# Investigations on the Application of Turpentine in Wood Processes with Acid Anhydrides

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## ABSTRACT

This study was devoted to investigations on possibilities of the application in the wood esterification process of a solvent of natural origin, namely turpentine. For purposes of comparison of wood reactivity with anhydrides, wood modification in the environment with three other organic solvents: N,N-dimethylformamide (DMF), dimethyl sulfoxide (DMSO) and xylene was also performed. The performed experiments involved modification of ground (0.5 to 1.0 mm) pine and beech wood using the following anhydrides: maleic, succinic and propionic. The efficiency of the treatment was determined by infrared spectroscopy (FTIR). The weight percent gain index (WPG) was determined for all products. Increases of sample mass were recorded following the esterification of pine ad beech wood in turpentine, DMF and xylene environments, whereas in the case of the DMSO environment, irrespective of the type of the applied anhydride, losses of mass were determined. From among the three acid anhydrides applied in the investigations, the modification of both pine and beech woods in the turpentine, DMF and xylene environments was found to be the most effective in the case of the succinic anhydride. It was also found that pine wood reacted with acid anhydrides easier than beech wood. In the majority of cases, higher WPG values were obtained for pine wood in the same conditions of the performed process. On the basis of the performed investigations, it can be concluded that turpentine can be employed as a solvent in the esterification process of wood with anhydrides.

## INTRODUCTION

The problem of the effect of modification on wood is very complex. In order to obtain modified wood of definite properties, it is necessary to select appropriate conditions of carrying out the process. There are many factors that can influence the degree of wood modification and changes of its properties, among others: wood species, time, temperature, pressure etc. The environment in which the reaction takes place also exerts a strong impact.

Literature descriptions of the esterification of lingocellulosic materials in the environment of different organic solvents include: dimethylformamide (DMF), dimethyl sulfoxide (DMSO), 1,2-dichloroethane, tetrahydrofuran, xylene and pyridine (Hill 2006). In addition, the process can also take place without solvent participation at the temperature of 60-200$^{o}$C and at the presence of catalysers (Matsuda et al. 1984; Li et al. 2000). In the experiments on wood esterification carried out so far, the authors employed xylene as the solvent (Doczekalska et al. 2007). However, xylene is as a highly flammable and noxious substance characterised by a strong and irritating smell. It exerts its harmful effect via the respiratory system as well as by skin contact. In

additions, xylene vapours have an irritating influence on the mucous membranes of eyes, nose and throat.
That is why the presented study was devoted to investigations of the possibility of application for the wood esterification process of a less harmful solvent of natural origin, i.e. turpentine. For purposes of comparison of wood reactivity with acid anhydrides, wood modification in the environment with three other organic solvents: N,N-dimethylformamide (DMF), dimethyl sulfoxide (DMSO) and xylene was also performed.
Turpentine is a liquid, volatile constituent of resins of coniferous trees, primarily pine. From the chemical point of view, it is a mixture of various hydrocarbons of the terpene type and their oxygen derivatives such as: alcohols, aldehydes, ketones, oxides and acids, thanks to which it found a very broad application in the paint and lacquer industry as a solvent.

## EXPERIMENTAL

### *Wood*

The experimental material comprised two most common Polish timber species pine wood (*Pinus sylvestris* L.) as a softwood species and beech wood (*Fagus sylvatica* L.) as a hardwood species. The size of wood sawdust ranged from 0.5 to 1.0 mm.Wood dried for 24 h at the temperature of 70$^{o}$C was treated at room temperature with the aqueous solution of sodium hydroxide at 10% concentration for 1.5 h (Borysiak and Doczekalska 2008). 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. About 20 g of activated wood material was introduced into a flask containing 200 ml of one of the solvents: DMSO, DMF, xylene or turpentine. The entire flask content was heated to the temperature of up to 90-100$^{o}$C and then one of the anhydrides was added in the amount corresponding to the concentration of the reaction mixture of 1 mol/dm$^3$. The performed experiments involved modification of sawdust using the following anhydrides: maleic (MERCK), succinic (MERCK) and propionic (MERCK). The modification was carried out for 4 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, v/v) 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$^{-1}$.

### *Weight percent gain index (WPG)*

The extent of reaction was calculated as weight percent gain (WPG) determined by the differences in oven dry weight of the samples after mercerization ($W_1$) and after esterification ($W_2$) according to equation (1):

$$WPG\ (\%) = (W_2 - W_1)/W_1 \times 100 \qquad (1)$$

## RESULTS AND DISCUSSION

In order to enhance the efficiency of the wood modification process, the initial activation of its surface was carried out. The mercerization applied in the investigations consisted in the treatment of the wood with the aqueous solution of NaOH. Mercerization treatment is also believed to improve the fiber surface adhesive characteristics by removing natural impurities such as pectin, waxy substances and natural oils. Several authors suggest (Hon and Ou 1989) that wood alone does not react significatively with etherifying/esterifying reagents since the hydroxyl groups in wood are not readily accessible. Hence, the raw material must be pretreated with NaOH.
In order to confirm the occurrence of the esterification process, FTIR spectroscopic investigations were carried out of products modified in the environment of four anhydrides used in the study. Figures 1 and 2 show spectrograms of wood products modified in a turpentine environment.

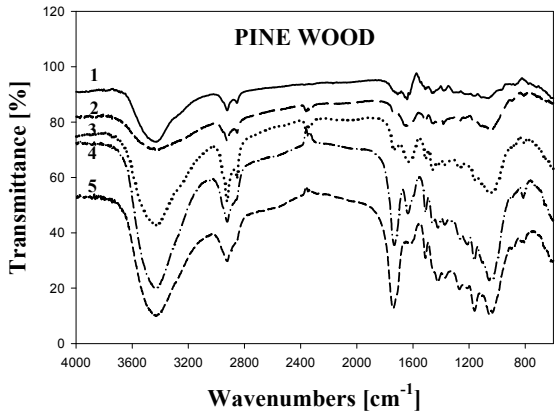


***Figure 1: FTIR spectra of pine wood esterified in turpentine: 1-untreated; 2-mercerized; 3-propionic; 4-maleic; 5-succinic***

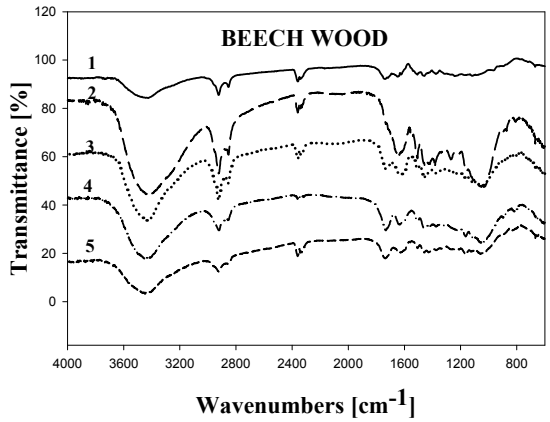


***Figure 2: FTIR spectra of beech wood esterified in turpentine: 1-untreated; 2-mercerized; 3-propionic; 4-maleic; 5-succinic***

In the case of all FTIR spectra, irrespective of the employed solvent, the presence of strong, narrow bands in the range of 1745-1728 $cm^{-1}$ was determined confirming unequivocally the development of ester bonds between wood and anhydrides. The evaluation of the effect of solvents on the degree of wood modification was carried out on the basis of the determined weight percent gain (WPG) indices. The results are presented in Figures 3 and 4.

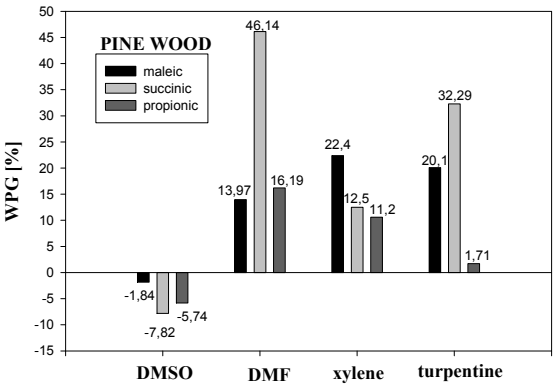


*Figure 3: WPG values determined for esterified pine wood*

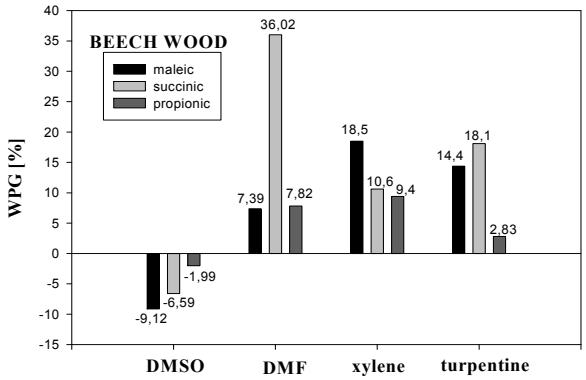


*Figure 4: WPG values determined for esterified beech wood*

The percentage index of weight changes of wood samples following the esterification process in the DMSO environment is negative indicating losses of sample weight. This wood weight loss can probably be attributed to the dissolution of hemicelluloses and lignin contained in wood. Lignin solubility depends on the properties of the organic solvent (it increases with the increase of the Hildebrand solubility parameter) as well as the capability of the solvent to form hydrogen bonds. It is clear from the literature on the subject that the highest capability of dissolving lignin is found in liquids with the Hildebrand solubility parameter ($\delta$) close to 11, and for DMSO $\delta$ =13.4 (Fengel and Wegener 1989).

In the case of DMF, xylene and turpentine as the environments for the esterification reaction with acid anhydrides, the weight percent gain index (WPG) is positive for both wood species which indicates that the weight of the examined samples increased. Investigations on the DMF influence on the course of pine wood esterification show that, in this environment, it is the succinic anhydride that reacts with wood easiest. Much higher values of the WPG index were obtained for both wood species in comparison with the remaining anhydrides. On the other hand, maleic anhydride was found to react most readily in the environment of xylene with wood (WPG amounted to about 20%). Propionic and succinic anhydrides reacted less readily and their WPG ranged from 10 to 12%.

When turpentine was used in the process of wood esterification, the highest WPG was observed for the esterification products with succinic anhydride and the lowest – for esterification products with propionic anhydride. It should be emphasised that values of WPG indices obtained during the modification with the succinic and maleic anhydrides in the turpentine environment were comparable with those obtained in the xylene or DMF environments. Products of very small degree of esterification were obtained only for the propionic anhydride. Therefore, on the basis of the obtained results, it can be recommended to apply turpentine as a solvent in the process of wood esterification using the following two acid anhydrides: maleic and succinic.

## CONCLUSIONS

From among the three acid anhydrides applied in the investigations, the modification of both pine and beech woods in the turpentine, DMF and xylene environments was found to be the most effective in the case of the succinic anhydride. It was also found that pine wood reacted with acid anhydrides easier than beech wood. In the majority of cases, higher WPG values were obtained for pine wood in the same conditions of the

performed process. On the basis of the performed investigations, it can be concluded that turpentine can be employed as a solvent in the esterification process of wood with succinic and maleic anhydrides. Investigations on the recognition of the mechanisms of reactions occurring in the environment of this solvent as well as on the structure of the obtained products should be continued.

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