

PREPARATION AND CHARACTERIZATION OF COMPOSITES COMPRISING MODIFIED HARDWOOD AND WOOD POLYMERS/POLY(VINYL CHLORIDE)

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Chemical modification of hardwood sawdust from ash-tree species was carried out with a solution of maleic anhydride in acetone. Wood polymers, lignin, and cellulose were isolated from the wood sawdust and modified by the same method. Samples were characterized by Fourier transform infrared spectroscopy (FTIR), providing evidence that maleic anhydride esterifies the free hydroxyl groups of the wood polymer components. Composites comprising chemically modified wood sawdust and wood polymers (cellulose, lignin)-as variable weight percentages-, and poly (vinyl chloride) were obtained and further characterized by using FTIR spectroscopy and scanning electron microscopy (SEM). The thermal behavior of composites was investigated by using the thermogravimetric analysis (TGA). In all cases, thermal properties were affected by fillers addition.

Keywords: Composites; Fillers; Poly (vinyl chloride); FTIR spectroscopy; Thermogravimetric analysis

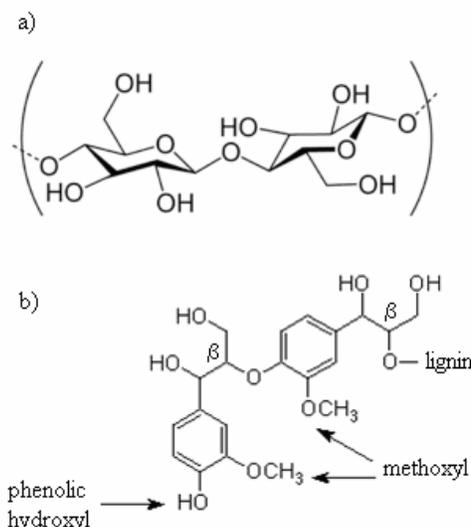
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INTRODUCTION

The production of lignocellulosic fibers-based polymer composites has become in recent years an important application for recovering, reuse, and recycling a variety of by-products related to industrial exploitation of natural resources.

Lignocellulosic materials (wood fibers, wood flour, agro-residues) are attractive fillers for thermoplastic polymers mainly because of their low cost and large availability. According to their botanical source, these renewable materials present large variations in their composition. Main elements are cellulose, hemicelluloses, and lignin, which are known to present a very complex structure (see Scheme 1).

Wood fibers offer a number of advantages over the currently used reinforcing inorganic materials (e.g., glass fibers) in terms of cost on a unit volume basis, as well as flexibility during processing (Matuana et al. 1998; Mengeloglu et al. 2000; Bledzki and Gassan 1999). Wood modification can change important properties of the wood, including biological durability, dimensional stability, hardness, and UV-stability by converting hydrophilic OH-groups into larger, more hydrophobic groups. Specific wood modification processes designed for the production of wood-plastic composites may be developed having in view the properties of the wood component in the composites, but also the improved interaction, e.g. by means of grafting processes.



Scheme 1. Structural representation of main wood polymer components: a) cellulose; b) lignin

The use of lignocellulose filler-thermoplastic polymer bio-composites has been rapidly increasing in the field of construction (wood decks, window frames, bathroom interiors, etc.) and the automotive industry (dashboards, etc.). In these composite systems, thermal properties, such as thermal stability and thermal expansion, are very important factors that affect the quality of the final products.

The technological performance of wood fiber – thermoplastic polymer composites depends strongly on the quality of the wood fiber-matrix interface, i.e., the establishment of a strong adhesive bond between reinforcing fillers and the polymer matrix. Although PVC/wood fiber composites have many outdoor applications, considerable problems arise from their photo-degradation induced by the terrestrial sunlight. This degradation is mainly due to the high susceptibility of both wood fibers (Lu et al. 2000) and PVC matrix (Torikai and Hasegawa 1999) to degradation when exposed to such factors as long-term solar ultraviolet (UV) radiation, rain, snow, and pollutants.

However, wood fibers and thermoplastics commonly used are not compatible enough to produce composites with appropriate properties for some particular applications, especially when high resistance to breakage is required. The incompatibility between lignocellulosics and thermoplastics is related to polarity differences, since the high content of hydroxyl (OH) groups in lignocellulosics (wood and wood polymers - cellulose, hemicelluloses, or lignin) makes them hydrophilic by nature; however, thermoplastics commonly used as matrix (polyethylene, polypropylene, or polyvinyl chloride) are low polarity compounds. Thus, in order to obtain a composite based in non-polar thermoplastics with competitive final properties, it is necessary to achieve a good compatibility between filler and matrix, generally by the modification of the filler surface or by the addition of chemical coupling agents. Most often treatments are performed on the lignocellulosic reinforcements (Gauthier et al. 1998).

At present, there is a tendency to use mercerization (treatment with a sodium hydroxide solution) to improve the compatibility between the hydrophilic wood fibre and the hydrophobic polymer matrix. Several authors suggest that wood alone does not react significantly with etherifying/esterifying reagents, since the hydroxyl groups in wood are not readily accessible. Hence, the raw material can be pretreated with NaOH as a swelling agent, and water as a solvating agent (Hon and Ou 1989; Marcovich et al. 2001). NaOH can cause a complete lattice transformation from cellulose-I to cellulose-II (Fengel and Wegener 1984). Esterification without the alkaline pretreatment in order to eliminate some wood matrix elements is also possible, with the attainment of higher weight gains (Marcovich et al. 2005).

Extractives-free wood is the supposition for the determination of wood components like holocellulose, cellulose, hemicellulose, and lignin according to the TAPPI test methods. The cold water, hot water, and toluene-ethanol solution extractions can all greatly improve the permeability of the wood cell wall. This fact has a real significance for the further treatments of wood.

Lignocellulosic fibers esterified with maleic anhydride and used to prepare composites present reduced moisture absorption of both of fibers and the resulting composites in comparison to the untreated systems (Clemons et al. 1992; Mishra and Naik 1998; Iwamoto and Itoh 2005; Nenkova et al. 2006).

Although the coupling action in wood fibers polymer composites (WFPCs) is complicated, the primary forms of covalent bonds for coupling agents are esterification, etherification, and carbon-carbon double bonds (Lu et al. 2000). Anhydrides such as maleic anhydride (MA), succinic anhydride (SA), and phthalic anhydride (PHA) are popular coupling agents in WFPCs.

Chemical modification of wood fibers is performed to provide a good compatibility by reaction with anhydrides that blocks the hydroxyl groups in the wood chemical structure, thus improving wood properties and increasing its dimensional stability, UV resistance, biological resistance, and mechanical properties (Matsuda 1996; Cofta et al. 2006; Nunez et al. 2002). By now, there are many reports about the effect of chemical modification on solid wood and wood composites (Lu et al. 2000; Nunez et al. 2002; Sombatsompop et al. 2003).

FTIR spectroscopy is uniquely suited for studies of chemical reaction, because absorbance peaks are characteristic of chemical bonds rather than of atoms (Marcovich et al. 2005; Lu et al. 2000; Torikai and Hasegawa 1999; Matsuda 1996; Cofta et al. 2006; Nunez et al. 2002; Sombatsompop et al. 2003; Kim et al. 2004; Bodîrlău et al. 2007; Matuana et al. 2001). Infrared spectroscopy has been proven to be a highly effective means of investigating specific interactions between polymers. FT-IR can be used to qualitatively and quantitatively study the mechanism of inter-polymer interaction through hydrogen bonding.

Thermogravimetric analysis (TGA) is one of the methods of thermal analysis that can be used to measure the mass change, thermal decomposition, and thermal stability of composite materials (Hatakeyama and Quinn 1994; Cofta et al. 2006). Thermal investigation is extensively applied to investigate the thermal behavior of various materials as a function of temperature (Oksman and Lindberg, 1995; Simonsen and Rials 1996).

Scanning electron microscopy (SEM) is used to investigate the occurrence of thermoplasticity of the esterified wood fiber matrix (Timar et al. 2004).

The purpose of this study is to carry out structural and thermal characterization of composites comprising chemically modified wood sawdust and wood polymers - cellulose, lignin- and poly (vinyl chloride) by using FTIR, TGA, and SEM analysis methods.

EXPERIMENTAL

Materials

Wood sawdust from a native hardwood tree species (ash tree wood *Fraxinus excelsior* L., 52 years old, obtained from a local source, namely Forestry Agency, Iasi), and cellulose and lignin isolated from the same wood by using the common methods of wood chemistry (Nunez et al. 2002; according to the TAPPI standards) were subjected to similar chemical treatment. Wood sawdust from *Fraxinus excelsior* L. was selected for this work because of its availability and because this wood is widely used in Romania. The moisture content of wood samples was found to be between 5% and 6%. The major chemical components of hardwood species are carbohydrates (69-75%), lignin (21-26%), and extractives (5-9%) that can be removed by an ethanol-toluene treatment.

In the present work, only the wood sawdust fraction passed through a mesh sieve 0.63 mm was used. Wood sawdust was dried at 70°C for 24 h in a vacuum oven before extraction with organic solvents mixture in a Soxhlet extractor. The temperature of 70°C was chosen instead of the usual 100°C in order to avoid the possible degradation of extractive substances.

Wood sawdust and its main polymer constituents were subjected to chemical modification by reaction with maleic anhydride (MA). Maleic anhydride (>99%, Sigma) and poly (vinylchloride) (PVC, Teraplast SA Bistrita, Romania: plasticized PVC granules type YT1, density: 1.2 g/cm³; shore A hardness at 23±2°C: 56 to 60 °Sh; thermal stability at 180°C: 60 min) were used as received. All solvents were of analytical grade.

Soxhlet Extraction of Wood Sawdust and Separation of Wood Polymer Components

Firstly, the wood sawdust was extracted with organic solvents in order to remove the extractive substances that can influence the further chemical modification. The Soxhlet extraction was conducted according to the TAPPI norm T 204 om-88. The wood samples were first extracted with a 120-mL mixing solution of toluene and ethanol (2:1) for 4 h, followed by a second extraction with 120 mL ethanol for 4 h. The extracted wood samples were finally oven-dried at 100°C for 24 h to reach a constant weight. Main wood polymer components (cellulose, lignin) were determined according to the standard methods used in wood chemistry.

The cellulose content was determined as follows: 1 g (oven-dried) of extracted wood sample was placed in a 200-mL beaker to which 5 mL of concentrated HNO₃ (96%) and 20 mL of ethanol were added. The mixture was refluxed under shaking in a water bath for 60 min. After that, samples were filtered using a tared fritted disc glass

thimble. The 60-min refluxing cycle was repeated four times. Finally, the sample was washed with hot water until reaching neutral pH, and dried at 70°C in a vacuum oven until constant weight. The cellulose content was calculated.

The lignin content was determined accordingly to the Klason method. One gram (oven-dried) of extracted wood sample was placed in a 100-mL beaker to which 15 mL of 72% H₂SO₄ was added. The mixture was left at room temperature for 2 h, with occasional stirring. The solution was then transferred to a 1-L Erlenmeyer flask, diluted with 560 mL of deionized water to reach a H₂SO₄ concentration of 3%, and refluxed for 4 h. The mixture was then filtered, washed with hot water until the neutral pH, and the insoluble lignin was determined gravimetrically.

Chemical Modification of Wood Sawdust and Its Main Polymer Components

Maleic anhydride (MA) was used for chemical modification of wood sawdust and its main polymer components. MA is an α,β -unsaturated carbonyl compound, containing one carbon-carbon double bond (C=C) and two carboxylate groups (-COO-). The functional groups [- (CO)₂ O-] of MA interact with the polar groups [mainly hydroxyl groups (-OH)] of cellulose and lignin to form covalent or hydrogen bonding. It has been reported in the literature that wood cell wall polymers reactivity towards organic anhydrides (e.g. acetic anhydride) decreases in the order: lignin >/cellulose (Matsuda 1996).

Wood sawdust, cellulose, and lignin samples were dried at 70°C in a vacuum oven until constant weight, then were transferred to a vacuum desiccator and allowed to cool to ambient temperature, and weighed (W_1). All samples were treated with MA solution in acetone (10% w/w) and heated at reflux temperature (57±2°C) during 7 h. Samples were allowed to sit in the acetone for one hour before being transferred to the Soxhlet apparatus for solvent extraction for ten hours in acetone in order to remove the unreacted anhydride. Finally, samples were re-weighed (W_2) after oven drying (as detailed previously). Samples were free of the excess reactant, by-products and acetone after this procedure.

The extent of reaction was calculated as weight percent gain (WPG) determined by the differences in oven dried weight of the unmodified wood sample (W_1) and the modified wood after extraction of the non-reacted reagent and by-products not actually linked to the wood matrix (W_2) according to the equation [$WPG = (W_2 - W_1) / W_1 \times 100$]. Data were presented in a previous study (Bodîrlău et al. 2006).

Preparation of Wood and Wood Polymers-PVC Composites

A Brabender LabStation (Germany) with a mixer (30/50 EHT) was used for the melt blending of PVC with fillers. Mixing was performed with 60 rpm at 170°C. The material was compression moulded after 5 min heating at 170°C in a moulding press at 2-4 MPa pressure to get sheets. The sheets were allowed to cool to room temperature. Test specimens for different structural, morphological and thermal characterization tests were cut from these sheets. The filler-PVC composites were coded, the sample identification codes being presented in Table 2. In all cases, the weight percentage of modified filler will be indicated in parentheses, e.g. WS (10) indicates a composite made with modified wood sawdust in a 10:90 (filler:PVC) ratio.

Table 2. Sample Identification Codes

Code	Sample
PVC	poly (vinylchloride)
WS	modified wood sawdust
C	modified cellulose
L	modified lignin
WS(10); WS(25); WS(50)	modified wood sawdust -PVC composites
C(10); C(25); C(50)	modified cellulose-PVC composites
L(10); L(25); L(50)	modified lignin-PVC composites

FTIR, TGA, and SEM Measurements

The efficiency of the chemical treatment was verified using Fourier transform infrared spectroscopy. Due to its specificity, infrared spectroscopy was used to identify the qualitative changes in the chemical structure of wood brought about by chemical modification. The spectra were recorded in the range of 4000–600 cm^{-1} . Samples were dried, ground, and mixed with potassium bromide (KBr) in a ratio of about 1:100 and pressed under vacuum to form pellets. A KBr pellet was used as a reference. FT-IR analysis was performed by using a Digilab Fourier Transform Infrared (FTIR) Spectrometer, Model Excalibur FTS-2000.

The thermal behavior of the chemically modified fillers and their composites with PVC was determined by thermogravimetry (TGA). Both the TG and DTG curves were recorded on a derivatograph Q-1500D type MOM Budapest (Hungary). About 50 mg of sample, previously ground and oven dried, was used for each analysis. Determinations were made in air atmosphere (30 cm^3/min air flow). The heating rate was 10 $^{\circ}\text{C}/\text{min}$, and the temperature range was up to 600 $^{\circ}\text{C}$. Aluminum oxide was used as a reference sample. Three or four repeated readings (temperature and weight loss) were performed on the same TG curve, each of them having at least 15 points. Kinetic parameters of thermal degradation for each degradation step were determined by using Coats-Redfern method (Coats and Redfern 1964) by using a computer program that processed the thermogravimetric data.

For the SEM investigation, specimens with surface areas of about 5x5 mm were cut from the different oven-dried composite products. The cross-sections were smoothed by several successive microtome cuttings. The samples were mounted on special stubs using carbon tabs and were then coated with gold by sputtering under vacuum (10 $^{-2}$ mbar). The surface properties of specimens were investigated using a scanning electron microscope (QUANTA 200).

RESULTS AND DISCUSSION

Characterization of Wood Sawdust

In Table 1, the values obtained from chemical analysis of ash-tree wood sawdust are presented.

Table 1. Main Components of Ash-Tree Wood Sawdust

Ash, %	Organic Solvents Extractives, (%)	Hot Water Extractives (%)	One Percent NaOH Solution Extractives (%)	Cellulose (%)	Lignin (%)
0.66	3.53	6.38	18.80	41.58	26.39

Characterization of Chemically Modified Wood Sawdust and Wood Polymers

FTIR spectroscopic analysis

The efficiency of the chemical treatment was investigated by FTIR spectroscopy (Nelson and O'Connor 1964; Hergert 1971; Owen and Thomas 1989; Pandey 1999; Colom et al. 2003; Colom and Carrillo 2005; Sakakibara 1991). The spectrum of hardwood showed the same basic structure as all wood samples, as it was detailed in a previous paper (Bodîrlău et al. 2008). Band assignments according to the literature are listed in Table 3 (Pandey 1999; Colom et al. 2003).

Table 3. Assignments of IR Bands of Ash-Tree Wood

Band Position (cm ⁻¹)	Functional Group
3300-4000	O-H stretching
2800-3000	C-H stretching in methyl and methylene groups
1750-1730	C=O stretching in carbonyl
1640-1618	C=C alkene
1510-1504	C=C aromatic skeletal vibrations
1462-1425	CH ₂ cellulose, lignin
1384-1346	C-H cellulose, hemicellulose
1260-1234	O-H phenolic
1170-1153	O-H alcohols (primary and secondary) and aliphatic ethers
910	C=C alkenes

Different publications (Marcovich et al. 1996; Marcovich et al. 1998) have detailed the reactions expected to occur between the wood with the MA. The FTIR spectra for unmodified and modified wood samples are presented in Figure 1, showing the differences in the chemical structure of wood brought about by the chemical modification. These differences were mostly reflected in the region 1800-700 cm⁻¹. Due to the complexity of the spectra, only the peaks that best reflect the changes in the chemical structure are discussed below.

Figure 1 gives evidence of the chemical bonding occurring as a consequence of the reaction of wood hydroxyl groups with MA. The major difference between the spectra obtained for unmodified and modified wood samples is the presence of a clear and well-marked peak at 1726 cm⁻¹ (attributed to the carbonyl groups C=O). The carbonyl stretching vibrations appear in this region, and the increment in the intensity is due to the new ester bonds formed by reaction of the OH groups in the wood with the anhydride. The absorption in this region corresponds to both the C=O groups in acid and ester groups attached to the wood (Bellamy 1975).

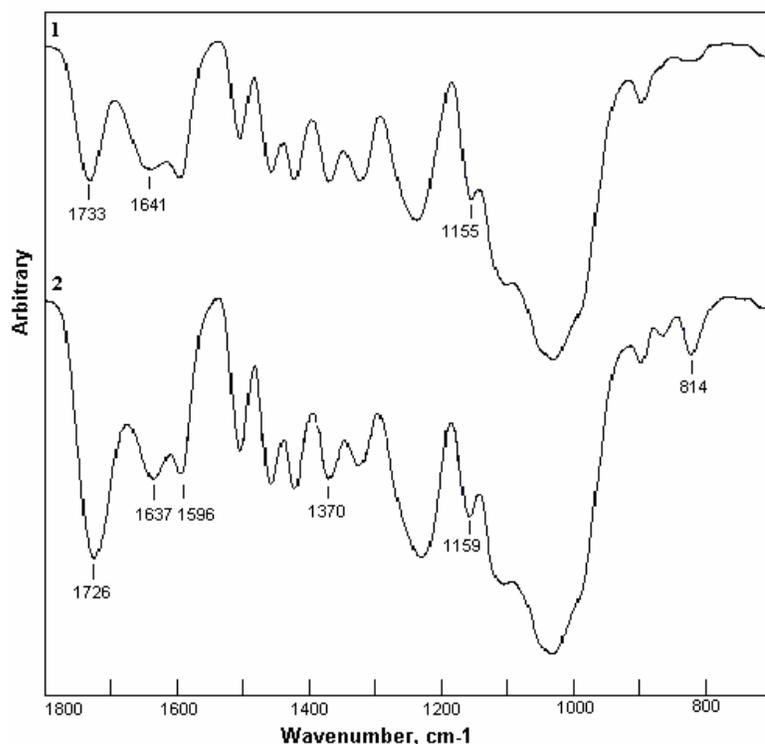


Fig. 1. FTIR spectra of unmodified (1) and chemically modified wood sawdust (2)

Moreover, the intensified peak at 1637 cm^{-1} and the new peak at about 814 cm^{-1} are attributed to the double bond in MA. The absence of a band at 1790 cm^{-1} , corresponding to the absorption of MA, proves that there is no more non-reacted MA in the samples. In addition, the peak at 1159 cm^{-1} becomes more intense as new ester groups are formed. In the treated wood spectrum, it is possible to observe a new peak at 822 cm^{-1} related to the absorption of cis C=C, in conjunction with the carbonyl group (Bellamy 1975).

The region between 1800 and 1100 cm^{-1} comprises bands assigned to the main components from wood: cellulose, hemicelluloses, and lignin (see Table 3), 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.

The higher xylan content in hardwood is evidenced by a stronger carbonyl band at 1733 cm^{-1} , for chemically modified wood this being shifted to a lower wavenumber value (1726 cm^{-1}). The enhanced carbonyl absorption peak at 1726 cm^{-1} (C=O ester), C–H absorption at 1370 cm^{-1} (–C–/CH₃), and –C–/O–/ stretching band at 1231 cm^{-1} confirmed the formation of ester bonds (Saikia et al. 1995). The absorption band observed at 1370 cm^{-1} is assigned to OH plane bending vibration, this band being specific to the wood components, cellulose and hemicelluloses (Pandey 1999). Two small bands at 1596 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.

The FTIR spectra obtained for the wood polymer components before and after the treatment with MA are not presented here, these showing no significant differences

Characterization of Wood Sawdust and Wood Polymers/PVC Composite Materials

FTIR spectroscopic analysis

The characteristic bands of PVC can be classified into three regions. The first is called the C-Cl stretching region in the range from 600-700 cm^{-1} . The second region is attributed to C-C stretching in the range from 900-1200 cm^{-1} . The third region is 1250-2970 cm^{-1} assigned to numerous C-H modes (Matuana et al. 2001).

The spectrum of PVC is presented in Fig. 2. Absorption bands of PVC are evidenced at 2959 cm^{-1} (C-H stretching from CH-Cl), 2929 cm^{-1} (C-H stretching from CH_2), 1461 and 1430 cm^{-1} (wagging CH_2), 1332 cm^{-1} (CH_2 deformation), 1272 cm^{-1} (C-H stretching from CH-Cl), 1072 cm^{-1} (C-C), 958 cm^{-1} (rocking CH_2), 703, 639 and 616 cm^{-1} (C-Cl stretching). Some oxygenated structures can be detected in the PVC chain, as evidenced by the absorption around 1723 cm^{-1} that can be assigned to an additive in the PVC product.

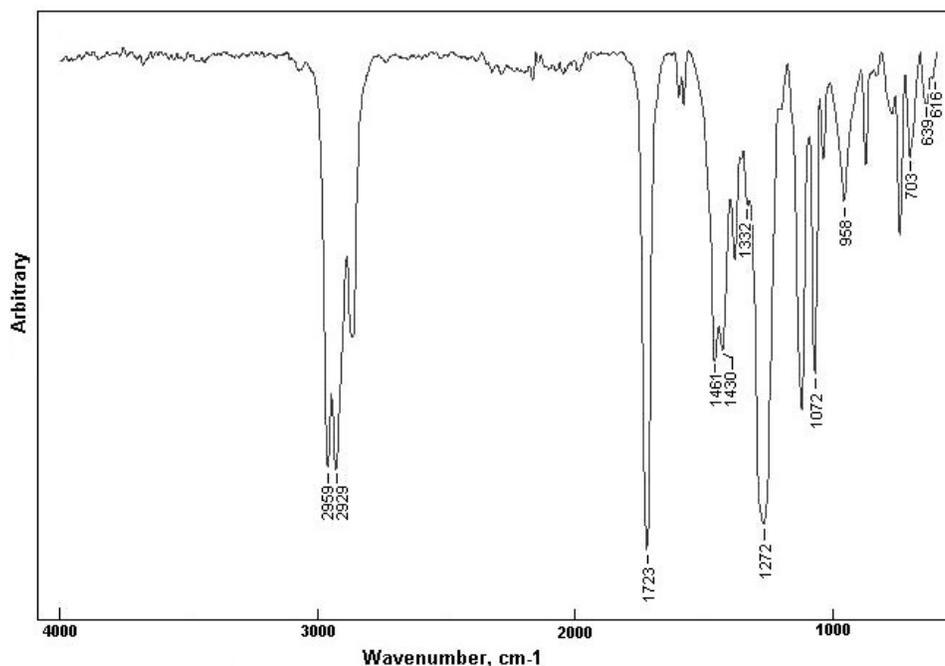


Fig. 2. FTIR spectrum of PVC used for wood composite materials

FTIR spectroscopy was used for the analysis of composite materials comprising WS, C, L, and PVC, these spectra being represented in Figs. 3-5.

FTIR spectra obtained for the WS(10), WS(25), and WS(50) composite samples are illustrated in Fig. 3.

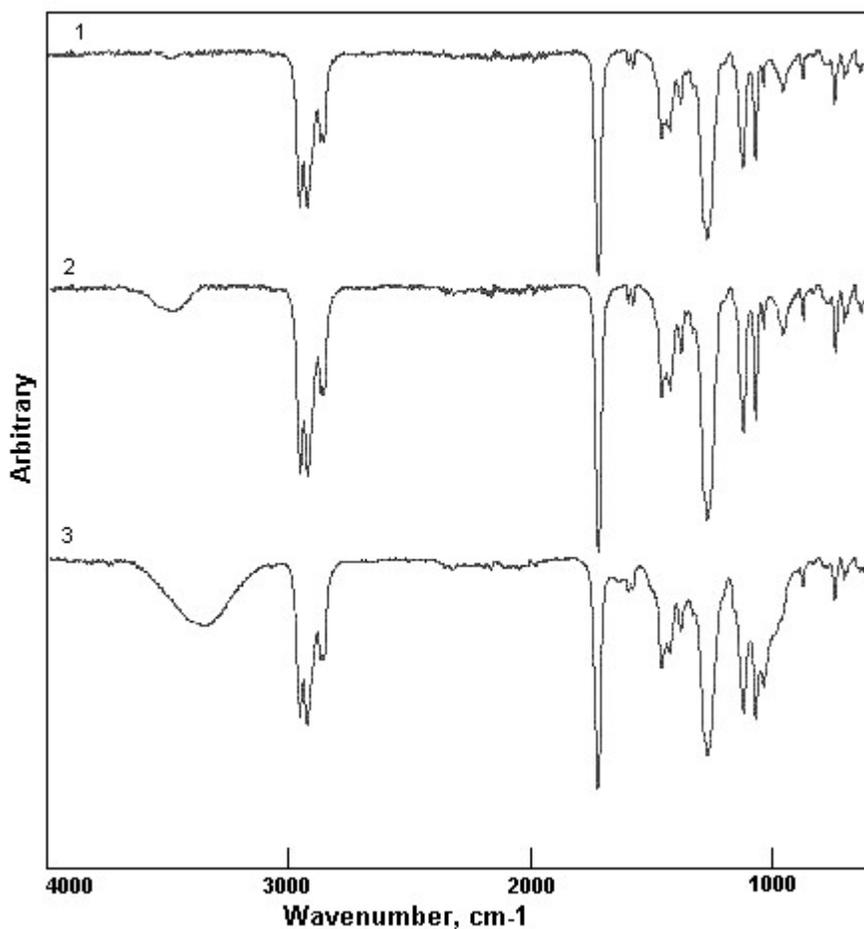


Fig. 3. FTIR spectra of modified wood sawdust-PVC composites 1-WS(10); 2-WS(25); 3- WS(50)

Absorption peaks at around 3400 cm^{-1} (broad) were observed in all the FTIR spectra (Fig. 3-5). These peaks are mainly attributed to intermolecular and freely bonded hydrogen of O-H stretching vibration of wood (Kuo et al. 1988). They were prominent in spectra for the composite samples with higher filler amount. However, the two bands in the $2929\text{-}2960\text{ cm}^{-1}$ were also prominent in all spectra, these being attributed to C-H stretching vibration in methyl and methylene groups of lignin and extractives, but also they are overlapping the bands characteristic to PVC (C-H from CH-Cl or C-H from CH_2). The broad peak occurring at 2929 cm^{-1} is also associated with -OH stretching in hydroxyl groups originating mainly from cellulose (Pandey 1999). The band at 2360 cm^{-1} observed in the samples belongs to the stretching asymmetric and symmetric vibration of CO_2 and appears in spectra for samples comprising cellulose and lignin filler.

The sharp peak at 1723 cm^{-1} is attributed to carbonyl C=O stretching vibration in conjugated ketones and ester carbonyl groups (Kuo et al. 1988; Anderson et al. 1991), being related to esterification of hydroxyl groups of the filler particles. This band is also associated with the formation of chloro-ketones by oxidation during the processing of composites (Decker, 1984). Bands at $1400\text{-}1500\text{ cm}^{-1}$ are due to benzene ring stretching vibration in lignin, but these may be also assigned to C-H groups of neat PVC. The

intensity of the band at 1430 cm^{-1} (C-H rocking of the ring) also appears due to the esterification of cellulose which corresponds to the decrease of hydrogen bonds.

The peak at 958 cm^{-1} , attributed to C-H bending vibration of the vinyl groups in PVC, became much less intense with increasing filler content in composite samples. This band is also characteristic for the β -(1,4)-linkage between sugar units in wood. The numerous acetyl groups present in the hardwood are released during the processing composites and induce a depolymerization of the wood polysaccharides. This process is also evidenced by the decrease of 1038 cm^{-1} and 875 cm^{-1} bands, characteristic to cellulose, with increasing filler content. The band at 1038 cm^{-1} is associated with both the C-O stretching in cellulose and the C-O deformation in the primary alcohols of lignin (Pandey 1999). The FT-IR spectra recorded for composites comprising C and PVC (Fig. 4) show bands at 1333 cm^{-1} , assigned to CH_2 wagging, and 1073 cm^{-1} , assigned to C-O stretching (Bellamy 1975).

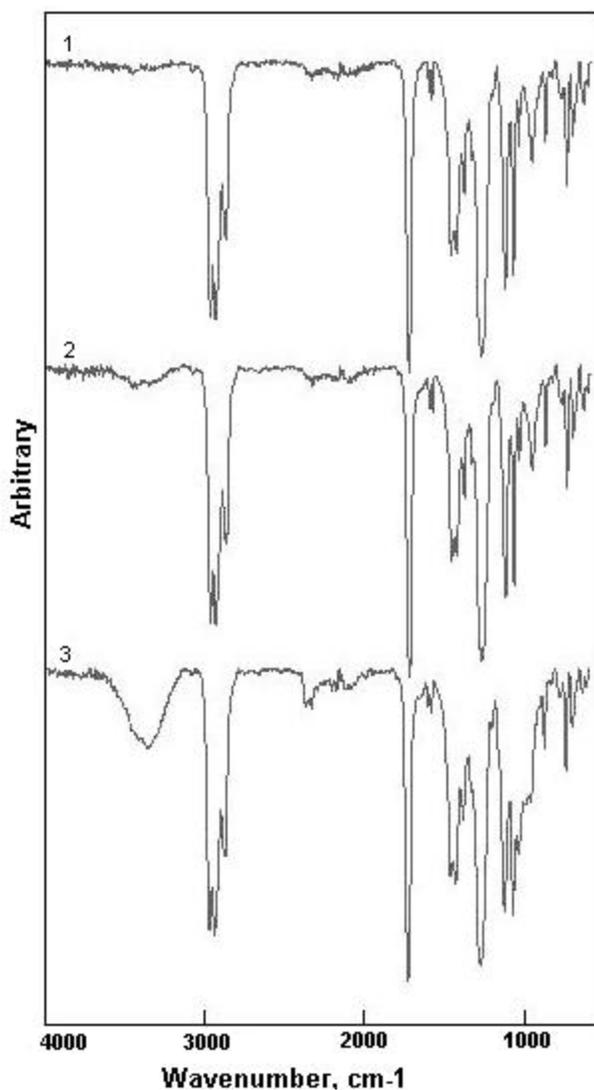


Fig. 4. FTIR spectra of modified cellulose-PVC composites: 1-C(10); 2-C(25); 3- C(50)

FTIR spectra for composites comprising L and PVC are represented in Fig. 5.

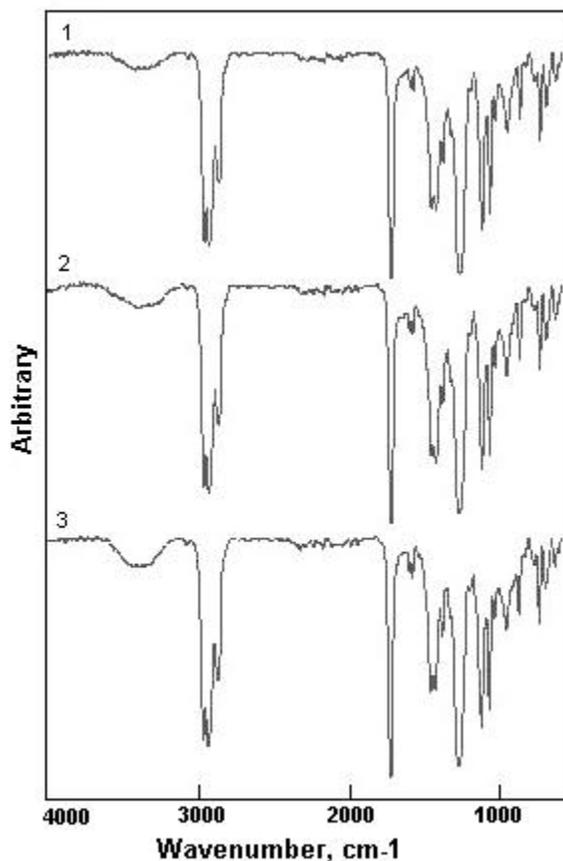


Fig. 5. FT-IR spectra of modified lignin-PVC composites: 1-L(10); 2-L(25); 3- L(50)

Thermogravimetric analysis (TGA)

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°C. Above this temperature the thermal stability gradually decreases and decomposition takes place. The thermal stability of wood is a very important parameter in the production of wood fibers plastic composites (WFPCs). 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 of wood (cellulose, hemicelluloses, lignin, and extractives) degrade at different temperatures. Hemicelluloses and lignin 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). There are evidenced two mass loss steps, an

initial mass loss below 100°C, which is due to the gradual evaporation of moisture, and a second mass loss from approximately 150 to 500°C, which is due to the decomposition of the three major polymer constituents of the wood: hemicelluloses mainly between 150 and 350°C, cellulose between 275 and 350°C, and lignin between 250 and 500°C.

The thermogravimetric analysis (TG) of untreated wood samples (Bodîrlău et al. 2008) indicated a loss of water of 6% between 20°C and 140°C. A loss of 3.5% of water was observed over the same temperature range for wood samples esterified with maleic anhydride. There were evidenced two other significant weight losses for wood polymer components: one of 47% in the 200-360°C range and another of 23% between 300°C and 350°C. The first weight loss is attributed to the decomposition of hemicelluloses (Nguyen et al. 1981).

The second weight loss is attributed to cellulose decomposition (Nguyen et al. 1981; Kosik et al. 1972; 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).

Characteristics of thermal decomposition of the PVC and chemically modified fillers (WS, C, L) are shown in Table 4.

After esterification of wood sawdust, a weight loss of 97.3% was observed until the temperature reached 600°C (see Table 4). The thermal analyses data of the composites comprising chemically modified fillers (WS, C, L) and PVC are summarized in Table 5.

Table 4. Thermal Characteristics of PVC and Chemically Modified Fillers (Wood Sawdust-WS, Cellulose-C, and Lignin-L)

Sample	T_i-T_f (°C)	T_m (°C)	W_{T_m} (%)	$W_{T_i-T_f}$ (%)	W_{600} (%)	T_{10} (°C)	T_{50} (°C)	E_a (Kj/mol)	n
PVC	200-345	283	31.6	66.22	85.8	271	285	149.3	1.4
WS	200-355	320	38.4	50.28	97.3	252	303	90.4	1.0
C	215-375	312	42.8	64.35	100	281	311	87.8	0.0
L	195-435	370	25.7	39.92	90.1	296	345	47.3	1.0

where: 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_{T_m} , $W_{T_i-T_f}$ and W_{600} - mass loss at T_m , T_i-T_f , and $T=600^\circ\text{C}$

E_a - activation energy, n - reaction order

Based on the data from all TG curves (not represented here), an initial small weight loss that occurred up to 100°C was mainly due to evaporation of water from the samples. Weight loss values for the 200-350°C temperature range significantly decreased in the presence of fillers in comparison with the polymer matrix (PVC). This aspect was more pronounced with increasing the filler weight percentage in composite samples (Tables 4 and 5).

Table 5. Thermal Characteristics of Composites Comprising PVC and Chemically Modified Wood Sawdust (WS), Cellulose (C), Lignin (L)

Composite Sample	T_f-T_i (°C)	T_m (°C)	W_{T_m} (%)	$W_{T_i-T_f}$ (%)	W_{600} (%)	T_{10} (°C)	T_{50} (°C)	E_a (Kj/mol)	n
WS(10)	210-335	290	39.11	60.8	85.3	273	287	122.5	0.0
WS(25)	200-350	295	41.15	60.0	83.2	266	287	127.4	0.9
WS(50)	200-350	290	35.67	57.0	97.0	257	286	138.9	1.3
C(10)	230-345	300	32.36	61.5	89.0	277	295	144.1	0.2
C(25)	200-350	300	46.21	63.4	89.5	267	294	155.3	1.1
C(50)	200-340	280	34.55	62.2	94.7	253	279	151.9	1.1
L(10)	220-345	295	39.11	62.8	87.8	274	290	119.7	0.8
L(25)	200-352	300	37.45	54.4	90.6	266	296	85.6	0.0
L(50)	180-347	293	20.49	43.0	84.8	250	298	96.4	0.6

where: 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_{T_m} , $W_{T_i-T_f}$ and W_{600} – mass loss at T_m , T_i-T_f and $T=600^\circ\text{C}$

E_a - activation energy, n – reaction order

The temperature corresponding to 50% weight loss (T_{50}) did not vary with increasing WS weight percentage in composite samples. For modified cellulose, T_{50} decreased with increasing the filler weight percentage, an opposite effect being observed for modified lignin (Table 5). This behavior may be related to the partially crystalline nature of cellulose, in contrast to the amorphous character of lignin. There can be noticed an increase of T_{50} mainly for the L(50) composite sample, indicating a different thermal behavior than that of composites containing WS or C as filler.

The temperatures of the maximum thermo-degradation rate obtained from the first derivative traces are related to the first and the second weight loss step after 150°C, respectively. The first weight loss corresponds to PVC thermo-degradation. The second step on composites thermo-degradation is related to the fillers, depending on their type and weight percentage (WS, C, L; 10%, 25%, 50%). PVC underwent two separate degradation steps under heating. PVC was stable at low temperatures. At around 280°C, its thermogravimetric percentage (TG %) significantly increased to 50%, a value of 60.8% being noticed at around 420°C. The TG% of PVC increased with another 25% until the temperature reached 600°C.

Thermal decomposition behavior of WS composites was closer to that of wood, mainly for those containing 10% WS. All composite samples had a gradual decomposition procedure. The decomposition behavior of WS composites was close to that of samples comprising C and L as fillers at low temperatures (< 200°C). However, TG curves of composites were different after temperatures greater than 300°C, the composites having varied composition. In particular, composites with 50% filler presented a distinguished deviation compared with those containing 10% filler. PVC had a large and sharp DTG peak at 300°C and a small and broad peak at about 420°C. For WS composites, a small and broad peak occurred at 100°C due to dehydration of wood, and a large and sharp peak at 300°C. The latter peak had a broad base, indicating that

another peak at around 275°C overlapped with it. The second DTG peak at around 420°C for PVC was much less evidenced in the DTG curves recorded for all composite samples.

Scanning electron microscopy (SEM) analysis

The SEM technique was used to establish the modified filler dispersion within the final composites. Figure 6 shows SEM micrographs that were obtained for the composite samples comprising modified filler (25%, respectively 50%) as follows: wood sawdust (6-a, b), cellulose (6-c, d), and lignin (6-e, f).

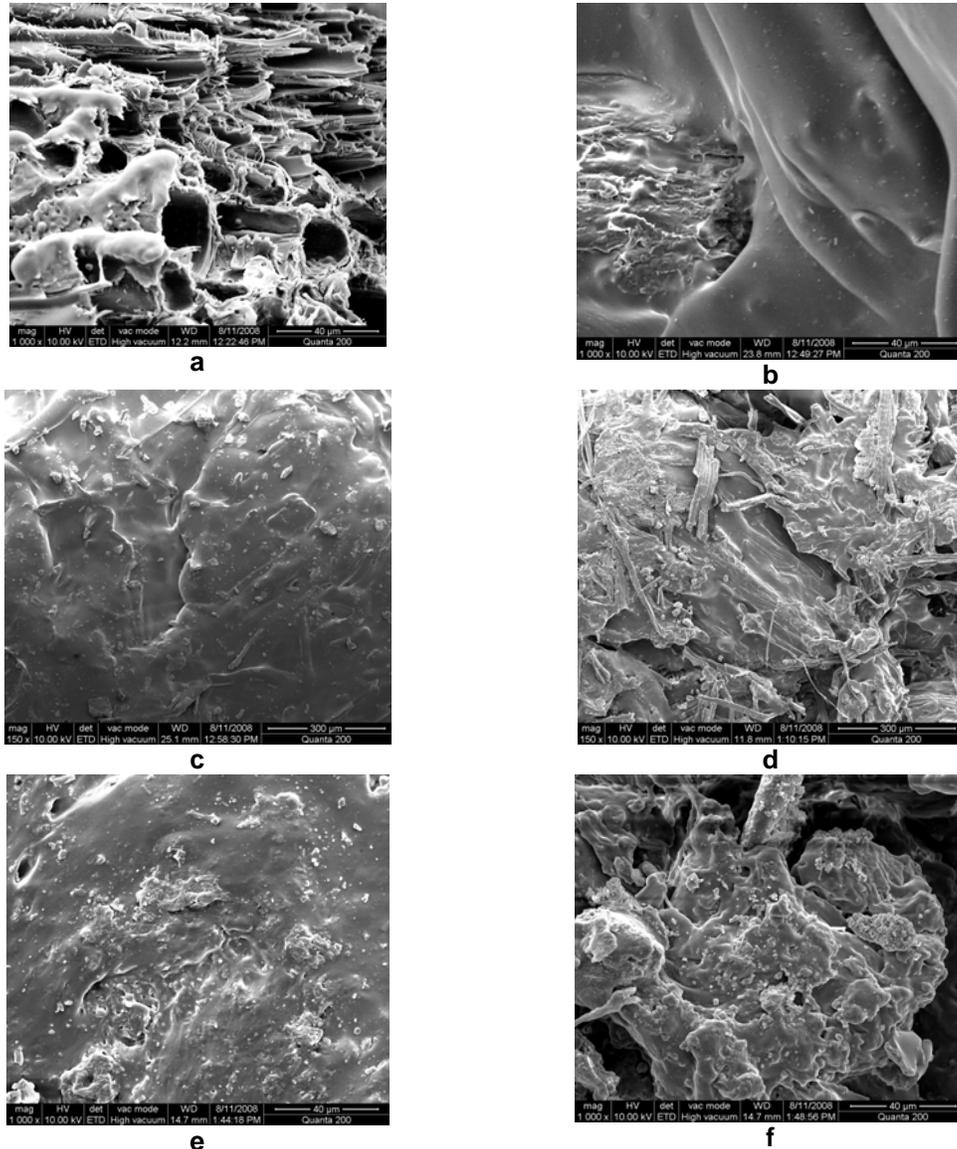


Fig. 6. SEM micrographs of: a) WS(25) sample; b) WS(50) sample; c) C(25) sample; d) C(50) sample; e) L(25) sample; f) L(50) sample

Comparing Fig. 6a and 6b, one can observe that the material processing leads to a homogeneous orientation of the wood sawdust particles (perpendicular to the cross section). The composite structure is evident, fibrous areas with cell walls and lumina being identified alongside homogeneous melted areas. The proportion of the melted areas depends on the degree of chemical modification expressed by the weight percent gain (Timar et al. 2004).

The cellulose and lignin particles seemed to be better coated by the PVC matrix than wood sawdust particles. This effect is related to the morphology of the fillers. Because cellulose and lignin particles have a more uniform shape, these are easier to be coated by a softened thermoplastic, such as heated PVC during the material processing. A lower content of filler leads to a more uniform cross-section.

Although the final composites were obtained by pressing the different sheets that were obtained in the press, each with a similar filler distribution, the moulding process seemed to cause a greater flow of PVC to both surfaces.

The filler particles near the surface appeared to be coated by the PVC matrix. For example, the wood sawdust particles near the surface of WS(25) and WS(50) samples were completely surrounded by the PVC matrix. This suggests that only small amounts of wood sawdust particles will be found at the surface, due to their strong tendency to be coated by the PVC.

The presence of the fillers seemed to increase slightly the roughness of the surface, creating a less homogeneous surface (as seen in Fig. 6). This increase can be related to the increasing content of the filler. A lower content of the filler leads to a more uniform cross section.

For high concentration of filler (e.g., 50% in weight), the polymer matrix was not continuously distributed and most filler particles directly contacted one another, causing a poor adhesion at the interface. It was also seen that the dispersion of the filler exhibits a significant particle aggregation for all composite types considered (Matuana et al. 1998; Bledzki et al. 2005). A good dispersion and alignment tendency of the fillers within the composites is observed at a lower loading level when the amount of thermoplastic was larger than that of the filler in weight.

CONCLUSIONS

1. Ash-tree wood sawdust and its main polymer components were previously chemically modified by reaction with maleic anhydride in order to improve their further exploitation for preparation of composites. Esterification was investigated through FT-IR spectroscopy. The presence of a clear and well-marked peak at 1726 cm^{-1} (attributed to the carbonyl groups C=O) was attributed to the new ester bonds formed by reaction of the OH groups in the wood with the anhydride. The absorption in this region corresponds to both the C=O groups in acid and ester groups attached to the wood.
2. Different composites comprising chemically modified hardwood sawdust and wood polymers - cellulose, lignin-(as different weight percentages) / poly (vinyl chloride)

were obtained by a melt blending process. These materials were further examined by FT-IR, TGA, and SEM analysis methods.

3. The composite samples were characterized by an intense band at 1722 cm^{-1} in the FTIR spectra, providing good evidence for the incorporation of carbonyl groups (specific to the wood components) into the PVC matrix during blending.
4. Thermal analyses data evidenced a decrease in weight loss for composites comprising modified cellulose and lignin in comparison with the weight loss for PVC for the same temperature domain (200-350°C). Thermal degradation of PVC may increase the polyene sequences by the cleavage of chlorine due to the strong hydrogen bonds with the fillers in composite samples.
5. In all cases, thermal properties were affected by the addition of the fillers. Weight loss values ($W_{T_i-T_f}$) for the main decomposition temperature domain decreased with increasing the filler content. Thermal behavior is improved mainly for composite samples comprising modified lignin. Samples containing modified cellulose present a lower thermal stability by comparison with WS and L samples.
6. Morphological characterization of composite samples showed a relatively uniform distribution of the filler in the polymer matrix. The presence of the fillers seemed to increase slightly the roughness of the surface, creating a less homogeneous surface. The SEM study of products from the hot-pressing of composites demonstrated that the modified wood had partially melted under pressure and temperature. The cellulose particles appeared to be better coated by the PVC matrix, this effect being related to their more uniform shape. A poor adhesion at the interface was observed for high concentration of filler (e.g., 50% in weight) because the polymer matrix was not continuously distributed and most filler elements directly contacted one another.

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