impregnated pre-treatment by curing the poplar wood at 160 °C under atmospheric conditions. The results showed that the thermal treatment played an important role in the chemical and mechanical performance. Such an approach not only can significantly reduce the hygroscopicity, but also can increase the bending strength and compressive strength parallel to grain. The positions of the XRD peaks did not change, which indicated that the structure of cellulose was not noticeably affected by the thermal treatment. The FT-IR analysis showed that the intensity of hydroxyl and carbonyl absorption peaks decreased significantly, which indicated that the NH-CH<sub>2</sub>-OH of methylolurea reacted with the wood carboxyl (C=O) and hydroxyl (-OH). The TGA showed that the thermal stability of treated wood improved. The SEM showed that the cell wall and vessels were filled with impregnated chemicals.

*Keywords: Thermal treatment; Methylolurea; Impregnation; Poplar wood*

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### INTRODUCTION

Heat treatment of wood has recently attracted a lot of attention as an environmentally friendly wood protection method both in Europe and North America. During the heat treatment, wood becomes more and more hydrophobic with increasing heat treatment temperature. As a result, it becomes dimensionally more stable than untreated wood. The high temperature thermal treatment of wood is an environmentally friendly method for wood preservation (Korkut and Budakci 2010). The improved characteristics of heat-treated timber offer the timber products industry many potential and attractive new opportunities (Brischke *et al.* 2011; Papadopoulos and Tountziarakis 2010). It is now well known that heat treatment can protect wood from biological degradation (Santos 2000). However, drying with the application of temperatures from 120 °C to 130 °C results in a decrease of about 8% to 9% in compression, bending, and tensile strength, and a decrease in shear strength of 30% to 35%. The wood also changes in color and becomes darker (Yildiz *et al.* 2006; Gonzalez-Pena and Hale 2009). Both Kamdem *et al.* (2000) and Ates *et al.* (2009) also reported that heat treatment can change the color of wood, bending strength, compression strength, hardness, amount of wood polymers, biological durability, *etc.* All these changes are caused by heat treatment process without any impregnated chemicals.

Khalil *et al.* (2011) noted that modification with propionic and succinic anhydrides to *Acacia mangium* wood can improve the thermal stability. The results showed that chemical modification with anhydrides improves the thermal stability of the *Acacia* wood.

The higher thermal stability of the anhydride-modified *Acacia* wood compared with unmodified wood was attributed to the reduction in the hydrophilic nature of the wood due to esterification. Tjeerdsma and Stevens (2000) showed that acetic acid is liberated from the hemicelluloses, which further catalyses carbohydrate cleavage, causing a reduction in the degree of polymerization of the carbohydrates. Furfural acid-catalyzed degradation results in the formation of formaldehyde, furfural, and other by-products. Some hemicelluloses and extractive compounds undergo degradation, which increases the relative proportion of lignin (Kamdern and Pizzi 2002). The thermal treatment of wood also can beneficially affect several properties of wood products (Retfalvi *et al.* 2009).

Although many studies have evaluated the heat treatment of wood, few studies have investigated the combined effects of heat and chemical treatment of wood. Chemical pre-treatment of wood is also a very widely studied area. A combination of heat and chemical treatments could lead to numerous complex chemical, thermal, thermo-chemical, and thermo-mechanical changes in wood.

The main wood components are cellulose, hemicelluloses, and lignin. A number of carbonyl and hydroxyl groups are present in the components of wood. The cross-linking reaction between wood and chemicals happens because of chemical activity during the heat treatment process. Significant cross-linking reactions occur by the formation of methylene bridges between organic acid and the benzene ring of lignin (Brito *et al.* 2008; Juodeikiene 2009). Wood was subjected to heat treatment under atmospheric pressure at varying temperatures for varying durations (Kamdern and Pizzi 2002). The test results of heat-treated Scots pine and control samples showed that properties including compression strength, bending strength, modulus of elasticity in bending, Janka hardness, impact bending strength, and tension strength perpendicular to grain suffered with heat treatment, and increase in temperature and duration further diminished these values of the wood specimens (Korkut *et al.* 2008). The FT-IR spectra of acetone extracts showed that lignin became partly acetone soluble after a heat treatment of 180 °C or greater. Increased levels of free phenolic hydroxyl groups were detected in lignin, probably due to cleavages of  $\beta$ -O-aryl ether inter-unit linkages. The amount of extractable lignin increased with increasing temperature, while the resin in the extracts decreased (Nuopponen *et al.* 2005). Thermally modified specimens have higher lignin contents and lower acid numbers compared to the untreated controls, indicating the degradation of some hemicelluloses and extractive compounds (Gao *et al.* 2004; Poncsak *et al.* 2009).

The present investigation aimed to study the influence of heat treatment on chemically modified wood. A chemical pre-treatment was introduced to improve the heat treatment of wood by impregnating it with methylolurea beforehand. The major motivation for this work was to enhance the dimensional stability of wood without reducing its physical and mechanical strength and without using high toxicity pesticides.

## EXPERIMENTAL

### Materials

The fresh poplar (*Populus euramevicana* cv. 'I-214') wood samples used during this study were obtained from Beijing, China. They had initial moisture contents that ranged from 60% to 70% before the impregnation.

## Synthesis of Methylolurea

A three-necked flask was charged with urea, formaldehyde, and ammonia at a certain molar ratio (Pu *et al.* 2009c). The reaction mixture was stirred and kept at 30 °C for 3 hr. Then, sodium hydroxide or hydrochloric acid was used to adjust the pH of methylolurea to within the range of 4 to 7. Actually, the methylolurea was a mixture of urea-formaldehyde oligomers, formed by methylation reaction. Finally, the reacted mixture was transferred into a container and sealed.

## Pulse-Dipping and Kiln Drying

The dimensions of the wood samples for impregnation were 200 mm in diameter and 1000 mm in length. The fresh poplar was impregnated with 15% carbamide (w/w) and 15% methylolurea (w/w) by a pulse-dipping machine at the pressure of 0.7 to 0.8 MPa for 30 min (Pu *et al.* 2009a). After soaking, the impregnated logs were sawn into blocks about 50 mm thick (tangential) × 120 mm wide (radial) × 1000 mm length (longitudinal) for kiln drying. It took approximately 120 hr for drying. The pressure on the timber was 0.5 MPa (Pu *et al.* 2009b).

## Heat Treatment

Heat treatment was performed under atmospheric air in an oven at 160 °C for 8 hr on wood with the dimensions of 40 cm (T) × 12 cm (R) × 5 cm (L). The oven temperature was increased by 20 °C min<sup>-1</sup> from room temperature to 160 °C.

## Chemical Composition and Mechanical Properties

Before chemical analysis, the specimens, including untreated wood, treated wood without heat (methylolurea-impregnated without thermal treatment), and treated wood with heat (methylolurea-impregnated with thermal treatment), were smashed in a granulator and then grinded to a size of 40 to 60 mesh. Benzene and alcohol extraction was applied to control and treat wood specimens according to GB/T 2677.6-94. Hot water solubility was determined by consulting GB/T 2677.4-93. Holocellulose analysis was done according to GB/T 2677.10-95. Lignin content was determined as acid-insoluble Klason lignin by GB/T 2677.8-94. Ten specimens of three kinds of wood were analyzed in a universal mechanical testing machine (AG-100KNIMO, Japan). Tests were carried out according to GB/T 1936.1-91, GB/T 1935-91, and GB/T 1933-91, respectively.

## Hygroscopicity

In order to measure the water absorption characteristics of untreated and treated wood, rectangular specimens were prepared with dimensions of 20 mm (L) × 20 mm (T) × 20 mm (R). The specimens were dried in an oven at 105 °C until the average quantity change was less than 0.02 g during every 2 hr. Then the specimens were cooled in a desiccator containing silica gel and immediately weighed. The specimens were immersed in distilled water for 72 hr. After immersion, the excess water on the surface of the specimens was removed by a soft cloth, and the weights of the specimens were immediately taken. The increase in the weight was calculated according to the formula,

$$H (\%) = \frac{m - m_0}{m_0} \times 100 \quad (1)$$

where  $m$  is the final weight and  $m_0$  is the original weight.

### **X-ray Diffraction (XRD) Analysis**

The crystallinity of the samples from untreated and treated wood was evaluated by XRD, using a Shimadzu diffractometer, model XRD 6000. The measurement conditions were: CuK $\alpha$  radiation with graphite monochromator, 30 kV voltage, and 40 mA electric current. The patterns were obtained within a 10 to 50° 2 $\theta$  angular interval with 0.05° step and a scan speed of 2° min<sup>-1</sup>. The degree of crystallinity was calculated as the ratio of the intensity differences in the peak positions.

### **Fourier Transform Infrared Spectroscopy (FT-IR) Analysis**

The untreated and treated wood specimens of 120 mesh size were used in the FT-IR spectroscopy measurement. The dried specimens were embedded in potassium bromide (KBr) pellets and analyzed by using a Tensor 27 (Bruker, Germany) spectrometer. They were recorded in the absorption mode in the range of 4000 to 400 cm<sup>-1</sup> with an accumulation of 64 scans at a resolution of 4 cm<sup>-1</sup>.

### **Thermogravimetric Analyzer (TGA) Analysis**

A modulated TGA (DTG-60, SHIMIDZU, Japan) was used to characterize the decomposition and thermal stability of untreated and treated wood. The sample pan was placed on the Pt basket in the furnace and then heated from room temperature to 600 °C. The heating rate was 10 °C min<sup>-1</sup>.  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> was taken as the reference material. During testing, the heating unit was flushed under a continuous nitrogen flow at a pressure of 8 kPa.

### **Scanning Electron Microscope (SEM) Analysis**

A JSM 5900 model 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**

### **Chemical Composition and Mechanical Properties**

Table 1 shows the changes in chemical composition and mechanical properties of the poplar wood. As shown in Table 1, the benzene alcohol extractions of treated wood with and without heat were 4.23% and 5.47%, respectively, which were more than the untreated wood by 1.53% and 2.77%, respectively. The content of hot water extraction increased by 94% and 126%, compared with the untreated wood of 5.88%.

While the holocellulose content decreased from 71.26% to 61.26% and 63.77%, the content of lignin decreased from 21.53% to 20.93% and 19.73% for the treated wood without heat and treated wood with heat, respectively. All of the above values were caused by the impregnation and heat treatment. On the one hand, the wood modifier impregnation increased the extractive amounts. On the other hand, heat treatment caused substantial degradation of the material, resulting in a decrease of the amount of extractives. The extraction may be accelerated through volatilization as a result of the thermal treatment. The reduction in lignin content is consistent with the increase in extraction. Compared with the treated wood without heat, the increase of holocellulose content was due to the cross-linking reaction that occurred between the holocellulose and

methylolurea at high temperature (Wu *et al.* 2010), which substantially reduced the degradation. The polymerization products of methylolurea may be volatilized during the heat treatment process as well.

The density and mechanical properties are also shown in Table 1. The oven-dried density was increased by 36.6% and 34.1%, from 0.41 g·cm<sup>-1</sup> to 0.56 g·cm<sup>-1</sup> and 0.55 g·cm<sup>-1</sup>. The basic density also was increased by 24.3% and 18.9% from 0.37 g·cm<sup>-1</sup> to 0.46 g·cm<sup>-1</sup> and 0.44 g·cm<sup>-1</sup>. The density increase is due to the impregnation with wood modifier. For thermally treated wood, the oven-dried density and basic density were lower than the wood with only impregnation, because of the volatilization of extractives at higher temperatures. The bending strength and compressive strength parallel to grain were enhanced as a result of the modification. They increased by 44.6% and 73% with the impregnation and thermal treatment, respectively.

The results described above were different from the usual results of heat treatment (Gunduz *et al.* 2008; Kocaefe *et al.* 2008), indicating that the cross-linking reaction played an important role in the mechanical properties. Usually in the course of the high temperature thermal treatment the hemicelluloses are degraded to a greater extent than the other macromolecular components (Shafizadeh and Chin 1977). This results in the production particularly of acetic acid derived from the hemicelluloses; but additionally formic acid and methanol are formed, as well the production of noncondensable gases (mainly CO<sub>2</sub>), as the temperature is raised further. The heating of wood in the presence of water or steam results in the accelerated formation of organic acids (primarily acetic acid) that catalyse the hydrolysis of hemicelluloses, and to a lesser extent the amorphous cellulose (Mitchell 1988). First of all, the methylolurea impregnation helped to prevent the polysaccharide components from severe degradation by various kinds of reactions. That was one of the reasons why the treated wood with heat acquired better mechanical properties. In other words, heat treatment of wood would cause degradation, but to a lesser extent. More importantly, it was the high temperature that provided the necessary condition for methylolurea, and wood components reacted more deeply. In this way, the mechanical properties of treated wood with heat were enhanced.

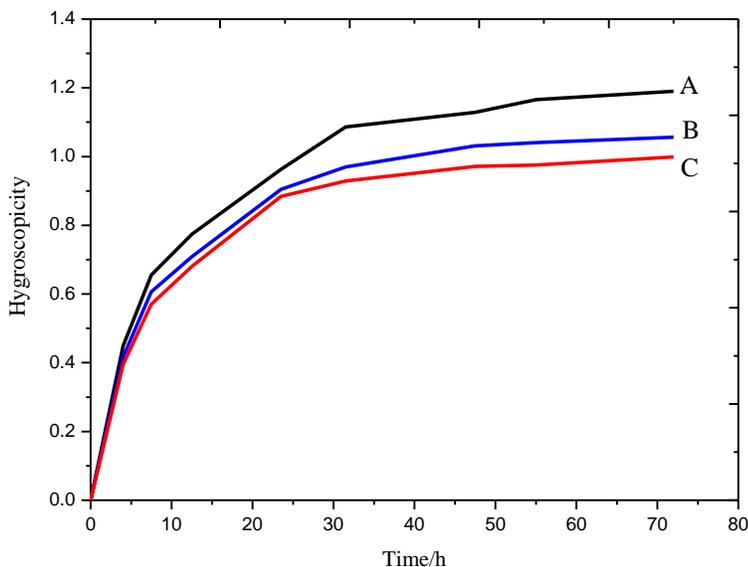
**Table 1.** Chemical Composition and Mechanical Properties

Properties	Untreated wood	Treated wood without heat	Treated wood with heat
Benzene alcohol extraction /%	2.70	5.47	4.23
Hot water solubility /%	5.88	13.27	11.39
Holocellulose /%	71.26	61.26	63.77
Lignin /%	21.53	20.93	19.73
Oven-dried density /g·cm <sup>-1</sup>	0.41	0.56	0.55
Basic density /g·cm <sup>-1</sup>	0.37	0.46	0.44
Bending strength /MPa	62.2	70.04	101.31
Compressive strength parallel to grain /MPa	39.3	46.35	80.19

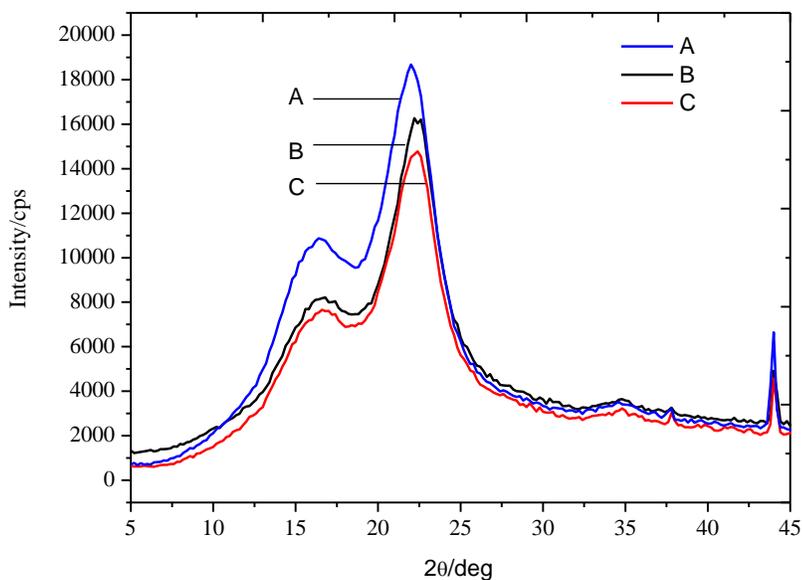
### Hygroscopicity

The hygroscopicity curve is shown in Fig. 1. The poplar wood became more water repellent after impregnation and heat treatment. In addition, the wood with heat treatment had a lower hygroscopicity. As has been stated earlier, the hygroscopicity is the most indicative characteristic of wood, with a major influence on both dimensional stability and durability (Akyildiz *et al.* 2009). The hygroscopicity of untreated wood was 119.2% after immersion in cold water for 72 hr, while the treated wood specimens were

105.6% and 99.9%, respectively. The hygroscopicity of both untreated and treated wood increased quickly within 24 hr. The treated wood had a lower hygroscopicity than the untreated wood because of the chemical reaction that occurred between the functional groups of wood and the modifier, which led to a decrease of hydroxyl groups in the wood. The hygroscopicity of treated wood with heat was lower than the wood without heat, due to the hydroxyl groups of wood further decreasing during the thermal treatment.



**Fig. 1.** The hygroscopicity curves of wood; A: untreated wood, B: treated wood without heat, C: treated wood with heat



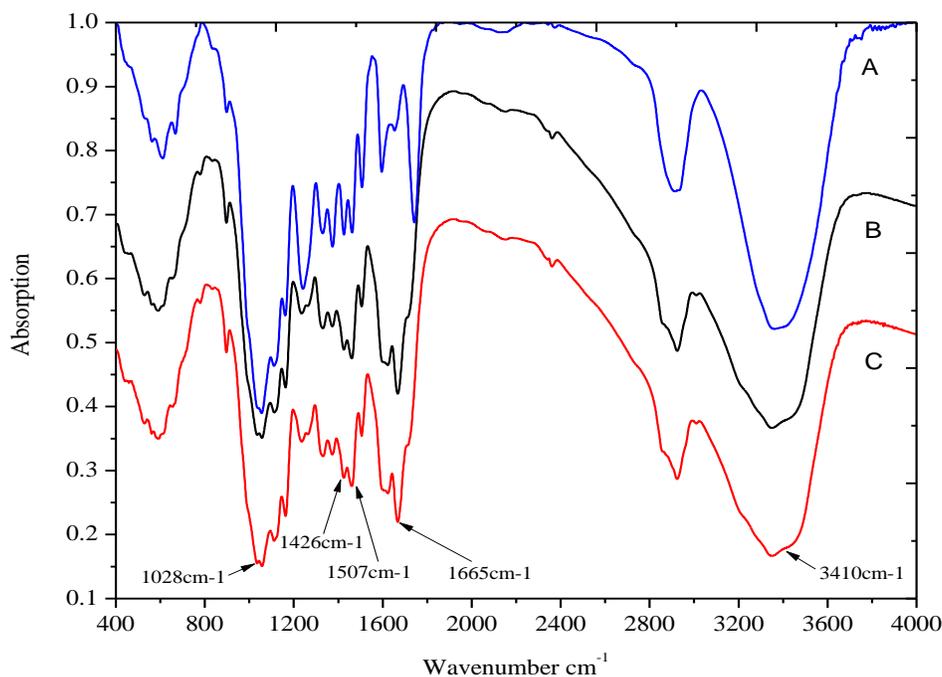
**Fig. 2.** XRD curves of wood; A: treated wood without heat, B: treated wood with heat, C: untreated wood

## XRD Analysis

A wide-angle XRD study was performed on untreated and treated wood. Figure 2 shows the XRD patterns of the wood crystalline phases, showing maxima at  $17.5^\circ$ ,  $22.5^\circ$ , and  $35.5^\circ$ . According to the results of experimentation, the crystallinity of the untreated wood was 35.4%, while the results for treated wood without heat and treated wood with heat were 38.55% and 37.47%, respectively. Comparing the three curves, the position of the peaks did not change, which indicated that the structure of cellulose was steady. The crystallinity increase of treated wood may be caused by the methylolurea, which could extend into the region between microfibrils of cell wall.

## FT-IR Spectroscopy

The nature of the chemical bonds in modified wood was characterized by FT-IR spectroscopy. The FT-IR spectra in Fig. 3 show the presence of characteristic peaks of untreated and treated wood. The vibrational band of modified wood was shown at  $3410\text{ cm}^{-1}$  for the hydroxyl groups, while the characteristic band of untreated wood was at  $3386\text{ cm}^{-1}$ . The reason for this may be attributed to intramolecular hydrogen bonding and -OH bending ( $1028\text{ cm}^{-1}$ ). The heat-treated wood showed a significant reduction of the -OH absorbance at  $3350\text{ cm}^{-1}$ , which indicated that the hygroscopicity decreased compared to the untreated wood. The band at  $1426\text{ cm}^{-1}$ , attributed to  $\text{CH}_2$  bending of cellulose, moved up with heat treatment compared to the untreated wood. The C=C stretching aromatic ring of lignin at  $1507\text{ cm}^{-1}$  evidently did not change after heat treatment. The band at  $1106\text{ cm}^{-1}$  that should belong to bridge C-O-C stretching of cellulose did not clearly change after heat treatment compared to the control wood sample. The absorption peak at  $1665\text{ cm}^{-1}$  was amide (N-C=O) from methylolurea. This was due to the bond between the  $-\text{NHCH}_2\text{OH}$  functional groups of methylolurea and the wood carboxyl C=O.

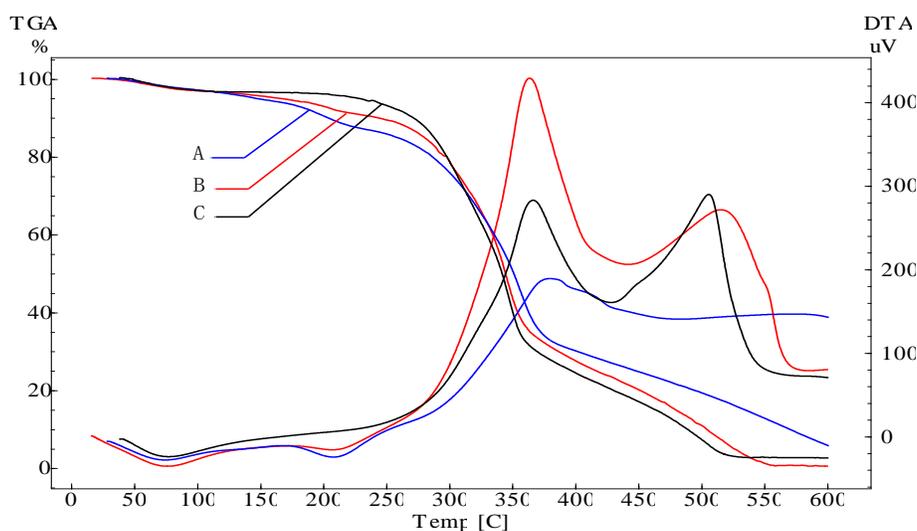


**Fig. 3.** The FT-IR curves of wood; A: untreated wood, B: treated wood without heat, C: treated wood with heat

All the occurrences described appear to be the consequences of reactions during the treatment that are well known in wood chemistry. The acetic acid liberated from the hemicelluloses, which further catalyzed methylolurea polymerization, causing the extent of reaction to increase between the methylolurea and the wood components.

### Thermogravimetric Analysis (TGA)

The thermogravimetric curves of untreated and treated wood are shown in Fig. 4. It was evident that there were four stages of thermal degradation. The mass loss at the temperature of 110 °C was about 4% in the first stage, which was due to the dehydration of wood powder. For the second stage, both the untreated and treated wood had a 37% rapid mass loss in the temperature range of 110 °C to 330 °C, which was because of the degradation during the heat treatment process. The methylolurea may also have been volatilized at the same time. However, the thermal degradation of treated wood without heat was faster than that of the heat-treated wood. That difference was attributed to a variety of processes occurring during thermal treatment of the treated wood. As wood is progressively heated to higher temperatures, production of condensable fractions occurs, with loss of water and volatile extractives at temperatures below about 140 °C. Above this temperature to 160 °C, the methylolurea could react more extensively with the wood components by the catalyzing substances derived from hemicelluloses (mainly acetic acid). That is to say, the treated wood not only had a much lower volatile extractives content, but also had much stronger cross-linking tendency between the modifier and the wood groups. These two phenomena would lead to an enhancement in the thermal stability of heat-treated wood. For the third stage, the oxidative decomposition of heated wood was faster than the other two. The large exothermic peak of heated wood at 362 °C in the DTA curve was due to the oxidation of flammable volatile products, compared with the treated wood without heat, which occurred at the relatively higher temperature of 380 °C. At the end of the third stage, 70% of the wood had been degraded because of oxidative decomposition.

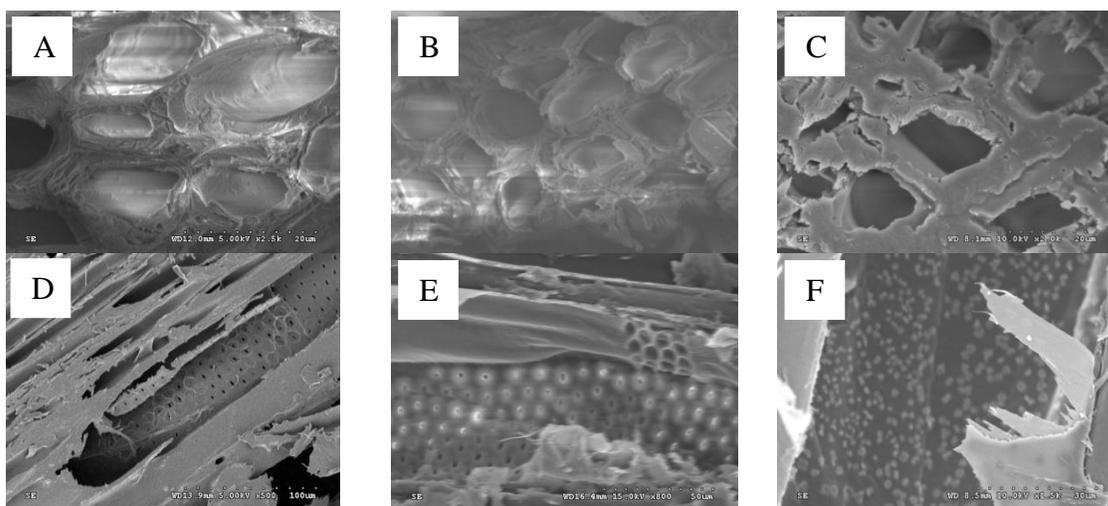


**Fig. 4.** The TGA curves of wood; A: untreated wood, B: treated wood without heat, C: treated wood with heat

After the oxidative decomposition stage, mass losses of the residual materials of wood were found to be slow within the temperature range 376 °C to 600 °C. The TG curve showed a mass loss of 30%. From the thermal analysis curves of wood, it was obvious that the oxidative decomposition of wood occurred at higher temperatures (>360 °C), and the heat release was distributed between two sharp and closely spaced isotherms, which indicated a high rate of heat release.

### SEM Analysis

The surface morphologies of untreated and treated wood were analyzed by SEM and are shown in Fig. 5. It can be seen that there was obvious precipitate on the surface of the impregnated wood, especially in Fig. 5 (F). The cell wall and vessels were also filled with impregnated chemicals after the drying process, which can be seen in Fig. 5 (C). In Fig. 5 (F) the chemical particles were distributed as rod-like objects or discontinuously in the wood cell, which means the chemical can be immersed in the wood fiber and other vertical cells under pulse-dipping pressure.



**Fig. 5.** SEM micrographs of untreated and treated wood; A: transection of untreated wood, B: transection of treated wood without heat, C: transection of treated wood with heat, D: radial section of untreated wood, E: radial section of treated wood without heat, F: radial section of treated wood with heat

### CONCLUSIONS

1. Thermal treatment of methylolurea-impregnated wood can improve the properties of natural wood, such as the density, the bending strength, and the compressive strength parallel to the grain. At the same time, the hygroscopicity was reduced significantly and cellulose crystallinity of the specimens did not change significantly.
2. The structure of cellulose did not change in comparison with the untreated wood. The positions of the peaks did not change according to the wood crystalline phases, which were revealed at 17.5°, 22.5°, and 35.5°.
3. The FTIR analysis showed that the intensity of hydroxyl and carbonyl absorption peak decreased significantly, which was because of the  $\text{NHCH}_2\text{OH}$  of methylolurea reacting with the wood carboxyl ( $\text{C}=\text{O}$ ) and hydroxyl ( $-\text{OH}$ ) groups.

4. The TGA showed that the thermal stability of heat-treated wood was enhanced. The SEM analysis indicated that the prepolymer was impregnated into the cell walls and the cell lumens of the wood.

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