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SOFTWOOD CHEMICAL MODIFICATION BY REACTION WITH ORGANIC ANHYDRIDES

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The fir (*Abies alba* Mill.) wood flour (30 mesh particle size) and discs 6.5 x 0.4 cm (diameter x length) were successfully chemically modified by treatment with succinic anhydride (SA) solution in xylene of different concentration values. The time of the reaction was changed between 180s and 1800s in several steps. The progress of modification was followed by the measurement of weight change and infrared spectroscopy investigation (FTIR). Further increase in reaction time influenced the weight change of fir wood. The reduction of surface tension led to significant changes in all interactions between the wood and other substances resulting in a considerable decrease of water absorption, which is the major benefit of modification. Water absorption of fir wood samples measured at 25°C and atmospheric pressure was investigated.

INTRODUCTION

The use of vegetable fibers and/or particles as reinforcement fillers for polymeric matrices has been enjoying a continuous growing interest in the past decade from the scientific and application points of view. Applications go beyond the widely used particleboard and efforts are being made to produce matrices for the construction, packaging and automotive industries among others. Because of the shortage of high-quality wood, reconstituted wood materials, such as particleboards, plywood, and fiberboards are important products of wood-based industries.[1] Moreover, natural fibers are very cheap, easily available, and renewable. Recently the interest in composite materials reinforced with wood flour and natural fibers increased considerably. [2, 3]

Wood is a complex composite material, which consists mainly of cellulose (40–45%), hemicelluloses (20–30%) and lignin (20–30%). Cellulose represents the crystalline part of wood, while the structures of hemicelluloses and lignin are amorphous.

Hardwood and softwood differ in several aspects, like fiber dimensions, chemical components composition, mainly the lignin and cellulose content. Hardwood contains a cell called a vessel element and has lignin containing guaiacyl and syringyl units, while softwood does not contain vessel elements and the lignin is composed of essentially only guaiacyl units.[4]

In recent years, a number of studies and method development work have been directed to apply chemical modification technology to solid wood in order to improve the durability and behavior of wood in adverse environments. The chemical modification of wood can be directed to improve the dimensional stability properties, hardness properties and/or durability properties of wood against decay.[5-7]

The dimensional modification, as well as biological degradation of wood has been attributed to the presence of numerous hydroxyl groups in various wood components. A blockade of such sites by larger groups swells the wood permanently and not only eliminates the moisture adsorption sites but prevents the highly specific enzymatic reactions. Environmental factors regulations about the use of biocides have renewed interest in chemical modification techniques, and efforts are being made to upgrade these techniques.

Besides acetic anhydride, other organic anhydrides, although to less extent, have been used as modifying agents for wood. For instance, modifications of wood with phthalic, succinic or maleic anhydrides have been reported to result in

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reduced tensile strength of the wood.[8] Organic anhydrides groups react chemically with the –OH groups of the wood and improve interfacial adhesion considerably. However, such a modification usually does not solve drawbacks like aggregation, appearance of the product, and water adsorption. Esterification or etherification of the hydroxyl groups is the most often applied approach for modification [9, 10] but attempts are made also for the impregnation of the wood with various monomers and their subsequent polymerization.[11-13]

The purpose of this paper is to investigate structural modification of fir wood as following succinic anhydride treatments. Chemical modification was followed by the measurement of weight change and infrared spectroscopy investigation (FTIR). Influence of dipping time and succinic anhydride concentration on weight change for un-extracted and extracted fir wood samples was investigated.

RESULTS AND DISCUSSION

Effect of chemical treatment on weight change of wood flour

The weight change of wood flour samples was significant as obtained for treatment with succinic anhydride 10% (w/w) in xylene (data not presented here). [14]

Characterization of wood flour by FTIR spectroscopy

The softwood chemical structure was investigated by FT-IR spectroscopy.[15] The FT-IR spectra of fir wood flour (previously extracted in solvents) treated with organic anhydrides confirmed the occurrence of wood-anhydride reaction (Figure 1). The strong vibration obtained in the region 1728-1730 cm^{-1} (C=O) was a distinct pattern present in modified samples which indicates the presence of new formed ester bond. As expected, such absorption band was not present in unmodified wood. An increase in the intensity of OH in plane bending vibration at 1219 cm^{-1} and 1214 cm^{-1} bands specific to wood components, cellulose and hemicelluloses, was also evidenced.

Effect of dipping time on weight change for wood discs

The effect of dipping time on weight change (%) during wood discs chemical modification in the presence of xylene was investigated in order to evaluate the extent of reaction. Experimental data are presented in Table 1. The increasing of dipping time increase weight change both for UW and EW samples, this effect being more significant for EW samples treated with SA solution 30 g/L in xylene.

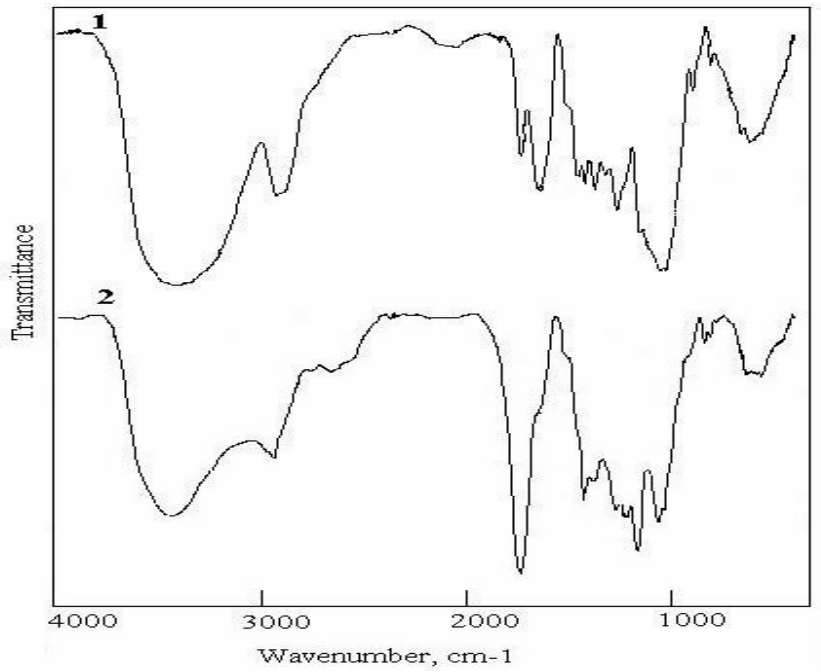

Fig. 1 – FTIR spectra for fir wood flour: 1.EWF; 2. EWF-SA.

Table 1

Weight change (%) for fir wood discs immersed in SA solution 30 g/L in xylene

Sample*	Dipping time, s			
	180	420	900	1800
UW	0.117	0.322	0.594	2.077
EW	0.499	1.066	4.288	7.343

*reported to oven-dried weight wood discs samples

Adsorption of SA on wood discs

Relationship between SA concentration and retention for UW and EW wood discs is presented (Figure 2 a). The retention of SA on wood samples was related to physical adsorption and grafting rate. A large number of succinic anhydride groups provided more opportunities for graft reaction. In general, the grafting rate increased with concentration and retention. For UW samples a higher grafting rate is noticed at most concentration levels (Figure 2 b). Although more hydroxyl groups were exposed on wood surfaces after Soxhlet extraction, the electrostatic blocking effect [16] significantly resisted the graft reaction for SA.

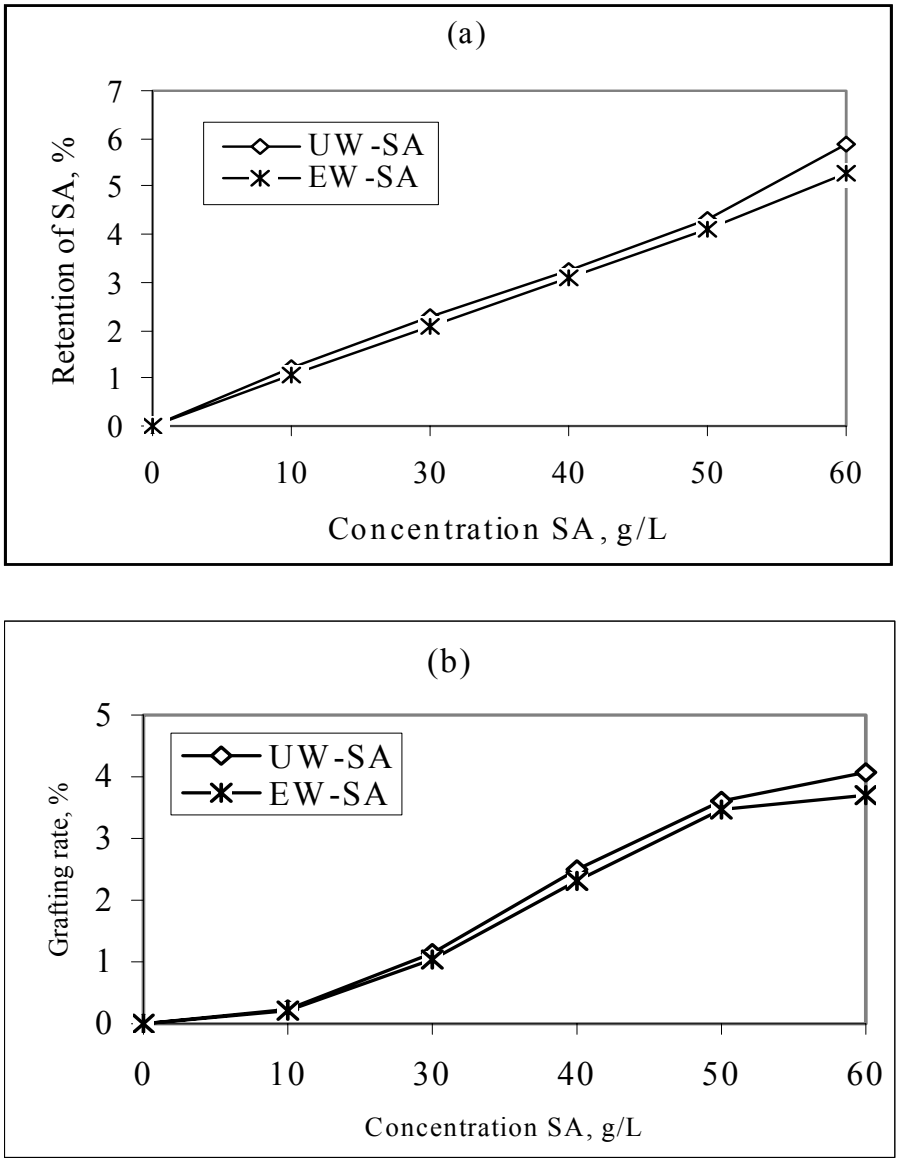

Fig. 2 – Variation of retention (a) and grafting rate (b) with SA concentration value (dipping time: 7 min).

Water absorption investigation for wood discs

In a series of water absorption studies with varying time period, the wood samples treated with succinic anhydride absorbed less water than the untreated ones. Water absorption after five hours decreases with increasing SA concentration value (Figures 3-4).

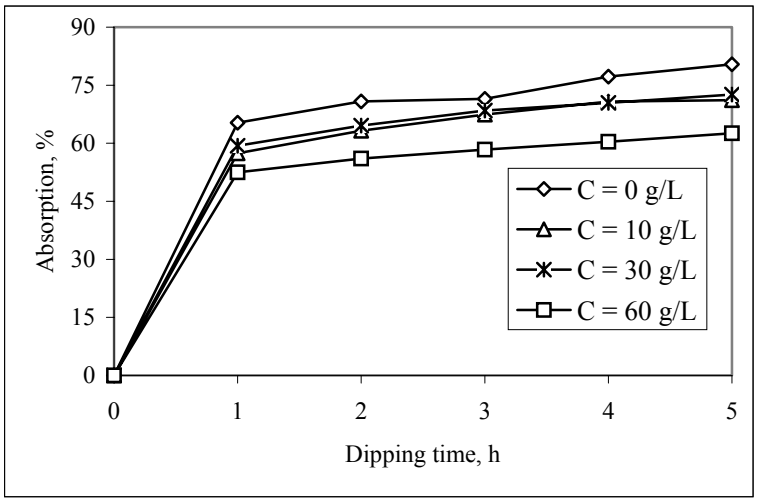

Fig. 3 – Water absorbtion of UW-SA samples for different SA concentration levels.

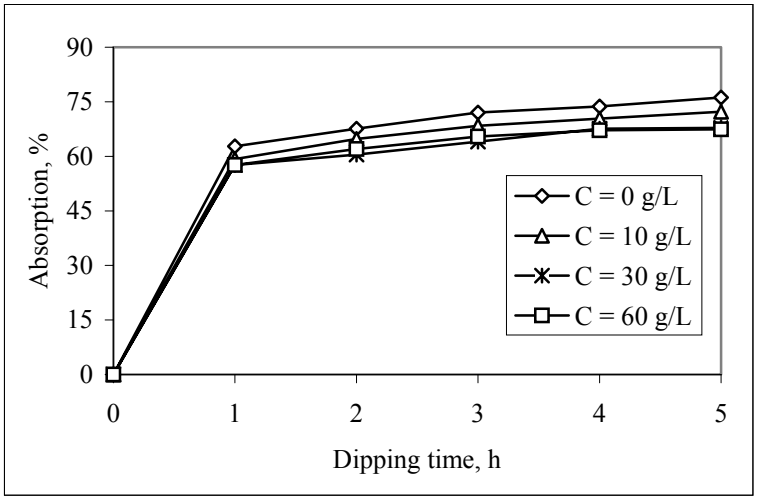

Fig. 4 – Water absorbtion of EW-SA samples for different SA concentration levels.

EXPERIMENTAL

Materials

Wood flour (30 mesh particle size) from a native fir wood species (*Abies alba* Mill.), provided from local sources, namely Forestry Agency, Iasi and discs 6.5 x 0.4 mm (diameter x length) were subjected to succinic anhydride chemical treatments. Moisture content of wood samples was 5-6%. The major chemical components of softwood samples were determined in accordance with TAPPI standards, their values being presented in Table 2.

Succinic anhydride (SA) was obtained from Aldrich (97 %) being used as received. Organic solvents were analytical grade.

Table 2

The main components of fir wood flour

Ash, %	Extractable substances (%) in :			Celullose, %	Lignin, %	Holocelullose, %
	Hot water	NaOH 1%	Ethanol/toluene			
0.25	1.65	9.57	1.53	54.21	30.17	81.12

Chemical modification of wood samples

Fir (*Abies alba* Mill.) wood flour and discs were prepared from dried logs (maintained at ambient temperature for one year). Wood samples (flour and discs) were placed individually in a Soxhlet extractor for solvent extraction using toluene/ethyl alcohol mixture (2:1 by volume) for eight hours. Samples were dried in an oven at 103ºC±2ºC until constant weight. Prior to weighing, samples were transferred to a desiccator and allowed to cool at ambient temperature.

Weighed wood flour samples were further transferred to a flask containing succinic anhydride 10% solution in xylene. The reaction time of wood flour samples was three hours at 120ºC.

Weighed wood discs samples were placed in the succinic anhydride solution under continuous stirring with a magnetic stirrer. The dipping time in succinic anhydride solution in xylene for softwood discs samples were 180, 420, 900, respectively 1800 seconds. Three succinic anhydride concentration levels (*i.e*. 0-control, 10, 30, and 60 g/L) at the same dipping time (7 min) were used to treat unextracted and extracted softwood discs samples. The SA solution was heated on a hot plate with a magnetic stirrer and was kept at 85-100°C. After complete dissolving of SA in xylene, the softwood discs samples were placed in the solution (at each concentration level) for 7 minutes under continuous stirring with a magnetic stirrer. All treated wood discs samples were cooled down to room temperature and finally oven-dried at 70ºC in a vacuum oven until constant weight was achieved. The oven-dry weight of each sample was re-weighted. For determination of the grafting rate, 25 treated wood discs samples underwent the secondary Soxhlet extraction for 24 hours in xylene, then oven-dried at 70ºC to reach a constant weight and weighted.

Sample identification codes are presented in Table 3.

Table 3

Sample identification codes

Code	Samples
EWF	extracted wood flour in toluene-ethyl alcohol
EWF-SA	extracted wood flour in toluene-ethyl alcohol and treated with succinic anhydride
UW	unextracted wood discs (control)
EW	extracted wood discs in toluene/ethyl alcohol
UW-SA	unextracted wood discs subjected to dipping in succinic anhydride solution in xylene
EW-SA	extracted wood discs subjected to dipping in succinic anhydride solution in xylene

Retention of succinic anhydride (Rt) and grafting rate (Gr) for treated wood discs samples were calculated as follows:

$$Rt, \% = [(W_1-W_0)/W_0] \times 100$$
$$Gr, \% = [(W_2-W_0)/W_0] \times 100$$

where: Rt - retention of succinic anhydride in a wood disc sample (%); Gr - grafting rate of succinic anhydride in a wood disc sample (%); W_0 - oven-dry wood disc sample weight after extraction and before chemical treatment (g); W_1 - oven-dry wood disc sample weight after chemical treatment (g); W_2 - oven-dry sample weight after chemical treatment and extraction with xylene (g).

Fourier transform infrared spectroscopy analysis

FT-IR spectroscopy is uniquely suited for studies of chemical reaction because absorbance peaks are characteristic of chemical bonds rather than of atoms.[17] FT-IR analysis was performed by using the KBr (potassium bromide) disk method with a Digilab Fourier Transform Infrared (FTIR) spectrometer, Model Excalibur FTS-2000. The samples were mixed with KBr to form the pellets that contained 1% powdered sample. These KBr disks were employed for FTIR analysis.

Water absorption

Five wood discs samples (6.2–7.2 g) were used to determine the degree of water absorption. The samples were first placed in an oven set at 60 °C, under reduced pressure, for 8 h. The oven-dried weight (W_D) was determined and used to calculate the water absorption as following[18]:

$$WA (\%) = [(W-W_D) / W_D] \times 100$$

where: W is the weight of the sample after water uptake in deionized water at 30 ºC dipping times 1-5 h and atmospheric pressure.

CONCLUSIONS

Wood chemical modification with succinic anhydride is influenced by many factors such as chemical treatment, reaction time, concentration, wood extraction in solvents.

The FT-IR spectra of fir wood flour, previously extracted in organic solvents and further reacted with SA, confirmed the occurrence of wood-succinic anhydride reaction, a strong vibration being observed in the region 1728-1730 cm^{-1} (C=O).

The increase of SA concentration determined increasing weight change, especially at 60 g/L for both UW and EW wood discs samples at dipping time 7 minutes. The increase of dipping time at 30 g/L SA concentration determines an increase of weight change both for UW and EW discs, this effect being pronounced for EW samples.

Retention of SA on fir wood discs increased with increasing SA solution concentration. At low concentration levels and low retention, SA molecules were mainly fixed on wood by

esterification. At high concentration levels, however, most SA molecules were deposited on wood by physical adsorption (such as capillary adsorption).

Water absorption after five hours decreases for both UW and EW discs treated with SA for the same dipping time. The wood discs treated at higher concentrations of SA solution in xylene present reduced water absorption.

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