VERSITA

Cent. Eur. J. Chem. • 11(12) • 2013 • 2098-2106
DOI: 10.2478/s11532-013-0337-x

Central European Journal of **Chemistry**

Physico-chemical properties investigation of softwood surface after treatment with organic anhydride

Research Article

Ruxanda Bodîrlău[1], Carmen-Alice Teacă[1*], Dan Roşu[2],
Liliana Roşu[2], Cristian-Dragoş Varganici[2], Adina Coroabă[2]

[1] *"Petru Poni" Institute of Macromolecular Chemistry,*
Department of Natural Polymers,
Iasi, 700487 Romania

[2] *"Petru Poni" Institute of Macromolecular Chemistry,*
Center of Advanced Research in Bionanoconjugates and Biopolymers,
Iasi 700487, Romania

Received 2 July 2013; Accepted 4 August 2013

Abstract: Wood originating from a softwood species was subjected to chemical treatment by reaction with succinic anhydride in *N, N*-dimethylformamide at different concentration values. Fourier transform infrared spectroscopy and X-ray photoelectron spectroscopy analysis were used to study changes that occurred on a softwood surface. The extent of chemical treatment on softwood was evaluated by determining the weight percent gain values. Thermal properties of modified softwood and the water absorption were also evaluated. The chemical treatment with succinic anhydride influenced the thermal stability of the softwood samples with increasing anhydride concentration levels.

Keywords: *Softwood • Organic anhydride • IR spectroscopy • XPS spectroscopy • Thermochemistry*

1. Introduction

Wood represents a versatile, multi-component polymeric system constituted mainly of three biopolymers, namely cellulose, lignin and hemicelluloses, with many potential applications which are renewable, biodegradable and susceptible to structural changes. In addition to these polymer components, wood may contain extractives in more or less large quantities, depending on the wood species. Wood extractives include several classes of organic compounds ranging from hydrophilic sugars, flavonoids, tannins, and resins to hydrophobic terpenes and fatty acids. Generally, wood extractives influence the wetting resistance of wood surfaces. Extractives are generally soluble in different organic solvents, but some can become covalently bonded to the wood structure or can induce an alteration which is inevitable during the extraction process.

When wood is exposed to the environmental conditions without any protection [1,2] – *e.g.* outdoor exposure is mainly represented by sunlight (especially UV and visible light) and humidity – its surface deteriorates relatively fast. Degradation of wood cells walls causes separation and strength loss of the material [1]. This damage is evidenced through appearance of micro-fractures which further induce surface cracks by swelling and shrinking of the wood as a result of water absorption and drying processes [2-5]. An increase of wood surface roughness is also observed through leaching action of rain water which removes photo-degraded fragments (originating mainly from lignin component) from the wood surface.

Surface coating and bulk treatment of wood are two effective methods which can be applied, individually or in conjunction, for protection of wood surface from degradation. A physical barrier that protects the wood

---

* *E-mail: cateaca14@yahoo.com*

Table 1. The main chemical components of *Abies alba* softwood.

Ash	**Extractable substances (%):**			**Cellulose**	**Lignin**	**Holocellulose**
(%)	Hot water	NaOH 1%	Ethanol/toluene	(%)	(%)	(%)
0.25	1.65	9.57	1.53	54.21	30.17	81.12

surface from the damaging effects of environmental factors, including moisture, solar radiation, stain and decay fungi [6] can be achieved by wood coating. Thus, a dimensional stability, a decrease of capillarity and an improved fungal resistance can be obtained.

The bulk treatment of wood refers to its chemical modification by reaction with a reagent which can penetrate into wood cell wall and/or can induce a cross-linking process involving wood polymers [7,8]. In this context, an improvement of the weathering resistance and coating performance can be achieved through wood modification with acetic anhydride [9]. In treatments with cyclic anhydrides such as succinic anhydride, the carboxylic acid formed through esterification reaction is now attached to the wood. If the free acid were to esterify as well, not only would the hydrophobic properties be improved, but also an extra cross-link would stabilize the material even better. Thus, the wood becomes more water resistant with improved dimensional stability and decay resistance [10].

Surface spectroscopy techniques are needed to characterize changes occurring on wood surfaces due to modification, including infrared spectroscopy, scanning electron microscopy (SEM), and X-ray photoelectron spectroscopy (XPS). Fourier transform infrared spectroscopy (FTIR) is a very useful technique for analyzing the surface of wood and wood polymer components, to measure the chemical modification of wood [11-13].

XPS is a non-destructive surface analytical technique that provides information on the oxidation or chemical bonding state of elements. XPS has been used in several applications in wood science to investigate the surface of different wood species [14-17], chemically modified pulp and wood [18-20], surface lignin on cellulose fibers [21], and weathering of wood and wood–plastic composites [22,23].

This paper describes how wood originating from a softwood species was subjected to chemical modification by reacting with succinic anhydride in N, N-dimethylformamide (DMF) at three different concentration levels. The extent of chemical treatment was estimated by means of weight percent gain (WPG) values. Evidence of softwood structural changes after chemical treatments was discussed by FTIR and XPS methods. The thermal decomposition of softwood samples was investigated by TG-DTG analysis. This preliminary approach has been performed considering the potential use of wood in outdoor applications after coating using an epoxy functionalized vegetable oil in order to improve its weathering protection.

2. Experimental procedure

2.1. Preparation of wood specimens

Softwood specimens shaped as discs with diameters of 60.0 mm and 3±0.02 mm thickness were prepared from logs of softwood *Abies alba* L. and dried at ambient temperature for one year. Softwood samples were polished with sandpaper (400 P) prior to use. The chemical composition of softwood samples was determined in accordance with TAPPI standards, and is displayed in Table 1.

Succinic anhydride (SA) was obtained from Aldrich (97%) and used as received. Dimethylformamide (DMF), sodium hydroxide, ethanol and toluene were analytical grade and supplied by Merck and Chimopar S.A. (Bucharest, Romania).

2.2. Chemical treatment of softwood

Through the chemical treatment, the molecular structure of the cell wall components is changed and some wood properties can be modified (*i.e.*, hydrophilicity). Cyclic anhydrides (*i.e.*, SA) do not yield a by-product when reacting with the hydroxyl groups of wood [24].

Wood reaction with anhydride can result in a single ester function and a free carboxylic group (Fig. 1A) or di-ester structures (Fig. 1B).

Prior to the chemical modification, the softwood samples were extracted for 8 h with DMF. The extraction was performed in a Soxhlet apparatus to decrease the material extractives influence on the chemical modification of the softwood. The extracted softwood samples were dried for 24 h in an oven at 70°C to obtain a constant weight. For esterification, the dried softwood samples were dipped in SA, dissolved previously in DMF and heated for one hour at 100°C, under continuous stirring. The concentration level of SA

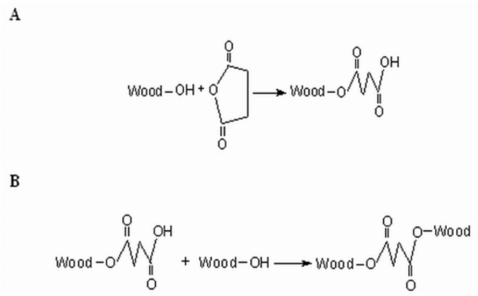

Figure 1. Chemical reaction of wood with succinic anhydride.

in the solution was designed to be 60%, 80%, and 120% (w/w), respectively.

After modification, the wood specimens, coded as MW60, MW80, respectively MW120, were removed from the solutions and cooled to room temperature. A new extraction with DMF for 8 h was performed to remove the non-reacted SA. Finally, the specimens were vacuum oven-dried for 24 h at 70°C to reach a constant weight. A total of 40 samples were designated for this study, namely 10 samples for each concentration value and 10 non-treated samples (R).

2.3. Evaluation of weight percent gain

The extent of chemical modification of softwood was evaluated by weight percent gain (WPG) calculation. After treatment with SA, the softwood specimens were removed from solution, pre-dried at room temperature for 24 h and subsequently vacuum oven-dried at 70°C for 24 h until constant weight was obtained. The WPG values were calculated by means of Eq. 1 from the softwood dry weight before and after treatment with SA for ten reference specimens (for each SA concentration value).

$$\text{WPG, \%} = [(m_{treated} - m_{untreated}) / m_{untreated}] \times 100 \qquad (1)$$

where: $m_{untreated}$ and $m_{treated}$ represent the dry weight of wood samples before and after treatment with SA.

2.4. FTIR analysis

FTIR spectroscopy of softwood samples was performed on a Bruker FTIR spectrometer (Vertex 70) equipped with the MIRacle ATR accessory designed for single or multi-reflection attenuated total reflectance. The single-reflection sampling plate of the accessory had a 1.8 mm round crystal surface which allowed a reliable analysis of the small samples. The ATR crystal plate was from Diamond, and solid materials were placed into close contact with the sampling area through high-pressure clamping and which yielded high-quality and reproducible spectra. Spectra were registered in the range from 400 to 4000 cm^{-1} at a spectral resolution of 4 cm^{-1}, 64 scans were averaged. The bands from FTIR spectra for softwood samples were attributed using literature data [5,12,18,23].

2.5. XPS analysis

The surface characterization of wood samples was performed on a KRATOS Axis Nova (Kratos Analytical, Manchester, UK) spectrometer, using a monochromatic AlKa source (1486.6 eV), with 10mA current and 15 kV, and base pressure of 10^{-8} to 10^{-9} Torr in the sample chamber. The incident mono-chromic X-ray beam was focused on a 0.7×0.3 mm^2 area of the surface.

The XPS survey spectra of the samples were collected in the range of -10¸1200 eV with a resolution of 1 eV and a pass energy of 160 eV. The high-resolution spectra for all the elements identified from the survey spectra were collected using a pass energy of 20 eV and a step size of 0.1 eV. The binding energy of the C_{1s} peak was normalized to 285 eV. To determine the type of O–C bonds present, a chemical bond analysis of carbon was accomplished by the deconvolution of the curve into five peaks. Data were analyzed using the Vision software from Kratos (Vision 2.2.10).

2.6. Water uptake

Four softwood specimen discs with a diameter of 60 mm and a thickness of 3±0.02 mm thickness were used for each formulation to measure water absorption [25]. The specimens were dried in an oven at 50°C for 24 h before being immersed in to distilled water until a constant specimen weight was reached. Following this process, softwood specimens were placed in distilled water at 25°C. The immersion times varied from 0, 5, 24, 48, 72, 96, to 120 h. For each measurement, the specimens were removed from the water, and the surface water was wiped off using blotting paper. The percentage of water absorbed by the specimens was determined by weighing the specimens with a precision of ± 0.0002 g. The water absorption at any time M(t) was calculated using Eq. 2:

$$M(t) = \frac{W_t - W_0}{W_0} \text{ x } 100 \ [\%] \qquad (2)$$

where: W_0 was the oven dried weight, W_t the weight of wood specimen at a given immersion time t.

2.7. Thermal analysis

A thermal analysis of softwood was performed with a thermal analyzer STA 449 F1 Netzsch (Germany). Samples (» 5 mg) were placed in Al_2O_3 crucibles and heated under nitrogen from 50°C to 700°C with a 10°C

Table 2. Weight percent gain values for non-modified (R) and modified wood (MW).

Sample	R	MW60	MW80	MW120
WPG (%)	0	10.93	21.83	39.45

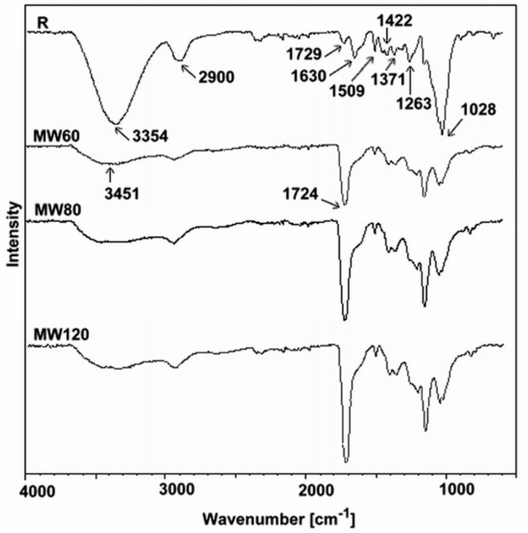

Figure 2. FTIR spectra for non-treated (R) and treated (MW) softwood.

min^{-1} heating rate. TG and DTG curves recorded with a ±0.5°C precision were analyzed with Netzsch Proteus analysis software.

3. Results and discussion

The chemical reagent concentration plays a significant role on WPG values. The amount of moisture present in the wood and wood polymers is also important. Content of moisture (~5%) seems to be needed for an optimal reaction between wood and SA. Above this level, the water hydrolyses anhydride to a corresponding carboxylic acid. The esterification rate decreases as moisture content increases [26]. After the chemical reaction of softwood with SA at different concentration levels for 1 h, the calculated weight percent gain values increased from ~11% to 39%, depending on the SA concentration. WPG values are presented in Table 2.

FTIR spectroscopy was used to study chemical changes on the surface of softwood before and after chemical treatment with SA (Fig. 2). Usually the broad peak around 3354 cm^{-1} is associated with a 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 a characteristic absorption of conjugated carbonyl group C=O of lignin in wood samples.

The band around 1509 cm^{-1} (Fig. 2) can be attributed to the stretching and bending vibration of an aromatic ring framework in lignin of wood. The peak 1028 cm^{-1} corresponds to C-O group stretching mainly in cellulose and hemicelluloses of wood samples [11,12].

The vibration from 1422 cm^{-1} is specific to CH_2 bending related to the structure of cellulose and/or aromatic skeletal vibrations. The peak from 1371 cm^{-1} characterizes the deformation vibration of C-H groups and O-H bending vibrations in phenols from lignin. The signal from 1263 cm^{-1} was attributed to C-O vibrations of guaiacyl unit in lignin.

In all, the spectra of the modified softwood samples with SA (MW60, MW80 and MW120) the absorbance intensity from 3451 cm^{-1} decreases and enlarges to lower wavelength values. This behavior is an indication of a decrease of the hydroxyl group content during the reaction between softwood and SA (Fig. 2, MW). Signal broadening through lower wavelength 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. 1A, can explain the presence of these signals in FTIR spectra.

The band from 1729 cm^{-1}, attributed to the carbonyl groups C=O, is changed to the lower wavelength values (1724 cm^{-1}) and significantly increases as intensity is registered. This increase of band intensity is correlated positively with the SA concentration level (Fig. 2). The carbonyl stretching vibrations appear in this region (1800-1000 cm^{-1}). The absorption increase is due to the formation of ester groups after chemical treatment. The spectral changes confirmed a reaction between softwood and succinic anhydride. As expected, the absence of an absorption region 1800-1760 cm^{-1} in spectrum (MW) indicated that the wood sample was free of organic anhydride.

XPS analysis was used to investigate the changes that occurred during the wood treatment with organic anhydride. The O/C atomic ratio was calculated to indicate softwood surface oxidation. The literature generally corroborateswith the assignment of deconvoluted peaks C1s and O1s for lignocellulosic materials [27-29].

The results from the XPS analysis for non-modified and modified softwood samples are summarized in Table 3. The O/C ratio and distribution of carbon and oxygen atoms of chemical modified softwood samples differ from those obtained for non-modified wood. The

XPS spectra data evidenced an O/C ratio of 0.45 for non-modified softwood which increased over 0.55 after chemical treatment with SA.

Table 4 presents the binding energies of C1, C2, C3, C4, C5 and the C4/C2 ratios.

Table 4 shows a decrease forC1, C2 and C3 and an increase for C4 after treatment. A class C5 representing the CO-CH_3 and/or CO-CH_2 groups is presented in chemically treated softwood. This class (C5) was characterized through a binding energy value approximating that of the C1 class (consisting of C–C or C–H groups). It partially overlapped the C1 class and contributed to the chemically modified softwood with 12.85-19.51% which was dependent on the SA concentration level (Table 4). This is consistent with the SA concentration level observed with FTIR spectra.

For chemically modified softwood, the highest amount from the carbon peak components was found for C2 class consisting of C-O linkage of carbon (32-35%).

Fig. 3 shows the high-resolution spectra of C1s carbon and O1s oxygen for non-modified (R) and SA modified softwood (MW). The analysis of the survey spectra indicates the presence of carbon, oxygen and small amounts of nitrogen, which represent the expected elements in softwood. High-resolution scans of the XPS spectra of C1s and O1s levels are also presented with their decomposition into components.

The C1s peaks indicated a significant decrease in the area of the C1 peak for treated softwood, known to originate from lignin and extractive substances. At the same time, a diminution in the C2 peak area (mainly originating from cellulose and hemicelluloses) was observed with increase in the SA concentration, indicating that more cellulose and hemicelluloses on the wood surface chemically reacted (Fig. 3).

The C4 class consisting of an O-C=O linkage of carbon showed a significant increase for treated softwood (comparative with R), whereas C3 class consisting of C=O and/or O-C-O linkage of carbon represented 11.95% for non-modified softwood and asignificant decrease (5.5-6.8%) for modified softwood (Table 4); this may be caused by the complexity of chemical reactions between softwood constitutes and succinic anhydride.

Since the ratio of C4/C2 increased after the chemical treatment, largely due to an increase in the C4 area, it can be inferred that the components of the content with carboxyl structure in the softwood surface increased (Table 4).

It has been reported that pure cellulose contains only C2 and C3 carbon [30], thus the C1, C4 and C5 carbons can be characterized for SA modified softwood.

Table 5 presents the binding energies of O1, O2 and O3 as well as the O1/O2 ratios.

Table 3. Percent values of C1s, O1s and oxygen/carbon atomic ratio.

Sample	C 1s (%)	O 1s (%)	O/C
R	67.19	30.15	0.45
MW60	63.18	35.80	0.57
MW80	62.68	36.20	0.58
MW120	63.63	34.90	0.55

R: non-modified softwood; MW: modified softwood

Table 4. Subpeak area fractions of C1s and ratio of C4/C2.

Softwood sample	Relative area of C 1s peaks (%)					C4/C2
	C1 (285.0 eV)	C2 (286.7 eV)	C3 (280.0 eV)	C4 (289.2 eV)	C5 (285.5 eV)	
R	43.12	40.43	11.95	4.5	-	0.11
MW60	28.49	35.24	6.43	16.99	12.85	0.48
MW80	23.54	33.10	6.87	19.65	16.84	0.59
MW120	23.87	31.97	5.56	19.09	19.51	0.60

Table 5. Subpeak area fractions of O1s and ratio of O1/O2.

Softwood sample	Relative area of O 1s peaks (%)			O1/O2
	O1 (533.3 eV)	O2 (532.8 eV)	O3 (532.0 eV)	
R	24.04	65.06	10.90	0.36
MW60	24.13	63.05	12.82	0.38
MW80	34.38	45.18	20.44	0.76
MW120	39.16	37.20	23.64	1.05

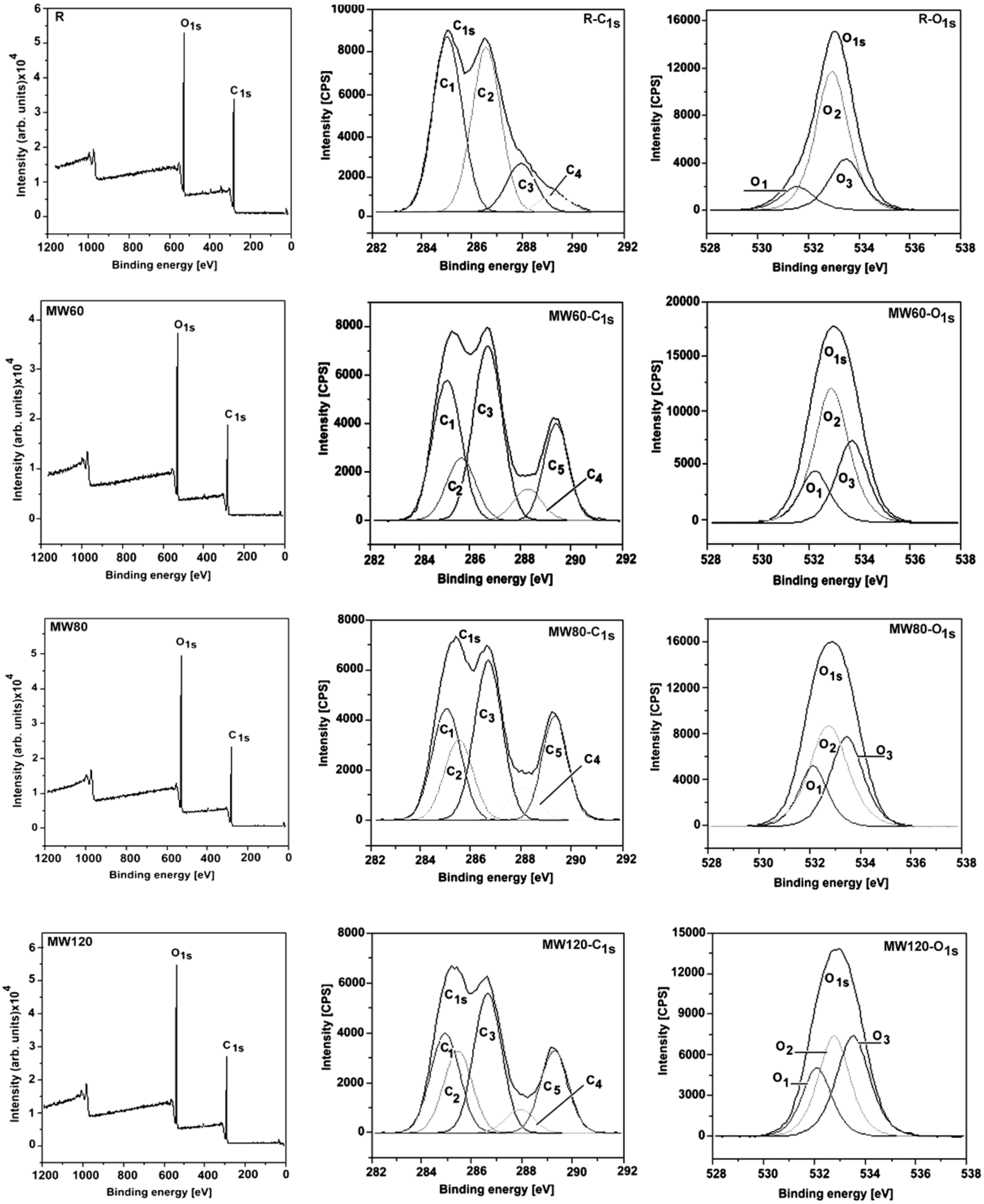

Figure 3. XPS spectra for non-modified and SA modified wood and C1s and O1s XPS survey spectra (R -C1s, R -O1s; MW60 -C1s, MW60 -O1s; MW80 -C1s MW80 -O1s; MW120 -C1s, MW120 -O1s).

The O1s peaks showed an increase in the O1 peak area originating from cellulose (O=C and/or O-C-O), especially for MW80 and MW120 comparative with the R sample. The O2 peak corresponding O-C/C-O-C showed a decrease from 65.0% for R at 37.2% for MW120 whereas the O3 peak consisting of O-C=O, showed an increase from 10.9% (for R) at 23.6% (for MW120) due to chemical treatment. It is also reasonable to conclude that the increase in the O1/O2 ratio for treated softwood is a result of the esterification reaction between softwood components and succinic anhydride.

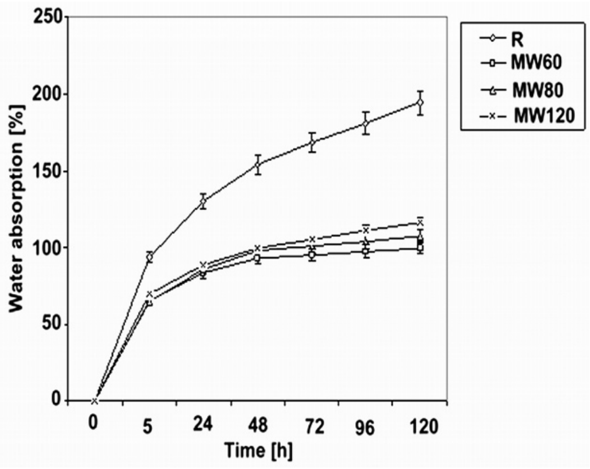

Figure 4. Water absorption of non-modified and modified softwood with SA.

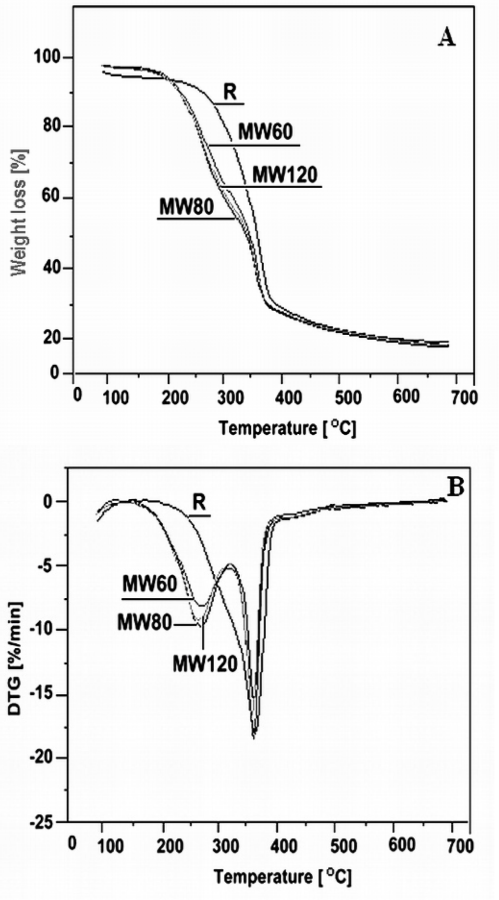

Figure 5. TG and DTG curves recorded at 10 K min⁻¹.

The XPS results are consistent with the observed IR absorption peaks in the range of 1739 cm^{-1} and 1724 cm^{-1} (for treated softwood) which suggest the formation of carbonylic groups.

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) increases with increasing distance from the polar OH group. Chemical modification of softwood reduced its hydrophilic character. A considerable lowering of water absorption is registered for modified softwood samples comparatively with non-modified softwood (Fig. 4).

During treatment, the hydrophilic OH groups from softwood are substituted with hydrophobic succinyl groups. The introduction of the succinyl group may reduce the cohesive forces between the main chains of cellulose and hemicelluloses from softwood samples.

The thermal decomposition of wood is a complex process because wood is comprised of many compounds with different decomposition temperatures. The thermal decomposition of the softwood 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 [31].

Fig. 5 shows the TG (Fig. 5A) and DTG (Fig. 5B) 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 chemical modified softwood were different from those of the reference sample (R). The DTG curves (Fig. 5B) show the presence of one main stage of thermal decomposition for the R sample while MW samples degrade in two main stages respectively. For all softwood samples the first stage exhibits a wide peak around 100°C, which can be associated with the maximum in the water loss rate.

The thermal characteristics recorded for both the MW and non-modified softwood (R) samples are presented in Table 6. These parameters include: T_i - temperature corresponding to 5% weight loss; $T_{50\%}$ - temperature corresponding to 50% weight loss; T_{mI}, T_{mII}, and W_{mI}, W_{mII} – temperatures and weight loss values corresponding to the maximum decomposition rate for each stage of thermal decomposition, respectively; T_f - final temperatures at which the process responsible for the mass change is completed; W_{rez} - mass of residuum resulted at 700°C. The increase of the SA concentration level in the reaction medium determines a significant increase in the starting temperature of thermal degradation (T_i) and restricts the range T_f–T_i. The structural modifications of softwood

Table 6. Some data evaluated from TG and DTG curves.

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_{Tf-Ti} (%)	W_{rez} (%)
R	109	365	372	75.5	-	-	388	229	75.5	19.4
MW60	203	355	279	33.7	368	43.9	383	180	77.6	19.3
MW80	199	352	276	38.2	368	41.50	380	181	78.7	19.0
MW120	196	350	277	38.8	368	40.0	381	185	78.8	19.1

through SA esterification reaction could explain the increase of T_i value. The evolution rate of thermal decomposition products increases in this case and restricts the range T_f–T_i.

This observation may also explain the lower $T_{50\%}$ temperature measured for MW samples compared with those of the R sample.

The first main weight loss (in the 200-360°C range) is usually attributed to the decomposition of hemicelluloses [32,33]. The temperature corresponding to the maximum rate of weight loss (T_{ml}) exhibits a significant decrease for treated wood compared to the reference samples. This could be due to the increasing susceptibility to decomposition of the hemicelluloses from wood after chemical treatment.

The residue content remaining after heating the samples at 700°C varies between 19.0% and 19.4% depending on the softwood structure.

T_{50} temperature exhibits a slightly decrease for chemically modified softwood in comparison to R, following the order:

R > MW60 > MW80 > MW120

The thermal stability of chemically modified softwood, as shown by thermogravimetric analysis, is higher compared to reference R if Ti is taken into account. This behavior could be attributed to some specific interactions between wood components and the chemical reagent which led to an increase in thermal stability [34].

4. Conclusions

The chemical treatment induced structural changes in softwood samples as evidenced by FTIR spectroscopy and XPS analysis.

Results obtained from XPS analysis indicated an increase in the O/C ratio value for chemically modified softwood which could be due to the oxidation process that took place during the chemical reaction.

The changes in chemical composition observed by the XPS analysis supported results reported in the literature. The increase in C4, O1 area, O/C, C4/C2 and O1/O2 ratio signified the occurrence of oxidation reactions in the chemical modification process. It can be concluded that the increase in these ratio values for treated softwood was a result of esterification reaction between softwood components and succinic anhydride.

The XPS results are consistent with the observed IR absorption peaks in the range 1739 cm^{-1} and 1724 cm^{-1} (for treated softwood) which suggest the formation of carbonylic groups.

The thermal decomposition of non-modified softwood or modified softwood is a complex process because the wood consists of many components with different thermal decomposition temperatures. Thermal analysis evidenced that the chemical treatment with SA influenced the thermal stability of the softwood samples, by making them more stable to thermal degradation with increasing SA concentration level.

The chemical modification of softwood reduced the hydrophilic nature of wood constituents. A considerable lowering of water uptake values was registered for the SA modified softwood comparatively with the non-modified softwood.

Acknowledgements

This work was supported by a grant from the Romanian National Authority for Scientific Research, CNCS-UEFISCDI - Project number PN-II-ID-PCE-2011-3-0187.

References

[1] D.N.S. Hon, Wood and cellulosic chemistry, 2nd edition (Marcel Dekker Inc. New York, 2001) 513

[2] D.N.S. Hon, S.T. Chang, J. Polym. Sci. Polym. Chem. 22, 2227 (1984)

[3] K.K. Pandey, Polym. Degrad. Stab. 90, 9 (2005)

[4] B. George, E. Suttie, A. Merlin, X. Deglise, Polym. Degrad. Stab. 88, 268 (2005)

[5] C. Clemons, R.A. Young, R.M. Rowell, Wood and Fiber Sci. 24, 353 (1992)

[6] P. Ahola, Holz Roh-Werkst. 49, 428 (1991)

[7] C.S. Hill, N.S. Cetin, Z. Ozmen, Holzforschung 54, 269 (2000)

[8] H-T. Chang, S-T. Chang, Biores. Technol. 97, 1265 (2006)

[9] P.D. Evans, A.F.A. Wallis, N.L. Owen, Wood Sci. Technol. 34, 151 (2000)

[10] R.M. Rowell, Wood Mat. Sci. Eng. 1, 29 (2006)

[11] X. Colom, F. Carrillo, F. Nogues, P. Garriga, Polym. Degrad. Stab. 80, 543 (2003)

[12] K.K. Pandey, J. Appl. Polym. Sci. 71, 1969 (1999)

[13] D. Rosu, C-A. Teacă, R. Bodîrlău, L. Rosu, 99, 144 (2010)

[14] H. Bouafif, A. Kouba, P. Perré, A. Cloutier, B. Riedl, J. Wood Chem. Technol. 28, 296 (2008)

[15] G. Nguila Inari, M. Petrissans, J. Lambert, J. J. Ehrhardt, P. Gerardin, Surf Interface Anal. 38, 1336 (2006)

[16] P. Nzokou, D.P. Kamdem, Surf. Interface Anal. 37, 689 (2005)

[17] G. Sinn, G.S. Reiterer, S.E. Stanzl-Tschegg, J. Mater. Sci. 36, 4673 (2001)

[18] H. Chtourou, B. Riedl, B.V. Kokta, J Adhes. Sci. Technol. 9, 551 (1995)

[19] L.M. Matuana, J.J. Balatinecz, R.N.S. Sodhi, C.B. Park, Wood Sci. Technol. 35, 191 (2001)

[20] G.K. Prakash, K.M. Mahadevan, Appl. Surf. Sci. 254, 1751 (2008)

[21] L.S. Johansson, J.M. Campbell, K. Koljonen, P. Stenius, Appl. Surf. Sci. 144-145, 92 (1999)

[22] L.M. Matuana, D.P. Kamdem, Polym. Eng. Sci. 42, 1651 (2002)

[23] I. Spiridon, R.N. Darie, R. Bodîrlău, C.A. Teacă, F. Doroftei, J. Compos. Mat. (2013) DOI: 10.1177/0021998312466906

[24] H. Matsuda, Wood Sci. Technol. 21, 75 (1987)

[25] A. Viksne, A.K. Bledzki, L. Rence, Mech. Compos. Mater. 42, 73 (2006)

[26] R.M. Rowell, Advances in Chemistry Series 207 (ACS Washington, DC, 1984) 175

[27] X. Hua, S. Kaliaguine, B.V. Kokta, A. Adnot, Wood Sci. Technol. 27, 449 (1993)

[28] X. Hua, S. Kaliaguine, B.V. Kokta, A. Adnot, Wood Sci. Technol. 28, 1 (1993)

[29] D.P. Kamdem, J. Zhang, A. Adnot, Holzforschung 55, 16 (2001)

[30] N. Maximova, M. Österberg, K. Kpljone, P. Stenius, Cellulose 8, 113 (2001)

[31] C. Schwarzinger, M. Leid, R. Putz, J. Anal. Appl. Pyrol. 83, 213 (2008)

[32] T. Nguyen, E. Zavarin, E.M. Barrall, J. Macromol. Sci.-Rev. Macromol. Chem. C 20(1), 1 (1981)

[33] R.M. Rowell, R.A. Susott, W.F. Degroot, F. Shafizadeh, Wood Fiber Sci. 16, 214 (1984)

[34] H.P.S. Abdul Khalil, I.O. Bakare, A.M. Khairul, J. Wood Chem. Technol. 31, 154 (2011)