FOURIER TRANSFORM INFRARED SPECTROSCOPY AND THERMAL ANALYSIS OF LIGNOCELLULOSE FILLERS TREATED WITH ORGANIC ANHYDRIDES[*]

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The chemical modification by esterification of hardwood sawdust and its polymer constituents (cellulose, lignin) using organic anhydrides has been investigated. It was found that the weight percent gain increased with an increment of reaction temperature and time. The characterization of modified hardwood, cellulose and lignin was performed by Fourier transform infrared spectroscopy (FT-IR) and thermogravimetry (TGA) studies. Thermal stability of chemically modified wood and wood polymers was found to be lower by comparison with unmodified samples.

Key words: wood, wood polymers, esterification, organic anhydrides, FT-IR, thermogravimetry.

1. INTRODUCTION

Wood residues can be considered polymeric composites made up primarily of cellulose, hemicelluloses, and lignin. These polymers make up the cell wall and are responsible for most of the physical and chemical properties exhibited by wood. Wood products have a well documented problem of water sorption and lack of dimensional stability, due to the associated abundant hydroxyl functionality. These groups are abundantly available in all the three major chemical components of wood or straw. They adsorb water from humid environments, which then enters the wood matrix. Since the adsorbed water is held by hydrogen bonding, wood moisture changes caused by dynamic humidity conditions generate swelling and shrinkage of wood products and physical degradation, sometimes leading to mechanical failure [1]. One strategy to improve the water absorption and dimensional stability of these products is to chemically modify the cell wall

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polymers, which will modify the physical properties of the lignocellulose composite. The chemical modification makes wood with superior qualities of possible tailor made products [2]. Wood can be modified as esters, isocyanates, acetals, epoxies etc., by using appropriate reagents [3].

Most of the research done in the area of chemical modification involves the reaction of the reactive chemical sites in wood, namely hydroxyl groups [4]. So far, the most studied of all the chemical modification treatments applied to wood has been acetylation. Acetylation of wood generally results in a chemically-modified material with superior resistance to biological decay, enhanced physical stability and less prone to surface degradation [5, 6]. Chemical modification of lignocellulose materials (wood and agro-based fibers) can also use dicarboxylic acid anhydrides such as succinic (SA), maleic (MA), and phthalic (PA) anhydrides [3, 7–9]. A schematic representation of chemical treatment of lignocellulose with anhydrides is depicted in Figure 1.
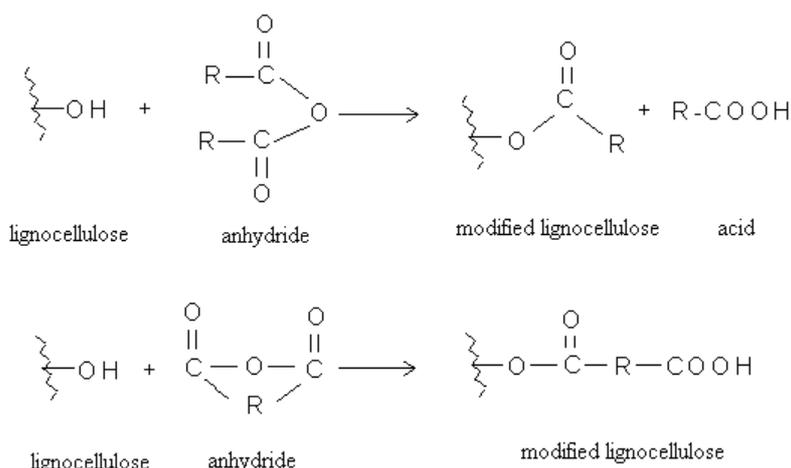

Fig. 1. ─ Chemical modification of lignocellulose by reaction with anhydrides.

Fourier transform infrared spectroscopy (FT-IR) is a useful technique for studying wood decay chemistry [10], as well as to characterize the chemistry of wood [11–13] and determine lignin content in pulp and wood. It is also useful for analyzing chemical and structural changes that occur in wood components due to different treatments [14–17].

The specific objectives of the present work were to modify wood and its polymer components through chemical modification using organic anhydrides as the esterifying agents. A second objective was to characterize the esterified wood and wood polymers. FT-IR analysis was performed to investigate the reaction. Thermogravimetric analysis (TGA) was carried out to study the thermal stability of esterified wood and to compare it with the control.

2. EXPERIMENTAL

2.1. INVESTIGATION METHODS

Sawdust from a native wood tree species (provided by Silvicultural Agency, Iaşi), and cellulose and lignin isolated from wood by using the common methods of wood chemistry (according to the TAPPI standards) were subjected to similar chemical modification treatments by reaction with organic anhydrides as described below. The moisture content of wood samples varied between 5–6%. The major chemical components of wood species are carbohydrates (69–75%), lignin (21–26%) and extractives that can be removed by a solvent (5–9%). In the present work, only wood sawdust fraction remained on the screen having the mesh size of 0.63 mm has been subjected to chemical treatments. Organic anhydrides (maleic MA, succinic SA, and phthalic PA anhydrides from Sigma-Aldrich) were used as the esterifying agents in the chemical modification.

2.1.1. Soxhlet extraction

Soxhlet extraction with ethyl alcohol-toluene mixture (1:2, v/v) was conducted according to the TAPPI norm T 204 om-88 to reduce the influence of wood extractives on the chemical modification. The extracted wood samples were finally oven-dried at 70°C for 24 h to reach a constant weight.

2.1.2. Chemical modification

Wood sawdust, cellulose and lignin samples were dried at 105±2°C in an oven until constant weight (W_1). The samples were treated with organic anhydride solution in acetone (10–100%, w/w). Afterwards it was heated at reflux temperature (57±2°C) during 3, 4, 5, 6 or 7 h. Sawdust samples were also treated with maleic anhydride solution in xylene 10% (w/w) heated at reflux temperature (136±2°C) during 3h. Samples were transferred to the Soxhlet apparatus for solvent extraction for ten hours in acetone (xylene) in order to remove non-reacted anhydride. Finally, samples were re-weighed (W_2) after oven drying 105±2°C.

The extent of reaction was calculated as weight percent gain (WPG) determined by the differences in oven dry weight of the sample before modification (W_1) and after modification (W_2) according to the equation [WPG = (W_2–W_1)/W_1 × 100].

2.1.3. Fourier Transform Infrared Spectroscopy analysis

The properties of the reaction products were characterized by FT-IR using a Digilab Fourier Transform Infrared spectrophotometer, Model Excalibur FTS-2000. The analyses were run using the KBr pellet technique.

The KBr pellets of samples were prepared by mixing (1.5–2.00) mg of samples, finely grounded, with 200 mg KBr (FT-IR grade) in a vibratory ball mixer for 20 s. The 13 mm KBr pellets were prepared under vacuum in a standard device under a pressure of 75 kN cm^{-2} for 3 min. The spectral resolution was 4 cm^{-1} and the scanning range was from 400 to 4000 cm^{-1}.

2.1.4. Thermogravimetric investigation

The thermogravimetric (TG) and differential thermogravimetric (DTG) curves were recorded on a Paulik-Erdey-type derivatograph, MOM Budapest (Hungary), under the following operational conditions: heating rate 12°C/min, temperature range 20–600ºC, sample weight 50 mg, using powdered samples in platinum crucibles, 30 cm^3/min air flow, as reference material α–Al$_2$O$_3$.

Kinetic parameters of thermal degradation for each degradation step were determined by using Swaminathan and Madhavan and Coats-Redfern methods [18, 19] by using a computer program that processed the thermogravimetry data.

3. RESULTS AND DISCUSSION

3.1. EFFECT OF REACTION CONDITIONS ON WEIGHT PERCENT GAIN (WPG)

The time of reaction plays a significant role on the values of WPG, and many of the properties of esterified samples depend on the method of esterification. The amount of moisture present in the wood and wood polymers is also important. The content of moisture (~ 5%) seems to be needed for best reaction, but above this level the water hydrolyses anhydrides to corresponding carboxylic acid. This loss by hydrolysis accounts for a 5.7% loss of anhydride with each 1 % of water in the wood. The rate of esterification decreases as moisture content increases. Here are presented only experimental data regarding the effect of time and maleic anhydride (MA) concentration on weight percent gain (WPG) during wood modification in the presence of solvent (acetone) and without catalyst, these reaction parameters being investigated in order to evaluate the extent of reaction.

3.1.1. Effect of MA concentration on WPG

Figure 2 evidences the effect of MA addition on WPG at reaction temperature of 57±2°C for hardwood samples. Generally, an increase of MA concentration determined an increase in WPG up to 3.1–8.7. A maximum WPG of 8.7 was obtained when wood sample was reacted with 100% (w/w) MA.
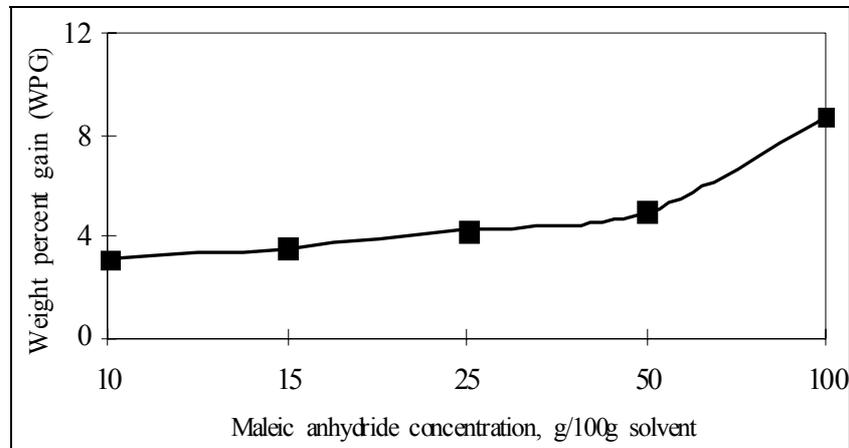
Fig. 2. – Effect of maleic anhydride concentration on WPG in hardwood modification
(reaction time: 7h).

3.1.2. Effect of reaction time on WPG

Effect of reaction time on WPG for wood sawdust samples modified with MA (50% w/w) is presented in Figure 3. As to be expected, the WPG increased with the increment of reaction time. Initially, the reaction time increasing up to 5 h did not result in significant increase of WPG. An increase in WPG for wood sawdust after 5h of treatment is noticed. This may be due to morphological and structural characteristics and degradation of the wood sawdust.
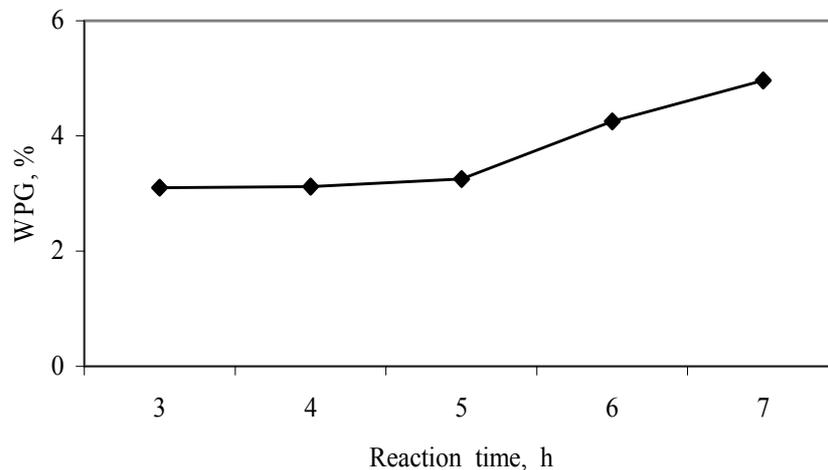

Fig. 3. – Effect of reaction time on the weight percent gain (WPG) in hardwood modification
(10% MA).

3.2. FT-IR ANALYSIS

The spectrum of hardwood shows the same basic structure as all wood samples: strong broad OH stretching (3300–4000 cm^{-1}), C–H stretching in methyl and methylene groups (2800–3000 cm^{-1}), and a strong broad superposition with sharp and discrete absorptions in the region from 1000 to 1750 cm^{-1} [20]. Comparing the spectra of holocellulose and lignin [20] reveals that the absorptions situated at 1510 and 1600 cm^{-1} (aromatic skeletal vibrations) are caused by lignin and the absorption located at 1730 cm^{-1} is caused by holocellulose; this indicates the C=O stretch in non-conjugated ketones, carbonyls and in ester groups [20, 21]. Appearance of the band near 1600 cm^{-1} is a relative pure ring stretching mode strongly associated with the aromatic C–O–CH$_3$ stretching mode, one of the main differences between softwoods and hardwoods being the large amount of metoxyl groups found in hardwoods [20]. The C=O stretch of conjugated or aromatic ketones absorbs below 1700 cm^{-1} [20] and can be seen as shoulders in the spectra. Band assignments according to the literature and band shifts are listed in Table 1 [10, 16].

Table 1

Assignment of the IR bands of functional groups in wood

Band position (cm^{-1})	Functional group
3450–3400	O–H alcohol
2930–2910	C–H methyl and methylene groups
1740–1730	C=O carbonyls
1640–1618	C=C alkene
1515–1504	C=C aromatic
1462–1425	CH$_2$ cellulose, lignin
1384–1346	C–H cellulose, hemicellulose
1260–1234	O–H phenolic
1170–1153	O–H alcohols (primary and secundary) and aliphatic ethers
910	C=C alkenes

Figure 4 shows the FT-IR spectra of unmodified wood (spectrum 1) and chemically modified wood (spectrum 2) – represented only in the fingerprint region between 1800 and 1100 cm^{-1}. This region comprises bands assigned to the main components from wood: cellulose, hemicelluloses and lignin (see Table 1), the spectra being very complex. Clear differences can be detected in the infrared spectra, both in the different absorbance values and shapes of the bands and in their location.

A decrease in the intensity of the O–H absorption band at 3456 cm^{-1} was observed (data not represented here), indicating that the hydroxyl group contents in wood were reduced after reaction. The higher xylan content in hardwood is evidenced by a stronger carbonyl band at 1740 cm^{-1}, for chemically modified wood this being shifted to a lower wavenumber value (1735 cm^{-1}). The enhanced carbonyl absorption peak at 1735 cm^{-1} (C=O ester), C–H absorption at 1381 cm^{-1} (– C– CH$_3$), and –C– O– stretching band at 1242 cm^{-1} confirmed the formation of

ester bonds [22]. Also, it is evidenced an increase in the intensity of OH in plane bending vibration at 1385 cm^{-1} band specific to the wood components, cellulose and hemicelluloses.

Two small bands at 1600 and 1637 cm^{-1} are assigned to the absorbed water and β-glucosidic linkages between the sugar units, respectively [20]. Weak absorptions between 1500 and 1400 cm^{-1} arise from the aromatic ring vibrations and ring breathing with C–O stretching in lignin. As expected, the absence of absorption region 1800–1760 cm^{-1} in spectrum 2 indicated that the product is free of the un-reacted organic anhydride. The lack of peaks at 1700 cm^{-1} for carboxylic group revealed that the products are also free of the by-product of carboxylic acid. Similar features were also observed between FT-IR spectra obtained for unmodified and chemically modified wood polymers.
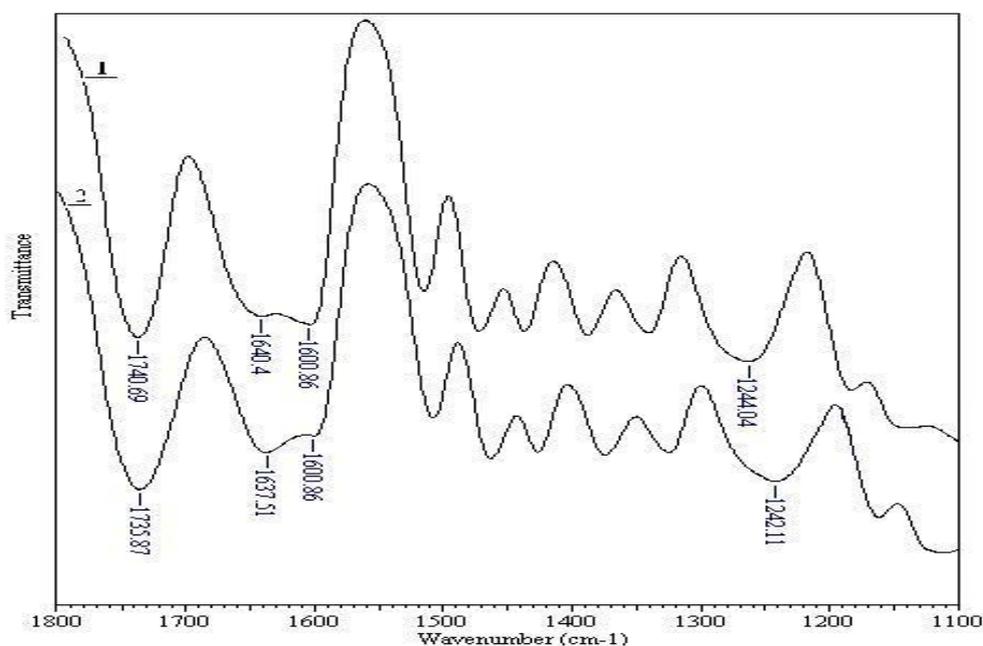

Fig. 4. ‒ FT-IR spectra of unmodified (1) and chemically modified (2) wood samples.

Structural units that undergo various changes are functional groups located on the glucose monomer in cellulose, observable in the FT-IR spectra. Carbon atoms occupying various positions in the ring (denoted as C-1, C-2, …C-6) loose their identity, gradually transforming into various carbonyl groups of different degrees of freedom, namely ketonic, aldehydic, and carboxylic groups.

Cellulose was separated from the wood samples by the common method used in wood chemistry using concentrated nitric acid and ethyl alcohol. The FT-IR spectra of cellulose samples (Figure 5) evidence some differences as follows:
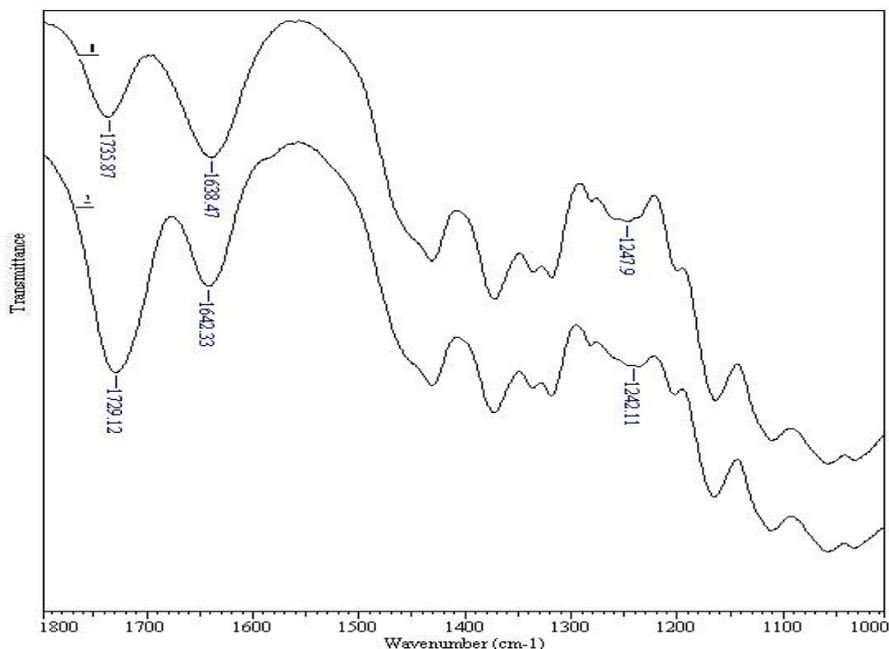
Fig. 5. – FT-IR spectra of unmodified (1) and chemically modified (2) cellulose samples.

1. a 1729 cm^{-1} band attributed to the spectral vibrations of CH=O and OH groups, characterized by an increase as intensity;
2. the carbonyl band assignment allows distinguishing aldehydic and carboxyl stretching vibrations as arising around 1642 cm^{-1}, with decreasing as intensity. These evidence the most profound changes upon esterification under various conditions.

The 1335–1316 cm^{-1} doublet is assigned to the cellulose component, and is related to the contents in crystallized I and amorphous cellulose [11].

The FT-IR spectra of lignin samples (Figure 6) show the bands assigned to the characteristic bending or stretching of different specific groups of lignin in the "fingerprint" region, these being in accordance with the literature [23]. There are evidenced, for example, intensities for the absorption bands specific to the carbonyl stretching (1716 cm^{-1} attributed to the non-conjugated ketone and carboxyl groups). Some bands that are assigned to lignin are not found (1770 and 1740 cm^{-1}) or the integral absorptions are very low (1604 cm^{-1}, 1423 cm^{-1} and 1080 cm^{-1}).

There are no significant differences between spectra for unmodified and chemically modified lignin samples. Some shifts of the absorption bands to lower wavenumbers (1080 cm^{-1} band attributed to the aromatic C-H in plane deformation, guaiacyl-type, and C-O deformation, primary alcohol; 1423 cm^{-1} band attributed to the syringyl ring breathing with CO stretching) are evidenced. These are caused probably by the interactions between the functional groups.
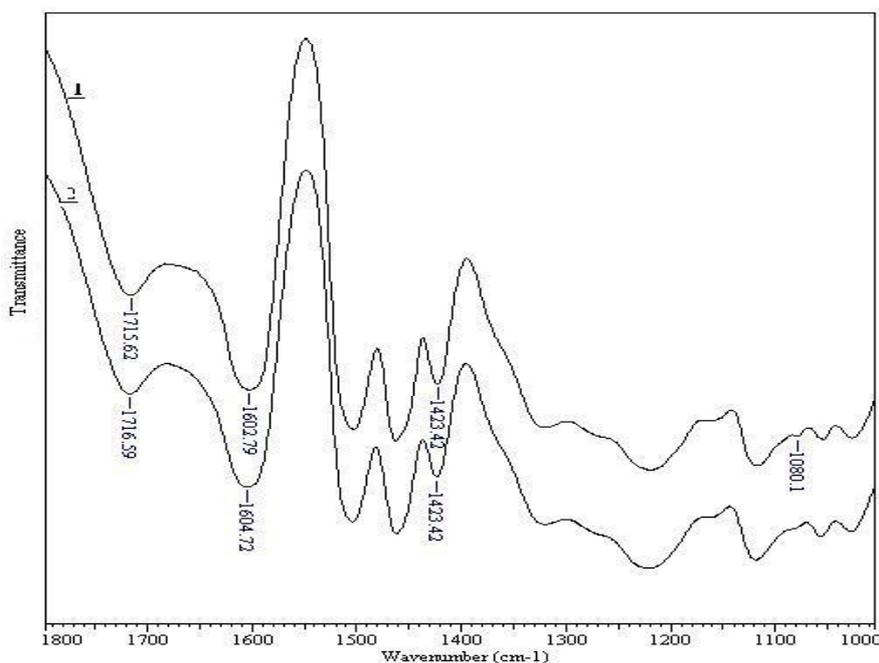
Fig. 6. – FT-IR spectra of unmodified (1) and chemically modified (2) lignin samples.

3.3. THERMOGRAVIMETRIC ANALYSIS

Experimental data regarding the effect of maleic anhydride treatment on the thermal properties of wood sawdust and wood polymers are presented in the Table 2. Cell wall polymers responsible for the wood thermal degradation follow the next diagram: hemicelluloses > cellulose >>> lignin.

Table 2

Thermogravimetry data for wood and polymer constituents untreated (U) and treated (T) with 100% (w/w) maleic anhydride

Samples	Temperature range (ºC)	T10 (ºC)		T50 (ºC)		Ea (Kj/mol)		n		Ea (Kj/mol)		n	
						Coats				Swaminathan			
		U	T	U	T	U	T	U	T	U	T	U	T
sawdust	190–360	242	219	278	261	126	113	1.3	2.0	114	72	1.3	1.4
	340–450	350	380	415	420	102	196	0.4	2.0	37	85	0.4	1.1
cellulose	190–350	260	249	276	278	247	98	2.5	0.7	222	118	2.5	1.3
	400–525	411	410	427	474	328	193	0.6	1.4	66	39	0.6	0.3
lignin	125–235	143	150	160	200	93	65	1.3	0.7	82	74	1.3	1.0
	240–420	293	265	349	320	92	78	0.1	1.1	20	14	0.1	0.1
	430–640	458	451	527	520	135	140	0.6	1.6	38	6	0.6	0.2

where: T10, T50 – temperature of decomposition at 10% respectively 50% weight loss; Ea – activation energy; n– reaction order

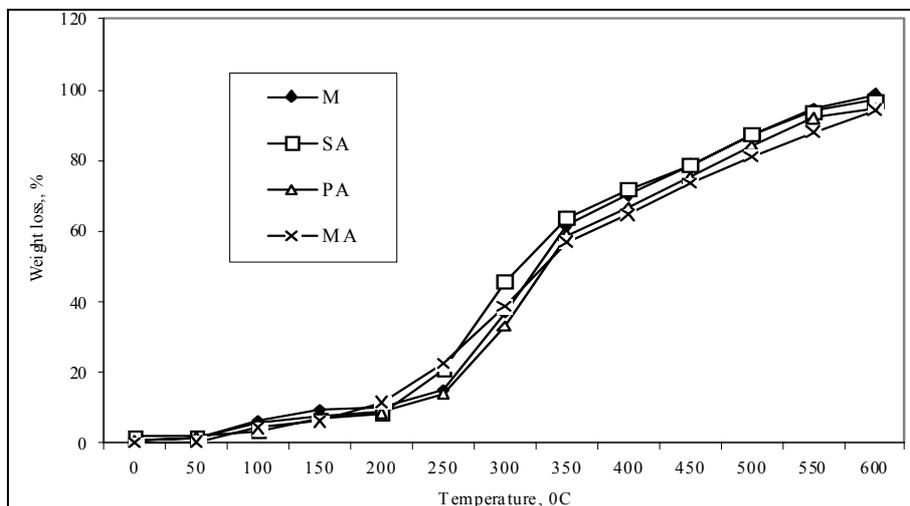The weight loss of wood sawdust untreated and treated with organic anhydrides is presented in Figure 7.

Fig. 7. – Weight loss for hardwood untreated (M) and treated with succinic (SA), phthalic (PA) and maleic (MA) anhydrides.

Table 3

Thermogravimetric data for chemically modified hardwood

Hardwood treated with:*	Ti, °C	Wi, %	Tm, °C	Wm, %	Tf, °C	Wf, %	Ea, Kj/mol	n
M	190	9.9	320	50.4	600	98.6	97.28	1.4
SA	170	7.3	270	31.6	570	95.6	96.75	1.3
PA	170	8.2	310	41.6	570	94.4	85.57	1.1
MA	130	5.8	310	38.2	570	92.0	51.99	1.0

*M-control, SA-succinic anhydride, PA-phthalic anhydride, MA-maleic anhydride where: Ti – initial temperature of decomposition; Tm – temperature of maximum decomposition; W – weight loss: Wi at Ti; Wm at Tm; Wf at the end of decomposition process; Ea – activation energy; n – reaction order.

4. CONCLUSIONS

Weight percent gain resulted for chemical modification of wood by reaction with maleic anhydride is positively correlated with the anhydride concentration and reaction time. A maximum WPG of 8.7 was obtained by reacting hardwood sawdust with 100% (w/w) MA.

FT-IR spectra have evidenced the occurrence of chemical modification of wood by reacting with anhydride. The enhanced carbonyl absorption peak at 1735 cm^{-1}

(C=O ester), C–H absorption at 1381 cm^{-1} (– C– CH$_3$), and –C– O– stretching band at 1242 cm^{-1} confirmed the formation of ester bonds. Similar features were also observed between FT-IR spectra obtained for unmodified and chemically modified wood polymers.

Thermogravimetric analysis evidenced that weight loss of chemically modified wood and its polymer constituents was lower by comparison with unmodified samples.

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