

## Homogeneous Esterification of Eucalyptus with Palmitoyl Chloride at Room Temperature

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Homogenous chemical modification of ball-milled eucalyptus wood with palmitoyl chloride was investigated using a dimethyl sulfoxide/N-methylimidazole solvent system at room temperature. The parameters were optimized, including the reaction time and the dosage of palmitoyl chloride. The results indicated that prolonging the reaction time from 15 min to 120 min resulted in an increase in the weight percentage gain (WPG) of eucalyptus from 9.5 to 22.8%, while a further increase of the reaction time to 180 min led to an increase in WPG of 19.3%. An increase of the mass ratio of palmitoyl chloride-to-wood from 1:2 to 5:1 resulted in an improvement of WPG from 8.7 to 46.0%, while a further increase of the mass ratio of palmitoyl chloride-to-wood to 6:1 led to a decrease in WPG (39.7%). The physico-chemical properties of the esterified wood were investigated with FT-IR and CP/MAS <sup>13</sup>C-NMR spectroscopies. The results indicated that the palmitoyl ester group was successfully attached to the eucalyptus. The esterification of lignin and carbohydrates occurred at room temperature and the thermal stability of eucalyptus increased after esterification.

*Keywords:* Esterification; Homogeneous; Room temperature; CP/MAS <sup>13</sup>C-NMR; DMSO/NMI

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### INTRODUCTION

Renewable and readily available lignocellulosic biomass has great potential for a wide variety of applications. The production of performance materials, platform chemicals, and biofuels from lignocelluloses has attracted significant attention due to the increasing environmental concerns about climate change. Hydroxyl groups susceptible to chemical reactions are the most abundant and reactive sites found on the three main constituents (*i.e.*, cellulose, hemicelluloses, and lignin) of plant cell walls (Gellerstedt and Gatenholm 1999; Mohanty *et al.* 2000). Hence, etherification, esterification, alkylation, hydroxyalkylation, graft co-polymerization, crosslinking, and oxidation can be conducted to produce a series of functional products. In recent decades, a series of modifications to lignocelluloses were investigated through hydroxyl group reaction to produce value-added products with or without solvents (Thiebaud and Borredon 1995; Vaca-Garcia and Borredon 1999; Liu *et al.* 2007a; Liu *et al.* 2008). It was reported that esterification of lignocelluloses with long-chain fatty acid chlorides could replace some of the hydroxyl

groups with lipophilic groups, improving their oil adsorption (Sun *et al.* 2002) and thermoplastic properties (Thiebaud *et al.* 1997). Esterification is significantly influenced by the nature of the reaction medium, depending on whether it is a swelling agent or a solvent for the lignocellulosic material or the derivatized products. Compared to heterogeneous reactions, a homogeneous reaction is simple and the degree of substitution of the products can be easily controlled and reproduced (Nawaz *et al.* 2012). However, due to the complexity of the plant cell walls, lignocelluloses' lack of solubility in water and most organic solvent constitutes a major obstacle for their homogeneous modification. Therefore, most research has focused on the heterogeneous derivatization of the whole plant cell wall and the homogeneous modification of isolated components from lignocelluloses (Thiebaud *et al.* 1997; Vaca-Garcia and Borredon 1999; Mohanty *et al.* 2000; Lu and Ralph 2003; Liu *et al.* 2007b; Xie *et al.* 2007; Li *et al.* 2009; Liu *et al.* 2009; Liu *et al.* 2010; Wen *et al.* 2011; Nawaz *et al.* 2012; Kono *et al.* 2013). However, heterogeneous reactions are generally controlled by the diffusion of reagents into the fibers, and depend heavily on the distribution of reactive functional groups. The hydroxyl groups are hard to access due to the complexity of the components and the thickness of the cell wall during heterogeneous reactions. As novel solvents for the dissolution of whole plant cell walls, ionic liquids have received attention for the derivatization of lignocelluloses (Xie *et al.* 2007; Wen *et al.* 2011). However, the dissolution of lignocelluloses into ionic liquids requires relatively high temperatures, which may cause the degradation of cellulose, hemicelluloses, and lignin (Yuan *et al.* 2010). The dimethyl sulfoxide/*N*-methylimidazole (DMSO/NMI, 2:1, v/v) solvent system can dissolve the whole plant cell wall at room temperature without any degradation (Lu and Ralph 2003), which gives this method the potential for functionalization of whole plant cell walls. In the present study, homogeneous functionalization of ball-milled eucalyptus wood with palmitoyl chloride (a long-chain fatty acid chloride) was performed using a DMSO/NMI solvent system at room temperature without any additional catalysts. The physico-chemical properties of unmodified eucalyptus and esterified eucalyptus were characterized with FT-IR, CP/MAS, and <sup>13</sup>C-NMR spectroscopy, as well as thermal analysis.

## EXPERIMENTAL

### Materials

*Eucalyptus tereticornis* (12ABL) was obtained from a paper mill in Guangzhou, China. Wood chips (already debarked) were utilized for this study. The chips were cut, ground, and screened to prepare 20 to 40 mesh size particles. The wood powder was oven-dried and extracted with toluene and ethanol (2:1, v/v), and then milled in a vibrating ball-mill for 36 h. All chemicals were obtained from Aladdin Reagent Co. (Shanghai, China), were of analytical reagent grade, and were used as received without any further purification.

### Dissolution of Wood in DMSO/NMI

The ball-milled wood sample (500 mg) was suspended in DMSO (10 mL) and NMI (5 mL). The mixture was agitated with magnetic stirring at room temperature for 5 h to guarantee the complete dissolution of the ball-milled wood meal in the solvent system.

The complete dissolution was monitored by observation and confirmed with the dark eyeshot of a polarizing light microscope.

### Homogeneous Esterification of Eucalyptus in DMSO/NMI

Homogeneous esterification of ball-milled eucalyptus was carried out in a DMSO/NMI (2:1, v/v) solvent system at room temperature with palmitoyl chloride as the esterifying reagent. Palmitoyl chloride was added into the wood solution and the resulting mixture was stirred at room temperature. After the required reaction time, the resulting solution was slowly poured into 100 mL isopropanol with agitation. The formed solid was filtered out, washed thoroughly with isopropanol to eliminate DMSO, NMI, palmitoyl chloride, and byproducts, and then freeze-dried. The weight percent gain (WPG) was calculated based on the initial oven-dried mass of the eucalyptus material:

$$\text{WPG (\%)} = [(\text{weight gain/original weight})] \times 100 \quad (1)$$

To reduce error and confirm the results, each esterification of eucalyptus wood was performed at least three times under the same conditions to make sure the standard deviation was lower than 5.0%. The WPG of each sample represents the average value.

### Characterization of the Untreated and Esterified Eucalyptus

FT-IR spectra of the underivatized and esterified eucalyptus were recorded on an FT-IR spectrophotometer (Nicolet 510) over the range 4000 to 400  $\text{cm}^{-1}$ . Finely ground samples were dispersed into KBr (at 1% w/w concentration) and pressed into pellets. Thirty-two scans were taken for each sample with a resolution of 2  $\text{cm}^{-1}$  in transmittance mode.

Solid-state CP/MAS  $^{13}\text{C}$ -NMR spectra were obtained on a Bruker DRX-400 spectrometer with a 5 mm MAS BBO probe employing both cross polarization and magic angle spinning (CP/MAS). Each experiment was recorded at ambient temperature. The spectrometer operated at 100 MHz. The acquisition time was 0.034 s, the delay time was 2 s, and the proton  $90^\circ$  pulse time was 4.85  $\mu\text{s}$ . Each spectrum was obtained with an accumulation of 5000 scans.

Thermal analysis of the underivatized and esterified eucalyptus samples was performed using thermogravimetric analysis (TGA) and derivative thermogravimetry (DTG) on a simultaneous thermal analyzer (SDT Q600, TA Instrument). The apparatus was continually flushed with nitrogen. The sample mass was between 8 and 12 mg and the scans were run from room temperature to 600  $^\circ\text{C}$  at a rate of 10  $^\circ\text{C}/\text{min}$ .

## RESULTS AND DISCUSSION

### Effects of Reaction Conditions on WPG

The esterification reaction for eucalyptus wood with palmitoyl chloride in the DMSO/NMI solvent system is shown in Fig. 1. The homogeneous reaction was carried out at room temperature and the effects of the main parameters (*i.e.*, reaction time and dosage of palmitoyl chloride (esterifying reagent)) were investigated. The esterification conditions and WPG of the modified eucalyptus are listed in Table 1.

As can be seen from Table 1, keeping the mass ratio of palmitoyl chloride-to-eucalyptus wood at 2:1 while increasing the reaction time from 15 min to 120 min resulted in an increase in WPG from 9.5 to 22.8%, indicating that wood esterification in the DMSO/NMI system occurred in a relatively short time. This unexpectedly easy achievement of esterification at room temperature was probably due to the important role of NMI as a solvent, base, and catalyst because of its special structure. A similarly important achievement of cellulose esterification with carboxylic acids was reported within 5 min in solid-state at a high temperature (180 °C) (Pantze *et al.* 2008). However, a further increase of reaction time to 180 min led to a decrease in WPG (19.3%). This decrease was probably due to the increased degradation of wood components in the presence of the HCl formed from the palmitoyl chloride esterification reaction. While holding the reaction time at 120 min, an increase of the mass ratio of palmitoyl chloride-to-wood from 1:2 to 5:1 resulted in an improvement of WPG from 8.7 to 46.0%. This favorable effect on esterification could be due to the greater availability of reactant molecules in the proximity of the reactive hydroxyl groups at a higher mass ratio of palmitoyl chloride-to-wood. However, a further increase of the mass ratio of palmitoyl chloride-to-wood to 6:1 led to a decrease in WPG (39.7%), indicating the detrimental effect of excessive palmitoyl chloride on the esterification of wood. Compared to the WPG of acetylated wood (about 17.5%) (Mohammed-Ziegler *et al.* 2008), the WPG of esterified eucalyptus wood in the range of 8.7-46.0% (only 1.6-8.3% expressed with acetate) under the given conditions was low, considering the different molecular weights of acetyl and palmitoyl groups. Solid-state acetylation of eastern cottonwood with acetic anhydride was investigated at 100-120 °C and the WPG ranged from 8-15.5% (Farahani and Taghizadeh 2010). The low WPG in the present study was probably due to relatively mild conditions (room temperature *vs.* 100-120 °C during solid-state reaction) and lower reaction activity of palmitoyl chloride than acetic anhydride.



**Fig. 1.** Esterification of eucalyptus wood with palmitoyl chloride in DMSO/NMI solvent system without additional catalysts at room temperature

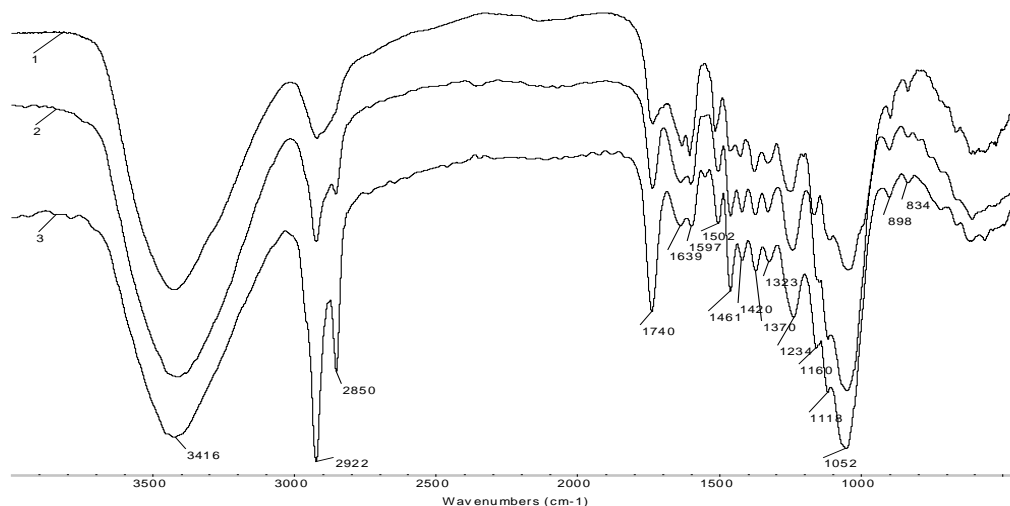
**Table 1.** WPG of Eucalyptus Wood Esterified with Palmitoyl Chloride in DMSO/NMI Solvent System at Room Temperature under Various Conditions

| Esterification conditions |  |                        | Esterified wood |            |
|---------------------------|--|------------------------|-----------------|------------|
| Esterifying reagent       | Esterifying reagent/wood <sup>a</sup><br>(g/g) | Reaction time<br>(min) | Sample No.      | WPG<br>(%) |
| Palmitoyl chloride        | 2:1  | 15                     | 1               | 9.5        |
| Palmitoyl chloride        | 2:1  | 30                     | 2               | 13.4       |
| Palmitoyl chloride        | 2:1  | 45                     | 3               | 18.1       |
| Palmitoyl chloride        | 2:1  | 60                     | 4               | 20.9       |
| Palmitoyl chloride        | 2:1  | 120                    | 5               | 22.8       |
| Palmitoyl chloride        | 2:1  | 180                    | 6               | 19.3       |
| Palmitoyl chloride        | 1:2  | 120                    | 7               | 8.7        |
| Palmitoyl chloride        | 1:1  | 120                    | 8               | 13.5       |
| Palmitoyl chloride        | 2:1  | 120                    | 9               | 22.8       |
| Palmitoyl chloride        | 3:1  | 120                    | 10              | 30.3       |
| Palmitoyl chloride        | 4:1  | 120                    | 11              | 34.1       |
| Palmitoyl chloride        | 5:1  | 120                    | 12              | 46.0       |
| Palmitoyl chloride        | 6:1  | 120                    | 13              | 39.7       |

<sup>a</sup>Mass ratio of esterifying reagent palmitoyl chloride to the dried ball-milled eucalyptus wood (g/g)

### FT-IR Spectra

Figure 2 shows the FT-IR spectra of the underivatized eucalyptus (spectrum 1) compared to the esterified eucalyptus samples 1 (spectrum 2) and 10 (spectrum 3). The spectra of the modified eucalyptus (spectra 2 and 3) provided evidence of esterification. The bands at 2922 and 2850  $\text{cm}^{-1}$  for C-H symmetrical and asymmetrical stretching of aliphatic groups, and the band at 1740  $\text{cm}^{-1}$  for C=O stretching of an ester (Jayakumar *et al.* 2000) significantly increased. In addition, the intensities of the bands at 1234 and 1160  $\text{cm}^{-1}$  for C-O antisymmetric stretching and C-O symmetric stretching in ester (Jayakumar *et al.* 2000; Ma *et al.* 2012), respectively, substantially increased. These changes indicated the successful attachment of the palmitoyl ester group onto the eucalyptus.

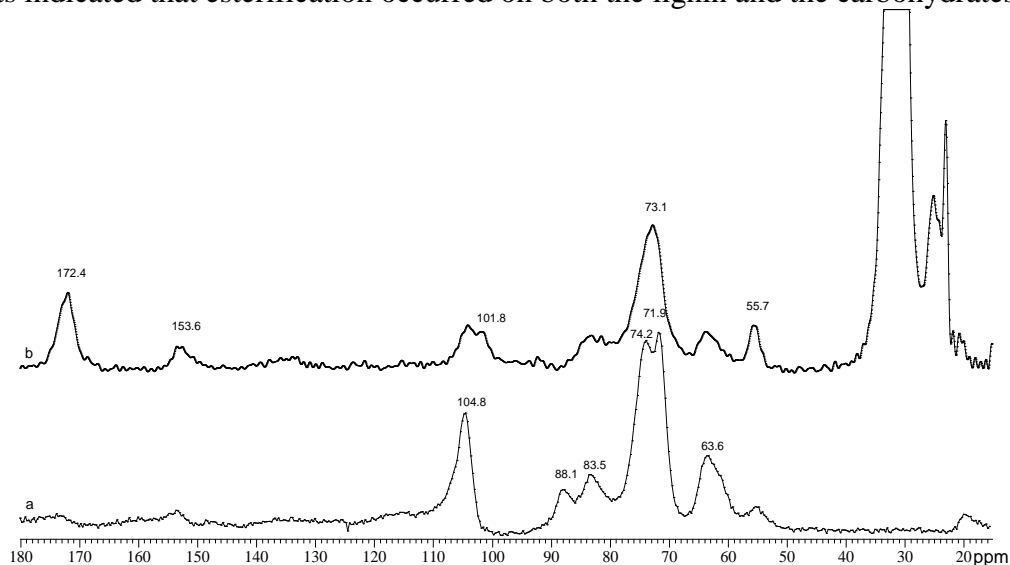


**Fig. 2.** FT-IR spectra of the unmodified eucalyptus (spectrum 1) and modified eucalyptus samples 1 (spectrum 2) and 10 (spectrum 3)

### Solid-state CP/MAS $^{13}\text{C}$ -NMR

Solid-state CP/MAS  $^{13}\text{C}$ -NMR spectroscopy is one of the most effective methods for the direct characterization of solid lignocellulosics without its dissolution into an NMR solvent. Figure 3 illustrates the solid-state  $^{13}\text{C}$ -NMR spectra of the unmodified eucalyptus (a) and modified eucalyptus sample 10 (b). In spectrum a, all of the noticeable signals in spectra have previously been reported (Maunu 2002; Liu *et al.* 2008; Li *et al.* 2009; Liu *et al.* 2009), and are distributed in four ranges: 170-155 ppm for carbonyl carbon range, 155-105 ppm for aromatic carbon range, 105-55 ppm for the carbohydrate carbon range, and 55-15 ppm for aliphatic carbon range.

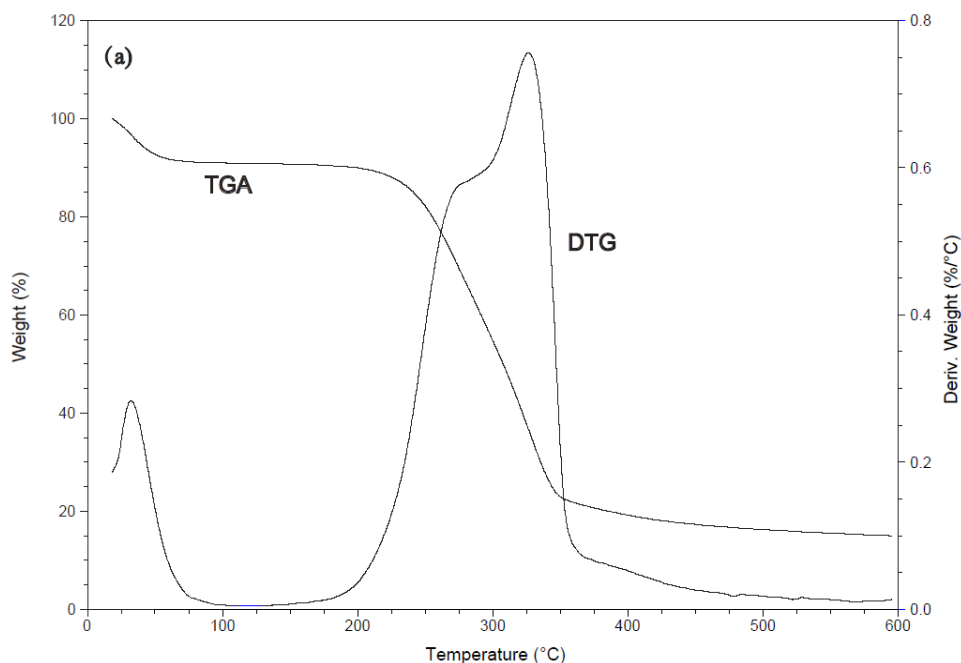
The signals at 104.8 (C-1 of cellulose and xylan), 88.1 and 83.5 (C-4 of crystal cellulose and amorphous cellulose, respectively), 74.2 and 71.9 ppm (C-2, C-3, and C-5 of cellulose; C-2, C-3, and C-4 of xylan), and 63.6 (C-6 of cellulose and C-5 of xylan) (Maunu 2002) were all observed prior to esterification. After esterification, the small shoulder at 101.8 ppm for the C-1 reducing end of cellulose and xylan indicated a noticeable degradation of wood components during esterification because of the presence of the HCl byproduct. More importantly, the intensity of the overlapping signals at 74.2 and 71.9 ppm attributed to C-2, C-3, and C-5 of cellulose and C-2, C-3, and C-4 of xylan decreased after esterification, as did the intensities of the signals at 63.6 ppm from C-6 of cellulose and C-5 of xylan. These decreases in signal intensities indicated that the esterification of the carbohydrates occurred. The small signals at 55.7 and 19.7 ppm belong to the  $\text{CH}_3$  carbon of the acetyl group in hemicelluloses and the methoxy group of aromatic moieties. After esterification, the signals in aliphatic carbon range increased significantly, which was derived from the palmitoyl group attached onto the eucalyptus. Moreover, the presence of 172.4 ppm for the carbonyl group also indicated the occurrence of esterification between palmitoyl chloride and eucalyptus. The resolution of lignin signals in the solid-state CP/MAS  $^{13}\text{C}$ -NMR spectra was very low, as shown in spectrum a in Fig. 3. The improvement of the intensity of the carbon signals in this region in spectrum b after esterification indicated the occurrence of lignin modification. These results indicated that esterification occurred on both the lignin and the carbohydrates.



**Fig. 3.** CP/MAS  $^{13}\text{C}$ -NMR spectra of unmodified eucalyptus (a) and modified eucalyptus sample 10 (b)

## Thermal Analysis

The TGA and DTG curves of unmodified eucalyptus (a) and esterified eucalyptus sample 10 (b) are shown in Fig. 4. The weight loss below 100 °C was due to the elimination of absorbed water. The thermal stability of wood is determined by the decomposition of its components: lignin, cellulose, and hemicelluloses. Hemicelluloses show the lowest thermal stability, while cellulose is relatively stable because of its highly crystalline structure. Lignin degrades over a wide temperature range. According to the TGA/DTG curves of the unmodified eucalyptus, there were two stages of decomposition: the first was mainly due to the degradation of hemicelluloses, and the second was due to the degradation of lignin and crystalline cellulose. The TGA/DTG curves of esterified eucalyptus shifted toward high temperatures, indicating the improved stability of the eucalyptus after esterification. From the TGA curves, the unmodified eucalyptus started to decompose at 207 °C, whereas the esterified eucalyptus (sample 10) began to decompose at 227 °C. At 50% weight loss, the decomposition temperature occurred at 312 °C for the unmodified eucalyptus *versus* 321 °C for the modified eucalyptus. Interestingly, the DTG curves exhibited significant differences in decomposition rate between the esterified and unmodified eucalyptus samples. After esterification, the high decomposition rate decreased compared to the unmodified eucalyptus, which was probably due to the decrystallization of the eucalyptus structure after homogeneous esterification.



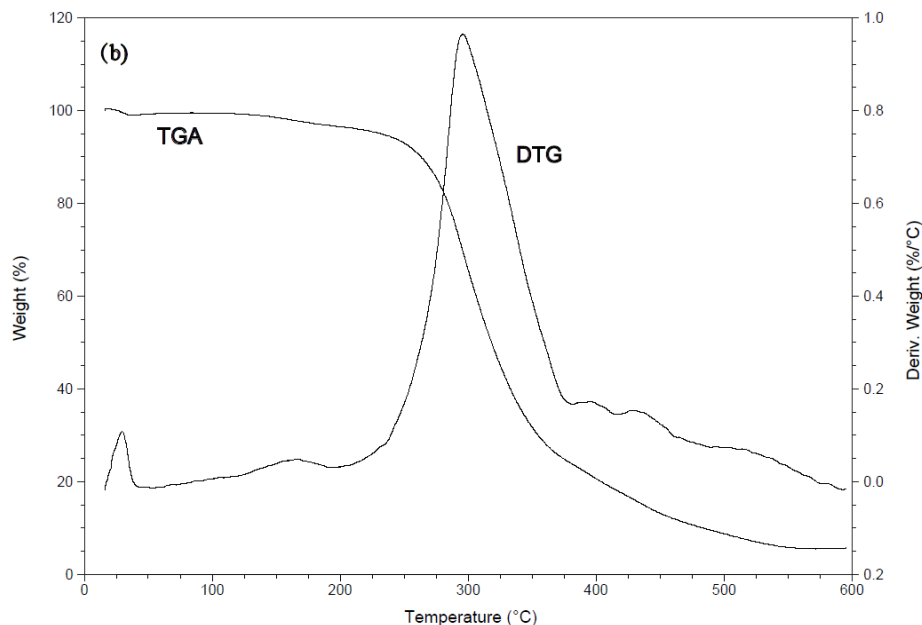


Fig. 4. TGA/DTG curves of unmodified eucalyptus (a) and modified eucalyptus sample 10 (b)

## CONCLUSIONS

1. Homogeneous esterification of eucalyptus with palmitoyl chloride in the dimethyl sulfoxide/*N*-methylimidazole (DMSO/NMI) solvent system was achieved at room temperature without additional catalysts.
2. Prolonging the reaction time from 15 min to 120 min resulted in an increase in weight percent gain (WPG) of eucalyptus from 9.5 to 22.8%, while a further increase of reaction time to 180 min led to a decrease in WPG to 19.3%. An increase of the mass ratio of palmitoyl chloride-to-wood from 1:2 to 5:1 resulted in an improvement of WPG from 8.7 to 46.0%, while a further increase of the mass ratio of palmitoyl chloride-to-wood to 6:1 led to a decrease in WPG of 39.7%.
3. The esterification of lignin and carbohydrates occurred at room temperature in the DMSO/NMI solvent system.
4. The thermal stability of eucalyptus wood increased after homogeneous esterification in DMSO/NMI at room temperature compared to the unmodified eucalyptus.

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