

WOOD ESTERIFICATION BY THE MALEIC ACID ANHYDRIDE

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ABSTRACT

The objective of this research project was to perform esterification of comminuted pine (*Pinus sylvestris* L.) wood with maleic anhydride and by lengthening the reaction time (2 to 8 hours) to obtain products of different degrees of modification. The assessment of the degree of wood modification was performed employing infrared spectroscopy (FTIR) and the titration method to determine the acid number (AN). In addition, using the thermogravimetric (TG) method, thermal properties of the obtained products were examined. It was found that with the lengthening of the esterification time, more and more wood functional groups underwent substitution and the obtained products were characterised by an increasing degree of esterification. Wood samples modified with maleic anhydride were characterised by worse thermostability in comparison with untreated wood.

KEY WORDS: chemical modification, maleic anhydride, thermal degradation, *Pinus sylvestris*

INTRODUCTION

Wood is exposed to the action of various atmospheric, biological and chemical factors. One of the most common methods of its protection against various elements is impregnation. One of the alternatives of its impregnation with wood protection agents is wood modification.

In recent years, there has been a dramatic increase of chemical methods of wood modification consisting in the reaction of active hydrophilic functional groups found in the major wood constituents, i.e. cellulose, lignin and hemicelluloses with modifiers. The modifiers include primary and secondary hydroxy, methoxy, carbonyl, carboxyl (ester), carbon-carbon, ether and acetyl groups (Hon 1996). The most frequent modifiers employed in the process of wood modification include: carboxylic acids, silanes, isocyanates, alkyl halides, lactones and nitriles (Rowell 1983, Kumar 1994, Hon 1996). However, out of the many methods of chemical wood modification, one of the most effective processes is its esterification with dicarboxylic acids: maleic (Marcovich et al. 1998, Chang and Chang 2001), phthalic (Matsuda et al. 1984 a), succinic (Hill and Mallon 1998) and crotonic (Cetin and Ozmen 2001) anhydrides. The esterification process can be carried out in the environment of organic solvents: in dimethyl sulfoxide (DMSO), in xylene or pyridine (Matsuda 1987). This process can also take place without solvent participation at the temperature of 60 – 200°C in the presence of Na₂CO₃ as a catalyst (Matsuda et al. 1984 b).

The purpose of the applied chemical modification is to improve mechanical properties, dimensional stability and biological resistance of wood (Rowell 1983). Wood modified in this way can also be used as a filler of thermoplastic polymers (Marcovich et al. 2001 a). The introduction into the polymer matrix of a lignocellulosic material sensitive to microbial decomposition can result in a partial or complete biodegradation of plastics (Morris and Cooper 1998).

The objective of this research project was to perform esterification of comminuted pine (*Pinus sylvestris* L.) wood with maleic anhydride and by lengthening the reaction time (2 to 8 hours) to obtain products of different degrees of modification. It was found (Marcovich et al. 1998) that mechanical, biological and thermal properties of lignocellulosic materials were strongly influenced by the degree of wood modification. The assessment of the degree of wood modification was performed employing infrared spectroscopy (FTIR) and the titration method to determine the acid number (AN). In addition, using the thermogravimetric (TG) method, thermal properties of the obtained products were examined.

MATERIALS AND METHODS

Wood

Comminuted (fraction 0.5 to 1.0 mm) Scots pine (*Pinus sylvestris* L.) softwood was used in the performed experiments. Wood dried in a vacuum oven for 24 h at the temperature of 70°C was treated at room temperature with the aqueous solution of sodium hydroxide at 10% concentration for 1.5 h (Borysiak and Doczekalska 2005). The material activated (swollen) in this way was rinsed with distilled water to neutralize excess sodium hydroxide and then it was dried for 48 h at ambient temperature.

Esterification

The modification process of wood was conducted in a three-necked flask of 500 ml volume equipped in a heat coat, reflux condenser, stirrer and a thermometer. Approximately 25 g of comminuted wood material was introduced into the flask containing 230 ml solution of maleic anhydride (MERCK) in xylene (1 mol/dm³). The esterification process was conducted for the period of: 2, 4, 6 and 8 hours. Once the esterification was finished, the product was filtered, washed several times with distilled water and then extracted using the ethanol- toluene mixture (2:1) in the Soxhlet apparatus for 8 h in order to remove the unreacted anhydride. The modified wood after extraction was dried at room temperature for 48 h.

Infrared analysis

Spectroscopic infrared (FTIR) experiments were carried out on an ANTI MATTSON Infinity Series FTIR spectrometer in KBr tablets at the range of 4000-500 cm⁻¹.

Determination of the acid number

The wood acid number (AN) before and after the modification process was determined using the method suggested by Matsuda (1987).

Approximately 0.3 g of wood was placed in a flat-bottom flask of 200 ml volume and 10 ml of 0.1 M aqueous solution of HCl and 100 ml of distilled water were added. This mixture was then titrated using 0.1 M aqueous solution of KOH in the presence of phenolphthalein as an indicator. The acid number was determined from the following formula (1):

$$AN = \frac{(V - H) \cdot N \cdot 56.1}{m} \quad [\text{mg KOH/g}] \quad (1)$$

where:

V – volume of 0.1 M KOH used for the titration of the solution [ml],

H – volume of 0.1 M KOH used for the neutralisation of 10 ml aqueous solution 0.1 M HCl [ml],

N – concentration of the KOH solution,

m – wood sample weight [g].

Thermo-gravimetric analysis

The analysis of the modified pine wood was carried out on a Labsys TM thermobalance of the Setaram Company in the following conditions: final temperature - 600 °C, rate of temperature increase - 5 deg/min, atmosphere – helium flowing at the rate of about 2 dm³/h.

RESULTS AND DISCUSSION

During the esterification process using the maleic anhydride, wood hydroxyl groups undergo substitution forming new groups: carbonyl, carboxyl as well as –CH=CH–. Therefore, wood modification with the assistance of the maleic anhydride can be presented as follows (Fig 1):

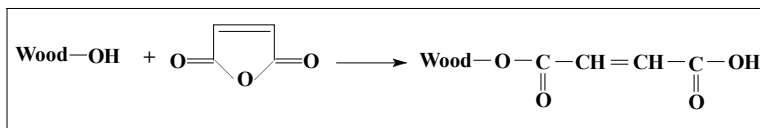


Fig. 1: Reaction scheme for modification of wood with maleic anhydride

It is evident from literature reports (Hon and Ou 1989) that in order to increase the efficiency of the modification process, wood should be subjected to surface activation using for this purpose the aqueous solution of NaOH. Wood mercerization increases adhesion by removing natural and artificial impurities (Sreekala et al. 1997)

Titration analysis

Results of the titration analysis are presented in Fig. 2.

On the basis of this analysis, it can be concluded that as the period of the esterification process of wood was expanded, more and more functional groups were substituted and gradually products

of increasing degree of esterification were obtained. The acid number for untreated pine wood was 1.1 mg KOH/g, whereas for the modified pinewood after 8-hour treatment - 34.4 mg KOH/g.

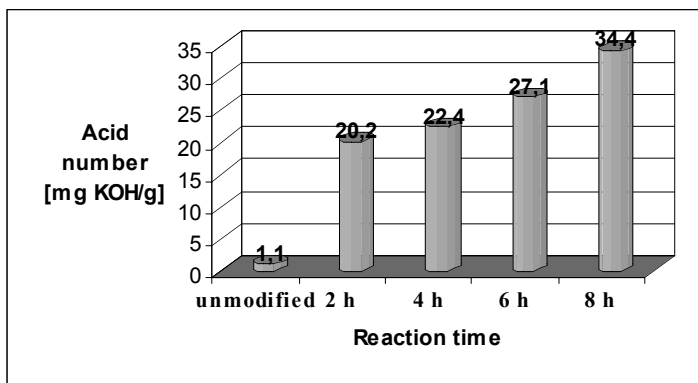


Fig. 2: Acid number of the pine wood as a function of the esterification reaction time

Infrared analysis

Infrared spectroscopic experiments were carried out on pine wood samples before and after their modification with the maleic anhydride (Fig. 3).

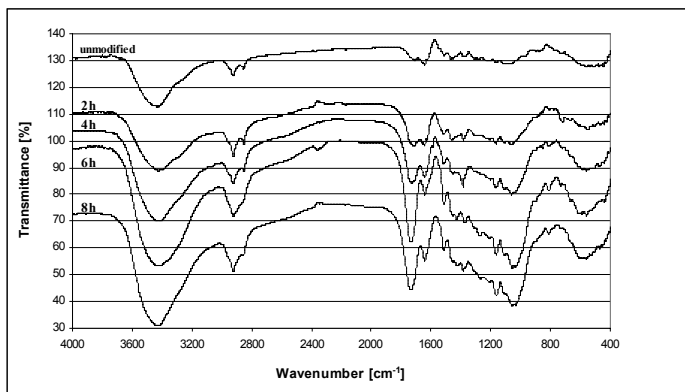


Fig. 3: FT-IR spectra: unmodified wood and esterified wood during 2,4,6 and 8 hours

On the basis of the analysis of the obtained spectrograms (Tab. 1), the 1730 – 1710 cm^{-1} absorption band can be considered as diagnostically the most valuable one. This band confirms the development, in the course of the modification process, of carboxyl and carbonyl groups. The absorption intensity of radiation in this range increased with the increase of the esterification time indicating the growing number of the substituted $-\text{OH}$ groups, hence the increasing degree of wood modification. In addition, the spectroscopic analysis revealed the presence of two other

absorption bands: 1650 – 1630 cm⁻¹ and 1170 – 1160 cm⁻¹ confirming the development of C=C and ether bonds.

Tab. 1: The peaks assignments of *Pinus sylvestris* L. for FT-IR analysis

Wave number	(cm ⁻¹)	Groups
Unmodified	Modified	
1080 - 1060		Alcoholic C-O stretch
1170	1170-1160	asymmetric C-O-C stretching
1310	1310	CH ₂ from holocelluloses
1390	1390	C-H from the cellulose and hemicelluloses
1460	1460	CH ₂ from cellulose
-	1650 -1630	-CH=CH-
-	1730 - 1710	Carbonyl C=O strong peak
1750	-	Very small peak showing very little C=O from holocellulose
3000- 2900	3000- 2900	C-H stretch in aromatic ring
3600 - 3200	3600 - 3200	Broad, strong band of the -OH group

Thermogravimetric analysis

On the basis of the obtained results of the thermo-gravimetric analysis, the authors determined:

- The initial temperature of decomposition of the examined samples T_d (at 2 % weight loss of dry wood),
- Two temperature ranges corresponding to individual stages of thermal degradation (DTG) as well as weight losses for each stage (TG),
- The amount of carbon residue at the final temperature measurement.

When analysing the obtained results (Tab. 2), the initial degradation temperature (T_d) of all samples subjected to the chemical treatment was found to decrease in comparison with the sample of unmodified wood (Marcovich et al. 2001 b).

Tab. 2: Thermal characteristic of unmodified wood and esterified wood

wood	T _d [°C]	Percentage mass loss to first step	First step		Second step		Residual char [mass %]
			Temperature [°C]	Percentage mass lost	Temperature [°C]	Percentage mass lost	
unmodified	275	6,1	235-300	5,4	300-600	68,0	20,5
2h	220	3,2	160-275	11,4	275-600	59,9	25,5
4h	230	3,5	160-275	9,9	275-600	60,7	25,9
6h	235	2,9	175-280	10,3	280-600	59,2	27,6
8h	230	3,8	175-265	9,5	265-600	61,8	24,9

The carbohydrate part of wood (hemicelluloses, cellulose) is the first to undergo degradation during wood thermolysis. The aromatic component of the wood tissue (lignin), because of its higher thermal resistance, is broken down next. The intensity of its degradation occurs at the temperature range 350-450°C (Antal 1982). This is confirmed on thermograms recorded in the course of the thermolysis of the examined samples of untreated and modified wood (Figs. 4 and 5).

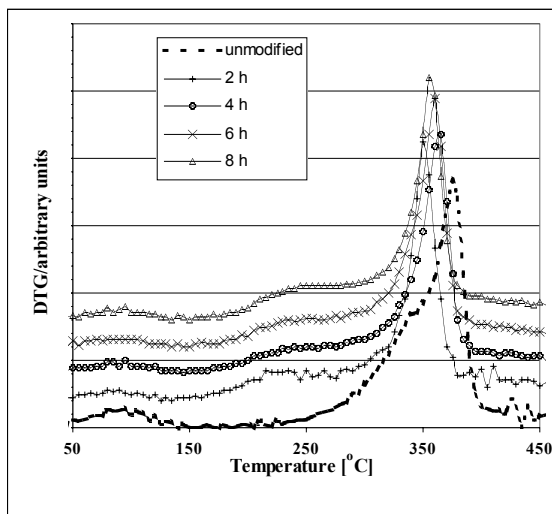


Fig. 4: DTG curves of unmodified and esterified wood

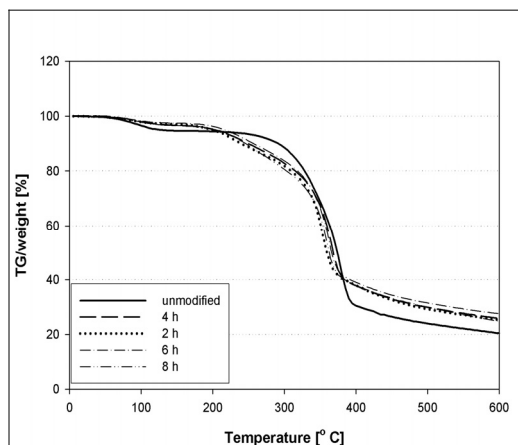


Fig. 5: TG curves of unmodified and esterified wood

Analysing the DTG curve runs (Fig. 4) of the untreated pine wood and all samples of esterified wood, two stages can be distinguished. During the first stage, the thermal degradation of the modified wood occurred at lower temperatures (160-280°C) than in the case of the untreated wood (235-300°C). On the other hand, the weight loss is higher for the modified samples (9.2 – 11.9%) in comparison with the sample of untreated wood (5.4%). Within the range of these temperatures (Marcovich et al. 2001 b), not only hemicelluloses and small-molecule lignin fractions undergo pyrolysis but also part of ester bonds developed during the modification process is destroyed. In the course of the second stage (Fig. 5), the weight loss of samples of the modified wood is lower (59.1-61.8%) than that of untreated wood (68.0%). The carbon residue after thermolysis constituted 20.5% in the case of untreated wood and ranged from 24.8% to 27.6% in the case of samples of modified wood.

CONCLUSIONS

It was found that with the lengthening of the esterification time (2 – 8 h), more and more wood functional groups underwent substitution and the obtained products were characterised by an increasing degree of esterification – the AN increased from 1.1 mg KOH/g (untreated pinewood) to 34.4 mg KOH/g (after 8 hours of modification). The spectroscopic evaluation of changes occurring in the wood revealed the following three absorption bands: 1730 – 1710 cm^{-1} , 1650 – 1630 cm^{-1} and 1170 – 1160 cm^{-1} confirming the development, in the course of the esterification process, of new carbonyl, carboxyl, C=C groups and ester bonds. On the basis of the performed TG and DTG analyses, it can be concluded that wood modification reduced the initial temperature of wood degradation (T_d) and the total weight loss of samples to the final temperature of the pyrolysis process.

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