

MALEIC ANHYDRIDE TREATMENT OF SOFTWOOD – EFFECT ON WOOD STRUCTURE AND PROPERTIES

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The chemical modification of wood can be directed to improve the dimensional stability properties, hardness properties and/or durability properties of wood against weathering. The chemical modification of *Abies alba* L. softwood samples (80 mm x 10 mm x 2 mm, length x width x thickness) was achieved using 60, 80 and 120% (w/v) organic anhydride – namely maleic (coded as MA) – in the presence of xylene as solvent (reaction time 1 h and 90 °C). Evidence of chemical treatment was also confirmed by FTIR-ATR spectroscopy. MA exhibited lower reactivity towards wood than SA, presumably due to chemical structure. Thermal properties of wood samples were studied through simultaneous thermal analysis (TG-DTG). Wood treatment with anhydrides influenced its thermal stability, which decreased by comparison with non-treated wood. Water sorption properties of softwood were also evaluated.

Keywords: softwood, maleic anhydride, FTIR spectroscopy, TG-DTG analysis

INTRODUCTION

As oil resources are depleting and global awareness of environmental issues is rising, the emergence of economically and environmentally friendly bio-based materials from lignocelluloses and green materials represents an important topic nowadays. The exploitation of bio-based materials as potential substituents for traditional petroleum resources is a sustainable alternative as these are renewable, biodegradable, recyclable, edible, and more energy efficient to process.^{1,2}

Wood is a lignocellulosic material comprising approximately 50-65% cellulose, 20-25% lignin, 1-10% extractives, and traces of ash. The ratio of these constituents differs based on wood species. Wood fibers may change dimensions in the presence of humidity because their polymer components present hydroxyl and other oxygen-containing groups, which capture water through hydrogen bonding.³ Hemicelluloses are mainly responsible for moisture sorption, but non-crystalline cellulose (which is more accessible), lignin, and the surface of crystalline cellulose are also involved and contribute to wood hygroscopic properties.

The environmental concerns regarding recycling and sustainability are continuously growing. In this context, there is a need to extend the life cycle of traditional building materials,

such as wood, to improve their properties and to recycle the raw material waste that occurs during manufacturing. Thus, wood plastic composites (WPCs) aim to increase the efficiency of wood usage by up to 40% compared to traditional wood processing. The properties of composite materials are determined by the interaction of individual constituents. In the case of WPCs, the mechanical properties of the wood are dependent not only on the fiber properties, but also on the level of adhesion between the wood fibers and the polymer matrix. An important issue is that WPCs are made up from two incompatible components and phases (wood fiber, which is hydrophilic in nature, and the plastic matrix, which is hydrophobic in nature) and the interaction of these components occurs at the interface, which can directly affect the strength properties.

Chemical modification provides a means of improving the properties and performance of wood and wood composites. Chemical modification is defined as chemical reaction between some reactive part of a lignocellulose material and a simple single chemical reagent, with or without catalyst, to form a covalent bond between them. This excludes a simple chemical impregnation treatment that does not form covalent bonds.⁴⁻⁸ Such a reaction leads to a

change in the chemical and physical properties of the wood substrate. For example, the acetylation of wood results in the substitution of hydrophilic hydroxyl groups with hydrophobic acetyl groups.^{5,8,9} Thus, such a chemical reaction also results in an increase in dimensions of the reacted wood species, because of swelling of the wood cell wall. In most cases, chemically modified wood has a lower capacity for water absorption, with lower equilibrium moisture content at a specified atmospheric relative humidity, comparatively with unmodified wood.

By replacing some of the hydroxyl groups on the wood polymers with organic anhydride, the hygroscopic properties of the wood are reduced. The reaction of maleic anhydride with wood is presented in Fig. 1.

The objective of this study was to investigate the changes in the structural and thermal properties of softwood after chemical modification using maleic anhydride. These treated wood samples can be further combined with other polymer matrices in order to obtain different composite materials.

EXPERIMENTAL

Materials

Softwood (*Abies alba* L.) was ground in a Retsch PM 200 planetary ball mill. Uniform wood fibers of 0.42 mm length were obtained through grinding and sieving. After that, the as-prepared wood samples were washed with distilled water for 1 h under constant stirring at 80 °C, and dried in an oven at 100 °C until constant weight was achieved. Xylene, as analytical grade reagent, was supplied by Chemical Company, Iasi, and was used as received. Maleic anhydride (MA) with purity > 98% was supplied by Fluka, Germany.

Chemical treatment of softwood

Through chemical treatment, the molecular structure of the cell wall components is changed and some wood properties can be modified (i.e. hydrophilic). Cyclic anhydrides do not yield a by-product when reacting with the hydroxyl groups of wood. The anhydride may react partially with wood, when a single ester function and a free carboxylic

group result, or completely to form di-ester structures (see Figure 1).

Prior to chemical modification, the softwood samples were extracted for 8 h with xylene. The extracted softwood samples were dried for 24 hours in an oven at 70 °C to obtain a constant weight. For esterification, the dried softwood samples were dipped in maleic anhydride (MA), dissolved previously in xylene and heated for one hour at 100 °C, under continuous stirring. The extracted softwood samples were dried for 24 hours in an oven at 70 °C to obtain a constant weight. The concentration level of MA in the solution was established to be 60%, 80%, and 120% (w/w), respectively.

After modification, the wood specimens, coded as W-MA60, W-MA80, and W-MA120 respectively, were removed from the solutions and cooled to room temperature. A new extraction with xylene for 8 h was performed in order to remove the non-reacted MA and, finally, the specimens were vacuum oven-dried for 24 hours at 70 °C to reach a constant weight. A total of 40 samples were designated for this study (10 samples for each concentration value and 10 non-treated samples (W)).

FTIR-ATR spectroscopy

FTIR-ATR spectra were recorded using a Vertex 70 model spectrophotometer (Bruker-Germany) in the range of 4000-400 cm⁻¹ with 4 cm⁻¹ resolution and a scan rate of 32. The spectrophotometer is equipped with a MIRacle™ ATR accessory designed for single or multi-reflection attenuated total reflectance (ATR). The ATR crystal diamond plate (1.8 mm diameter) allows solid materials to be put into intimate physical contact with the sampling area through high-pressure clamping, yielding high-quality reproducible spectra.

Thermal analysis

TG/DTG analysis was performed using a Netzsch STA 449 F1 Jupiter system under nitrogen atmosphere. The measurements were performed while heating the samples (~5 mg) placed in Al₂O₃ crucibles at a rate of 10 °C/min from room temperature up to 600 °C and using nitrogen as a purging gas at a flow rate of 50 mL/min. TG curves recorded with 0.5 °C precision were analyzed using Netzsch Proteus analysis software.

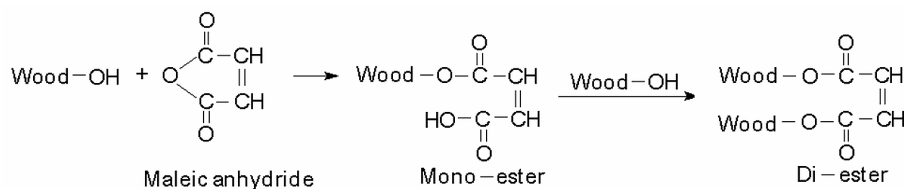


Figure 1: The reaction of maleic anhydride with wood

Water sorption properties

For investigating water sorption properties, the softwood samples were first placed in an oven set at 60 °C, under reduced pressure, for 8 h. The oven-dried weight (W_0) was determined and used to calculate water absorption (WA), as follows:

$$WA (\%) = [(W - W_0) / W_0] \times 100$$

where W is the weight of the softwood sample after immersion in distilled water (up to 188 h), at room temperature, and 85% relative humidity (RH).

RESULTS AND DISCUSSION

FTIR-ATR spectroscopy

FTIR spectroscopy was used to study chemical changes on the surface of softwood before and after chemical treatment with MA (Fig. 2a, b). Usually, the broad peak around 3354 cm^{-1} is associated with mixed OH stretching vibration mainly from cellulose and hemicelluloses. The vibrations from 2900 cm^{-1} characterize the C-H stretching in methyl and methylene groups. The signal from 1729 cm^{-1} corresponds to carbonyl stretching vibration in non-conjugated ketones and in the free aldehyde present in lignin and hemicelluloses. The peak around 1630 cm^{-1} is characteristic absorption of conjugated carbonyl group C=O of lignin in wood samples.

In all the spectra of the softwood samples modified with MA, the absorbance intensity from 3451 cm^{-1} decreases and shifts to lower wavelength values. This behavior is an indication of the decrease in hydroxyl group content during

the reaction between softwood and MA. Signal broadening through lower wavenumber values shows the presence of some new hydroxyl groups involved in hydrogen bonds. The new carboxyl groups that appeared during the reaction between the two components, as shown in Fig. 2, can explain the presence of these signals in the FTIR spectra.

The band from 1730 cm^{-1} , attributed to the carbonyl groups C=O, is shifted to lower wavelength values (1724 cm^{-1}) and a significant increase in intensity is registered. This increase of band intensity is positively correlated with the MA concentration level. The carbonyl stretching vibrations appear in this region (1800-1000 cm^{-1}), the absorption increase being due to the formation of ester groups after chemical treatment. The spectral changes recorded confirm the reaction between softwood and organic anhydride. As expected, the absence of the absorption region 1800-1760 cm^{-1} in the spectrum of the modified softwood indicates that the sample is free of maleic anhydride.

FTIR spectroscopy was used to determine the crystallinity index of non-treated and treated softwood samples.¹⁰⁻¹⁴ Also, the relative values of the hydroxyl index (HI) and carbonyl index (CI), as well as the optical density (RVOD) were evaluated from the FTIR spectra (data presented in Table 1).

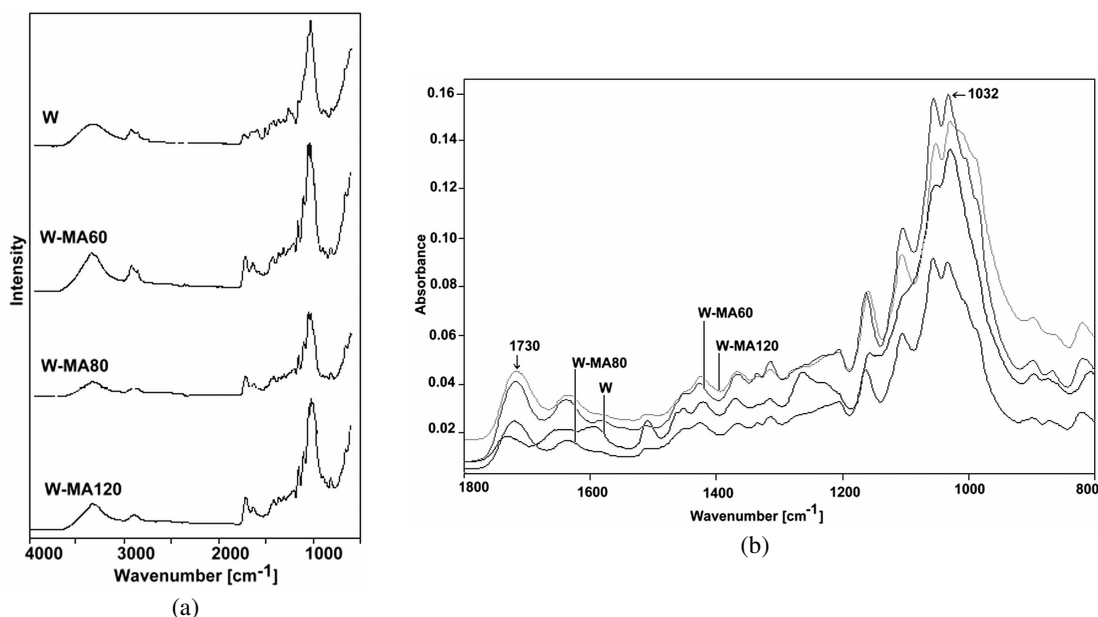


Figure 2: FTIR-ATR spectra of softwood samples – untreated (a) and treated with MA (b)

Table 1
Crystallinity index (χ_{IR}), hydroxyl index (HI), carbonyl index (CI), and optical density (RVOD) evaluation for wood samples

Sample	χ_{IR}		HI	CI	RVOD
	A_{1370}/A_{2900}	A_{1420}/A_{900}	A_{3400}/A_{2916}	A_{1716}/A_{2900}	A_{1505}/A_{1425}
W	1.4429	0.7556	1.2055	0.7705	0.7619
W-MA60	1.3932	0.8202	1.3859	1.2970	0.5687
W-MA80	1.7799	0.9311	1.4015	1.8275	0.5665
W-MA120	1.6840	0.6430	1.4412	1.6642	0.6468

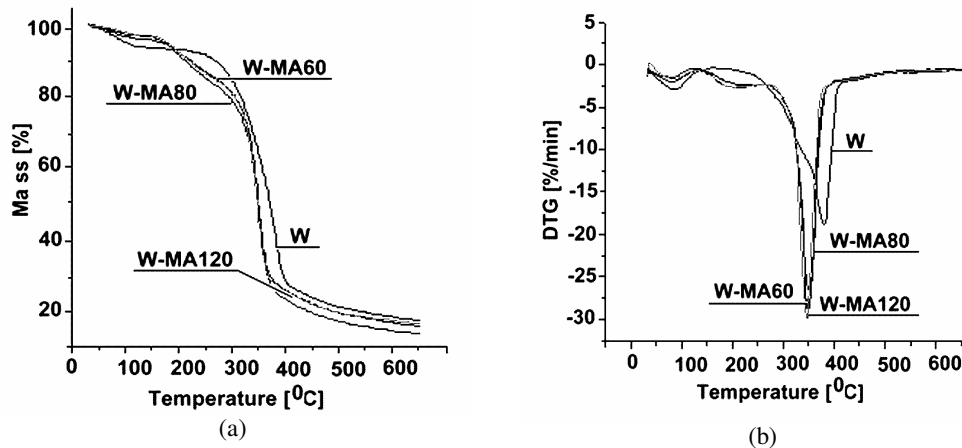


Figure 3: TG/DTG curves for softwood treated with MA

The absorbance values at 1420 and 900 cm^{-1} are sensitive to the amount of crystalline versus amorphous structure in the cellulose material, thus the broadening of these bands reflects a more disordered structure.^{13,14}

Crystallinity index (χ_{IR}) increased from 2.19 up to 2.71 through chemical treatment of wood. The results evidence that carbonyl index (CI) values significantly increased after chemical treatment comparatively with the hydroxyl index (HI) by using maleic anhydride for wood modification. The relative values of the optical density (RVOD) decreased from 0.76 to 0.56 after wood treatment (Table 1). This evolution indicates that some fragments of lignin from wood were removed by its reaction with maleic anhydride.

Thermal analysis

The thermal analysis of wood is difficult due to the composite nature of wood, which is constituted by a mixture of hemicelluloses, cellulose, and lignin. Through the thermal decomposition of softwood, it yields a wide range of products, of which the most characteristic are lignin-related guaiacol derivatives, cellulose-

related glucosan derivatives and hemicellulose-related furfural derivatives. Fig. 3 shows the TG and DTG curves of chemically modified softwood compared with non-modified softwood recorded at a heating rate of 10 K min^{-1} . It is observed that the TG and DTG curves of chemically modified softwood are different from those of the reference sample (W).

Table 2 presents some data extracted from the thermograms. The characteristic data for the modified softwood structures are compared with those of the non-modified softwood (W).

The increase of the MA concentration level in the reaction medium leads to a significant increase in the starting temperature of thermal degradation (Ti) and restricts the Tf–Ti range. The structural modifications of softwood through the esterification reaction could explain the increase of Ti value. The evolution rate of thermal decomposition products increases in this case and restricts the Tf–Ti range. This observation may also explain the lower $T_{50\%}$ temperature value measured for modified softwood samples compared with that recorded for the reference sample.

Table 2
Thermal characteristics of softwood samples under study

Sample	T_i (°C)	$T_{50\%}$ (°C)	T_{mi} (°C)	W_{mi} (%)	T_{mII} (°C)	W_{mII} (%)	T_f (°C)	$T_f - T_i$ (°C)	$W_f - W_i$ (%)	W_{rez} (%)
W	99	372	379	76.17	-	-	396	297	70.50	23.80
W-MA60	169	350	202	10.48	349	69.91	367	200	76.45	15.47
W-MA80	171	349	196	13.57	351	69.94	369	198	80.51	13.35
W-MA120	175	347	182	12.65	346	68.07	363	188	78.43	16.16

where: T_i , $T_{50\%}$ – temperatures corresponding to 5%, 50% mass loss; T_{mi} – temperatures that correspond to the maximum decomposition rate for each stage of thermal decomposition; W_i – mass loss; T_f – final temperature; W_{rez} – mass of residuum resulted at 700 °C

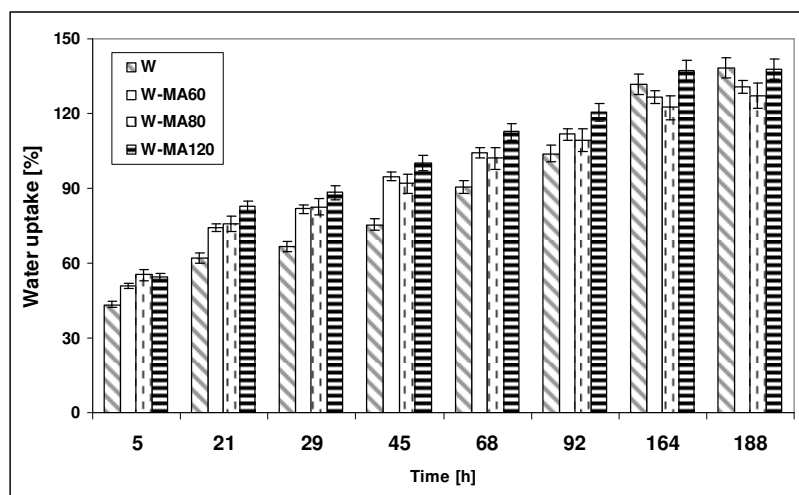


Figure 4: Water uptake evaluation for softwood samples, non-treated and treated with MA

Water sorption properties

The low water resistance is one of the disadvantages of wood. The OH groups influence water molecules more weakly, and this leads to their higher mobility. In such a way, several layers of water molecules are absorbed. The mobility of the water molecules (and the possibility of their removal) thus increases with the increasing distance from the polar OH group. Chemical modification of softwood reduced its hydrophilic character. A considerable lowering of the water uptake is registered for modified softwood samples comparatively with non-modified softwood (W) – see Fig. 4.

CONCLUSION

The spectral changes recorded through FTIR spectroscopy analysis confirmed the reaction of softwood with maleic anhydride.

Thermal analysis evidenced that chemical treatment with MA influenced the thermal stability of the wood samples, they becoming

more susceptible to degradation with increasing MA concentration. At the end of the thermal decomposition process, a slight increase in the weight loss percent for chemically modified softwood, comparatively with non-modified softwood, was recorded.

Chemical modification of softwood reduced the hydrophilic nature of its constituent polymers. A considerable decrease of the water uptake values were obtained for MA treated softwood samples, comparatively with those of non-treated samples.

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