CHEMICAL MODIFICATION OF BEECH WOOD: EFFECT ON THERMAL STABILITY

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Beech sawdust was reacted with phthalic (PA) and maleic (MA) anhydrides for chemical modification. The influence of reaction time and anhydride amount was investigated. IR spectra gave evidence of wood esterification. Thermogravimetric investigation of chemically modified wood indicated a better thermal stability (mainly for wood treated with phthalic anhydride) in comparison with the untreated wood.

Keywords: Wood; Chemical modification; Phthalic anhydride; Maleic anhydride; FT-IR spectra; TG analysis

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INTRODUCTION

Industries that use wood as raw material generate a large amount of by-product wastes, such as wood sawdust, during product manufacturing. Previous researchers have demonstrated that lignocellulosic materials properties (such as dimensional instability due to moisture and low durability due to biodeterioration) can be improved by chemical modification using etherification (Hon and Ou 1989; Norimoto et al. 1983), esterification (Efanov 2001; Hon and Xing 1992; Sereshiti and Rovshandeh 2003), and cyanoethylation (Hon and San Luis 1989; Liga et al. 1995) reactions. Lignocellulosic materials are favored as a new generation reinforcing materials in thermoplastics since they represent renewable natural resources. Besides, the increasing concern about our environment promotes recyclable raw materials and products, emphasizing the demand for lignocellulosic-thermoplastic composite materials (Mahlberg et al. 2001). Chemical modification of wood is defined as chemical reactions involving functional groups of wood-based components and a simple single chemical reagent that forms a covalent bond with the wood-based components (Rowell 1991; Kumar 1994). Dicarboxilic acid anhydrides such as phthalic (PA), maleic (MA) and succinic (SA) anhydrides have been used to esterify the lignocellulosic materials with the aim to produce a thermoformable product (Hassan et al. 2000).

Lignocellulosic materials may be used as filler for polymer materials, which are characterized through increased water and fire resistance in comparison with the wood (Lee et al. 2000; Rowell 1991). The esterification reaction applied to lignocellulosic materials may use different linear and cyclic anhydrides. The reaction between wood and linear anhydrides is a single-site reaction, yielding the corresponding carboxylic acid as a by-product of its reaction with wood. Figure 1 presents the reaction between wood and maleic and phthalic anhydrides.
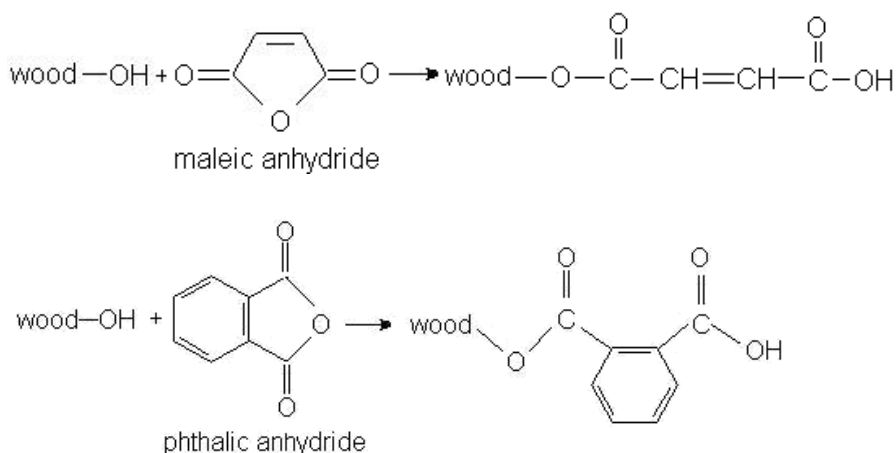
Fig. 1. Wood chemical modification by reaction with organic anhydrides

The first objective of the present work was to investigate the chemical composition of beech wood sawdust and its chemical modification by reaction with phthalic and maleic anhydrides. A second objective was to characterize the esterified wood to determine the optimum reaction conditions to obtain a minimum wood degradation process, as well as to investigate its thermal stability.

EXPERIMENTAL

Investigation of Wood Chemical Components

Wood from *Fagus sylvatica* was selected for this work because of its availability and because this wood is widely used in Romania. Beech sawdust of size 0.63 mm was extracted under reflux in a mixture of ethyl alcohol-benzene (1:2 v/v). Preliminarily, the chemical composition of beech wood sawdust was investigated according to the analytical methods used in wood chemistry as follows:

- humidity by oven-drying at 105^oC (TAPPI T 264 om-88);
- extractives by reaction with a 2:1 v/v mixture of benzene and ethyl alcohol, with a Soxhlet apparatus (TAPPI T 204 om-88);
- extractives by reaction with one percent sodium hydroxide solution (TAPPI T 212 om-88);
- extractives in hot water (TAPPI T 207 om-88);
- cellulose (by gravimetry), after reaction with a 1:4 v/v mixture of concentrated nitric acid and ethyl alcohol (Pettersen 1984);
- lignin (by gravimetry), after 72% sulfuric acid hydrolysis (Klason lignin method and TAPPI T 222 om-88);
- holocellulose (by gravimetry), after reaction with sodium chlorite (Pettersen 1984).

All the results are presented relative to the dry matter content (%DM).

Chemical Modification of Wood by Reaction with Organic Anhydrides

The extractives-free wood samples were dried in an oven set at 100°C for 24 hours. The dry wood sawdust was reacted with 10% solution of phthalic anhydride (PA) in benzene and 10% solution of maleic anhydride (MA) in acetone. The esterification reaction was performed at 57-60°C for various time intervals (180, 300, and 420 min) in a reactor vessel provided with an agitator. Phthalic anhydride (melting point 131°C) and maleic anhydride (melting point 53°C) are commercial products (Sigma), and were used as received.

At the end of the reaction, the reagent was decanted off, and the solvent (benzene or acetone) was added into the reactor to slow the reaction. The mixture was filtered through a pre-weighed crucible, and modified sawdust was further extracted in a Soxhlet apparatus for ten hours in benzene, followed by acetone, respectively. The modified lignocellulosic materials were oven-dried for 24 hours at 105°C.

Spectral and thermal Investigation of Wood Samples

The modified and unmodified wood samples were analyzed by using FT-IR spectroscopy (KBr disc method, a Bruker Vertex 70 FTIR spectrometer).

The KBr pellets of samples were prepared by mixing wood samples, finely ground, with KBr (FT-IR grade) in a vibratory ball mixer. The spectral resolution was 4 cm^{-1}, and the scanning range was from 400 to 4000 cm^{-1}.

The thermogravimetry (TG) and differential thermogravimetry (DTG) curves were recorded on a Paulik-Erdey derivatograph, MOM Budapest, under the following operational conditions: heating rate of 12°C/min, temperature 20-600°C, air flow, sample weight 50 mg, using powdered samples in platinum crucibles using as reference material α-Al_2O_3.

RESULTS AND DISCUSSION

Chemical Composition of Wood

The chemical composition of wood sawdust is presented in Table 1.

Table 1. Chemical Composition of Beech Wood

Index	Percent report to dry matter (%)
Content of cellulose	47.66
Content of lignin	25.53
Content of holocellulose	69.01
Substances extracted with benzene-alcohol	0.93
Substances extracted with hot water	2.18
Substances extracted with 1% NaOH	13.15
Mineral substances (ash)	0.3

Chemical Modification of Wood

The time of reaction is expected to have a significant influence on the values of weight percent gain (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. An intermediate 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. Experimental data regarding the influence of reaction parameters on the values of WPG were presented elsewhere (Bodirlau et al. 2006). The effects of the esterification treatments were evidenced by means of Fourier transform infrared spectroscopy and thermogravimetry analysis.

Fourier Transform Infrared Spectroscopy 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} (Owen and Thomas 1989). Comparing the spectra of holocellulose and lignin 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 (Owen and Thomas 1989; Hergert 1971). 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 (Owen and Thomas 1989). The C=O stretch of conjugated or aromatic ketones absorbs below 1700 cm^{-1} and can be seen as shoulders in the spectra. Band assignments according to the literature and band shifts are listed in Table 2 (Pandey and Pitman 2003; Colom et al. 2003).

Table 2. Assignments of IR Bands of Beech 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

Figures 2 and 3 compare the FT-IR spectra of the wood sawdust before and after the treatments with organic anhydrides. The region between 1800 and 1100 cm^{-1} comprises bands assigned to the main components from wood: cellulose, hemicelluloses,

and lignin (see Table 2), 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 (Saikia et al. 1995). Increase in the intensity of OH in plane bending vibration at 1385 cm^{-1} band is observed, this band being 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 (Owen and Thomas 1989). 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 organic anhydride. The frequency range 1800-1600 cm^{-1} is related to the formation of new ester groups between hydroxyl groups from the wood sawdust and the modifying agents.

Figure 2 shows the FT-IR spectra recorded for the unmodified and modified wood samples. These results provide evidence that the chemical bonding occurred as a consequence of the reaction of wood hydroxyl groups with phthalic anhydride.
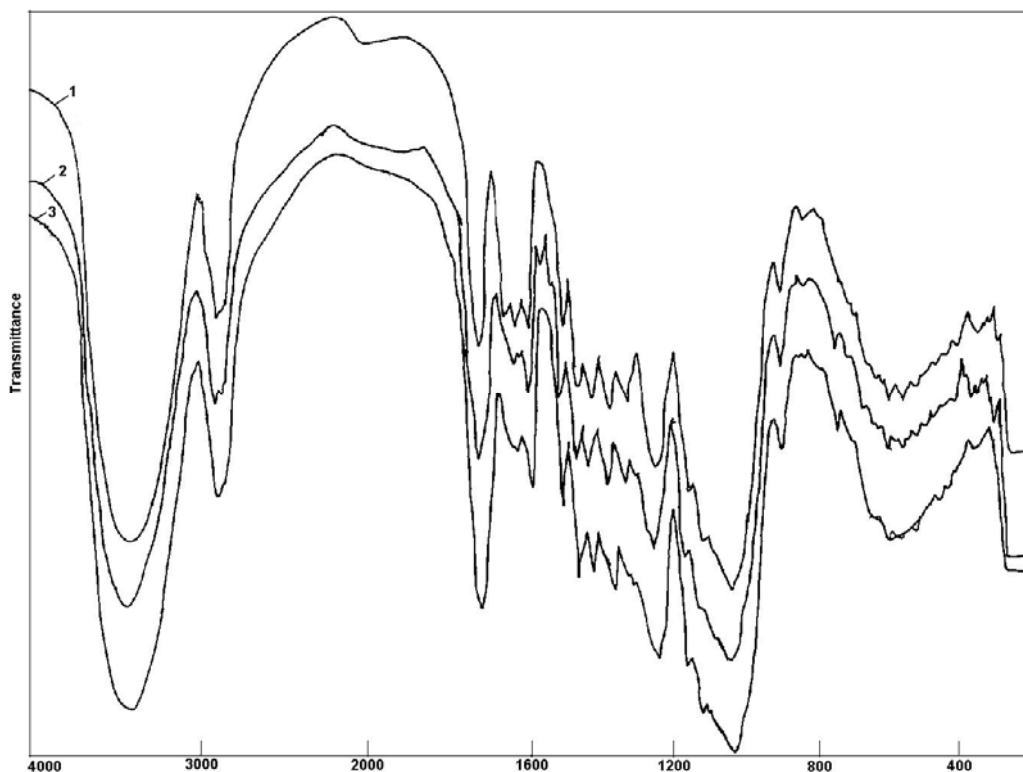

Fig. 2. FT-IR spectra of wood modified with phthalic anhydride 1. control; 2. 180 min; 3. 300 min.

The major difference between the spectra obtained for unmodified and modified wood samples is the presence of a clear and well-marked peak at 1735 cm^{-1} (attributed to the carbonyl groups C=O). The carbonyl stretching vibrations appear in this region and the absorption increase is due to the formation of bonded ester groups after esterification reaction.
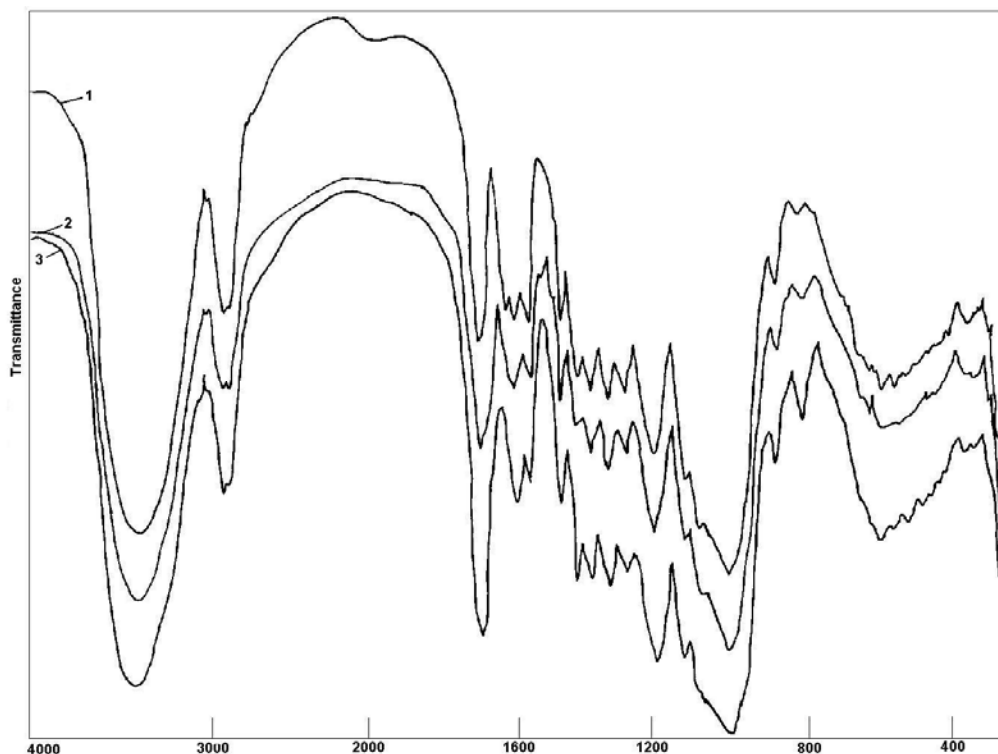

Fig. 3. FT-IR spectra of wood modified with maleic anhydride: 1. control; 2. 180 min; 3. 300 min.

The FT-IR spectra of wood modified with maleic anhydride evidence a more intense peak at 1735 cm^{-1} due to the esterification reaction (Fig. 3). At the same time, the shape of the 3700-3000 cm^{-1} broad band changes for maleic anhydride treatment, indicating a variation of intermolecular to intramolecular OH bonds.

Thermogravimetry Analysis

In thermogravimetric tests on wood sawdust a common behavior in all the samples is the dehydration process, in which 5-8 % of adsorbed water is removed. According with the literature (Wielage et al. 1999), it has been established that there is no degradation up to 160^{0}C. Above this temperature the thermal stability gradually decreases, and decomposition takes place. Figures 4 and 5 present the thermogravimetric curves obtained by dynamic scans for wood sawdust chemically modified with PA and MA.
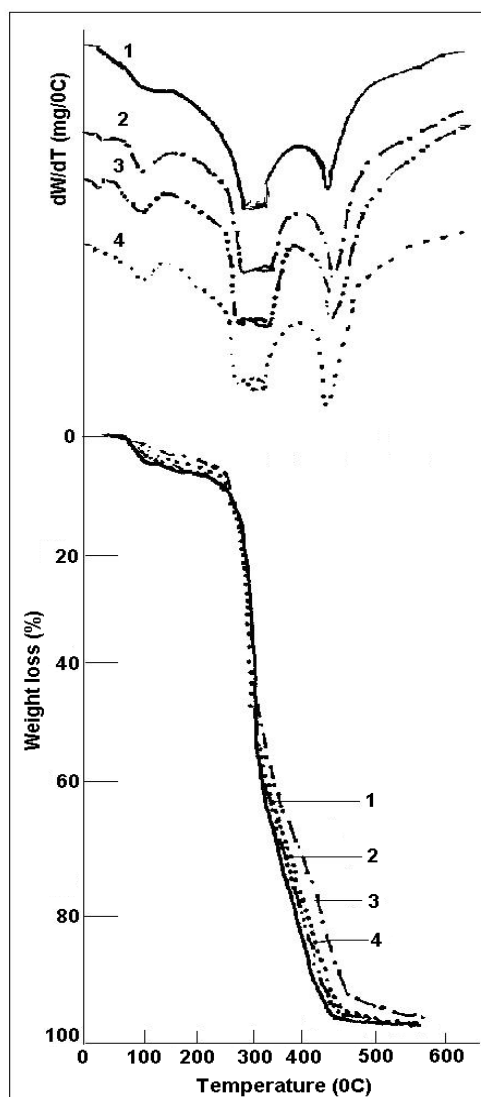
Fig. 4. DTG-TG curves for wood modified with phthalic anhydride: 1. control; 2. 180 min; 3. 300 min and 4. 420 min.

Table 3. Thermogravimetric Characteristics of Wood Modified with Phthalic Anhydride

Sample	T_i (^{o}C)	W_{Ti} (%)	Tmax (^{o}C)	W_{Tmax} (%)	T_f (^{o}C)	W_{Tf} (%)	T_{10} (^{o}C)	T_{50} (^{o}C)
1	198	8.0	274	50.0	361	75.5	231	274
2	149	4.2	303	75.5	351	71	231	298
3	123	4.0	308	50.0	351	69	223	303
4	130	6.0	308	51.0	351	72.5	220	303

T_{10}, T_{50} - temperature corresponding to 10 and 50%mass loss
T_m – temperature corresponding to the maximum rate of mass loss
T_i – temperature corresponding to the beginning of the decomposition
T_f- temperature corresponding to the ending of the decomposition
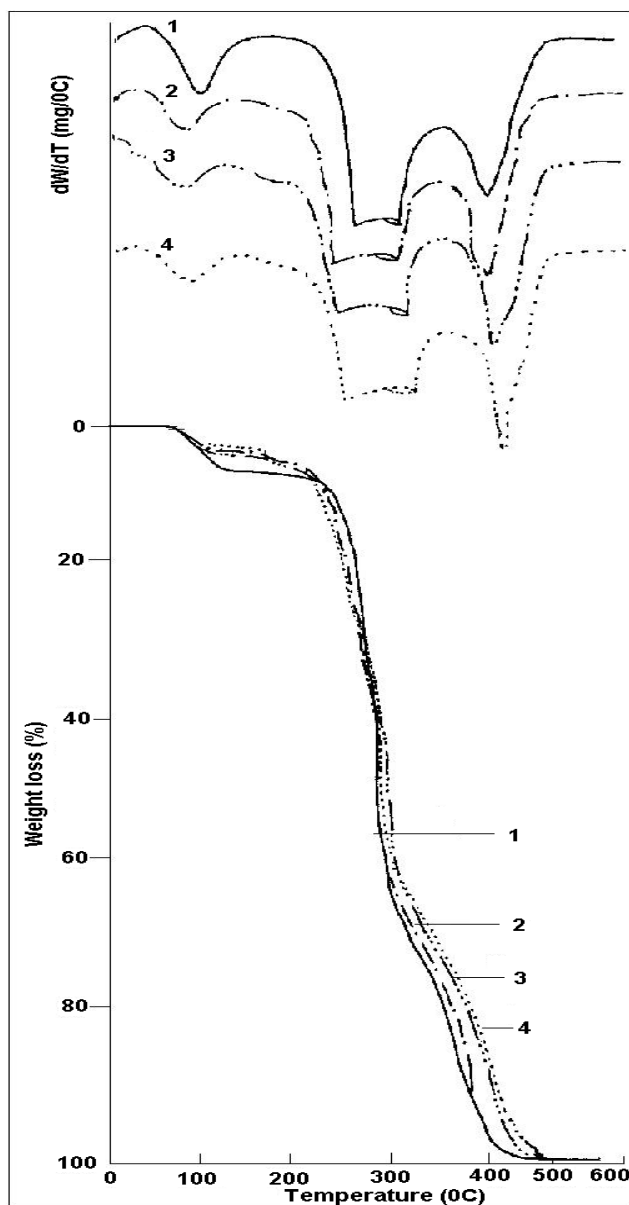W_{Ti}, W_{Tm} and W_{Tf} – mass loss at T_i, T_m and T_f

Fig. 5. DTG-TG curves for wood modified with maleic anhydride: 1. control; 2. 180 min; 3. 300 min and 4. 420 min.

Table 4. Thermogravimetric Characteristics of Wood Modified with Maleic Anhydride

Sample	Ti (^{o}C)	W_{Ti} (%)	Tmax, (^{o}C)	W_{Tmax} (%)	Tf, (^{o}C)	W_{Tf}, (%)	T_{10} (^{o}C)	T_{50} (^{o}C)
1	198	8.0	274	50.0	361	75.5	231	274
2	130	3.0	286	75.0	360	66.0	242	339
3	130	5.0	292	55.0	360	71.0	208	303
4	123	5.0	303	50.0	351	71.5	208	298

The thermal stability of wood is a very important parameter in the production of wood plastic composites (WPCs). They are usually manufactured by mixing wood and polymer at a temperature above the melting temperature of the polymer. Wood is used as a filler material and to improve mechanical strength in plastics that are processed at temperatures below 200°C (Nunez et al. 2002).

The major chemical components (cellulose, hemicelluloses, lignin, and extractives) degrade at different temperatures. Wood materials are known to present different degradation profiles depending on the wood composition. Cellulose is highly crystalline, which makes it thermally stable. Hemicelluloses and lignin, on the other hand, are amorphous and start to degrade before cellulose (Hill 2006). Hemicelluloses are the least thermally stable wood components, due to the presence of acetyl groups (Bourgois et al. 1989). Lignin degrades partly over a wide temperature range, starting at relatively low temperatures (Nassar and MacKay 1984).

The thermogravimetric analysis (TG) of untreated wood samples (Figs. 4-5) indicated a loss of water of 6% between 20 and 140°C. A loss of 5%, respectively 3.5%, of water was observed over the same temperature range for a sample of wood esterified with phthalic anhydride, respectively maleic anhydride.

There is evidence of two other significant weight losses for wood polymer components: one of 47 % in the 200-360°C range and another of 23 % between 360°C and 450°C. The first weight loss is attributed to the decomposition of hemicelluloses (Nguyen et al. 1981). The second one is attributed to cellulose decomposition (Kosik et al. 1972; Nguyen et al. 1981; Bouchard et al. 1986). These weight losses were followed by that of lignin at a temperature above 370°C (Nguyen et al. 1981; Bouchard et al.1986). In contrast, after esterification, only one weight loss of 88-90 % (reaction time 180 min), 89-90 % (reaction time 300 min), and 91-92 % (reaction time 420 min) was observed between 200°C and 450°C. This could be due to the greater stability of the hemicelluloses after esterification. This phenomenon has also been reported (Rowell et al. 1984). At 450°C, it was evidenced that from 1.5 up to 7 % (reaction time 180 min), 1-3 % (reaction time 300 min) and 0.5-1 % (reaction time 420 min) carbonized residue was obtained from esterified wood, against 5 % for untreated wood. This fact indicated that the phthalic and maleic groups in the esterified wood samples were eliminated with the volatile products and did not contribute to the carbonized residue.

The chemical modification of wood by reaction with organic anhydrides analyzed here slightly improves the thermal stability of wood, showing a higher temperature of decomposition and a lower weight loss rate than that of untreated wood sawdust (see Tables 3, 4). Both temperature corresponding to the maximum rate of weight loss (T_{max}), and that corresponding to 50% weight loss (T_{50}) exhibit a significant increase for chemically modified wood by comparison with the control samples. Weight loss at T_{max} increases for modified wood samples at 180 min time reaction, for higher values of time (300 min, respectively 420 min), this parameter being comparable with that of the control samples.

CONCLUSIONS

1. The reaction of any reagent with such a heterogeneous material as wood sawdust is complex, considering its main chemical constituents. FT-IR spectra indicate the occurrence of chemical modification of wood by reacting with organic anhydrides. 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. For the untreated wood sawdust the peak at 1735 cm^{-1} is less intense.
2. The TG and DTG curves for chemically modified sawdust shifted to higher temperatures, a fact that implies an improvement in thermal stability. This evolution becomes more pronounced by increasing the reaction time for treatment with anhydrides. The thermogravimetric data confirm that treatments with organic anhydrides influence wood thermal behavior, as indicated by the maximum peak and the temperature range of wood decomposition process.

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