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PHYSICO-CHEMICAL CHARACTERIZATION OF WOOD TREATED WITH POLYMERIC SYSTEMS

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Abstract: *In this investigation, silver fir wood (Abies alba) samples (FW) were impregnated with some polymeric systems, as follows: (1) a block copolymer of styrene-ethylene-butylene-styrene (SEBS) grafted with maleic anhydride (MA), denoted as SEBS-MA; (2) a block copolymer of styrene-ethylene-butylene-styrene (SEBS) grafted with maleic anhydride (MA), denoted as SEBS-MA, used in combination with ZnO for the preservation of wood surfaces applied by spraying on the wood surfaces pre-treated with a suspension of ZnO in isopropyl alcohol. The treated samples before and after UV irradiation were characterized by FTIR, Raman, chromatic parameters and mechanical analysis.*

Key words: *wood, SEBS-MA, Raman, FTIR.*

1. Introduction

Recently, wood-polymer composites are one of the most important products due to with various applications in the construction industry. Solid wood, a renewable resource, is one of the most used sources of structural materials, due to the low price and pleasant appearance [4]. Impregnation of wood with a monomer followed by catalytic polymerization or by gamma irradiation leads to the formation of Wood-Polymer Composites [5].

Composite materials based on wood polymers (WPC), represents one of the most important discoveries of the latest years, mainly due to their applications in industry and constructions fields. Massive wood represents a renewable source and that's why is so preferred as material but also due to its low cost and easy processing but also for its aspect. It is a natural mixture/composite based on cellulose, hemicellulose and lignin. Its properties are modified when are exposed to microorganisms and are vulnerable on humidity variations [3].

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This adhesion at pores level has direct influence over thermic and mechanic properties of composite materials. The obtained quality of wood composites is decreased imposing the development of new compatibility methods between polymers and wood, mostly for improving the interphase adhesion, e.g. wood treatment, matrix functionalization and/or the addition of an compatibility agent [1].

Recent investigations shown that using a block copolymer of styrene-ethylene-butylene-styrene (SEBS) grafted with maleic anhydride (MA), serve as toughening agents of polymers and nanocomposites mixtures [9].

Yao et al. [11] have studied mixtures of PLA and PPC (polypropylene carbonate) using maleic anhydride (MA) in order to modify the composite properties. The hardness have been improved meanwhile the strength remain the same after being added a very low content (0.9%) of MA into the mixtures [11].

Wilkinson et al. [10] observed the effects of SEBS-g-MA over the ternary mixtures of polypropylene/PA6/SEBS. Mechanical tests have shown that mixtures have low stretching properties, but improved impact strength compared to PP matrix [10].

In this workpaper, SEBS-g-MA is used as protection agent due to its impact resistance, good stability and mechanical properties [9]. Each sample of SEBS-g-MA treated wood was analyzed by mechanical, physical and chromatic characterization before and after UV irradition. This research provided a method of wood conservation.

2. Materials and Methods

2.1. Materials and sample preparation

Fir wood samples with size of 70 x 25 x 10 mm (length x width x thickness) were prepared by removing the roughness by polishing and dried in a hot air over at 105 °C for one hour. Poly(styrene-ethylene-butylene-styrene) with a 30% polystyrene content, grafted with 1.4% maleic anhydride chemical bounded (SEBS-MA) supplied by Kraton (Houston, United States of America) was used for coating obtaining. Zinc oxide (ZnO) supplied by Chemapol (Sweden) was previously milled at size <0.1 mm.

Treatment of fir wood surfaces with SEBS-MA + ZnO solutions

A 10% solution of SEBS-MA in toluene was obtained. After 1 hour of swelling, the polymer was dissolved by magnetic stirring at 500 rpm for 2 h at room temperature. Then 7.5% ZnO relative to the polymer weight was added and the solution was sonicated at room temperature for 10 minutes and magnetic stirred at 500 rpm for 1h.

ZnO (0.5 g) was dispersed into 100 ml isopropanol, sonicated for 10 minutes to remove agglomeration.

For an increased weathering resistance and improved optical properties, wood samples were first treated by spraying the ZnO solution and dried for 24h at room temperature. The surfaces were then reacted with SEBS-MA+ZnO solution by spraying, dried in a hot air over at 95 °C for 2 hours and cooled in desiccators.

Another set of samples were treated with the SEBS-MA in toluene solution under similar conditions.

Photostability of treated fir wood surfaces

The photostability of control and treated fir wood was analyzed by samples irradiation for 60 minutes with a medium pressure Hg polychromatic lamp (275 W) with maximum emission wavelength at 365 nm.

2.2. Methods

Colour measurements

The color changes of treated wood and due to the samples irradiation were determined using a Konica Minolta colorimeter. The color parameters analyzed were: Δ*L** - the change of color lightness, on different time intervals, compare with the initial value: $\Delta L^* = L_1^* - L_{initial}^*$; Δ*a** - the chromatic deviation of the *a** coordinates (red and green color), on different time intervals, compare to the initial value: $\Delta a^* = a_1^* - a_{initial}^*$; Δ*b** - chromatic deviation of the *b** coordinates (yellow and blue color), respecting the same mathematic formula: $\Delta b^* = b_1^* - b_{initial}^*$, and ΔE - color variation and stability that can be calculated using the Eq. (1) [4]:

$$\Delta E = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}\,, \tag{1}$$

Δ*E** value is an evaluation criterion of the overall change color. For values < 0.2 the difference is not visible, for Δ*E** between 0.2 and 2 a small difference in color can be observed, for values between 2 and 3, respectively between 3 and 6 highlights a color change visible with high-quality, respectively a medium-quality filter. At a value > 6 of Δ*E** the color is highly changed or even different.

Gloss parameter

For gloss parameters changes of control and treated samples before and after irradiation, expressed as gloss units (GU), a Specular GlossMeter 3nh_HG268 (China) instrument was used.

Mechanical strength

The mechanical strength test was performed using a Silver Schmidt Hammer Proceq (Zurich, Switzerland), type L, with impact energy of 0.735 Nm. The average of ten measurements was recorded for each sample obtained by treatment with ZnO and SEBS-MA solutions on dried and wet fir wood specimens. The compressive strength was

calculated using the Equation (2) (for 10th percentile curve range), after apparatus manual indications:

Compressive strength = 2.77*eˆ(0.048*Q), (2)

where Q represents the rebound number measured by the hammer.

Humidity test

For fir wood humidity measurement, specimens were weighted, dried in a hot air over at 105 °C for 2 hours and weighted again. The moisture content was calculated both for native and treated wood according to Eq. (3):

$$w = \frac{m_w - m_0}{m_0} * 100\,, \tag{3}$$

where w is the moisture content [%], m_w is the wet sample weight [g], and m_0 is the weight of the sample oven-dried [g].

Chemical characterization methods

FTIR spectroscopy was carried out using a Vertex 80v spectrometer (Bruker, Germany), with 0.2 cm^{-1} resolution, with ATR module with 0.1% T accuracy. For each sample, 32 scans were averaged in the spectral range of 4000 cm^{-1} - 400 cm^{-1}; the background was subtracted from the recorded spectra. Two replicate spectra per sample were measured.

A portable Raman spectrometer Xantus-2 (Rigaku, Germany) system with dual laser excitation (785 and 1064 nm) was used. Typical experimental parameters were: laser power - 400 mW, exposure time - 3 s, scans - 3, which led to a total acquisition time of 10 s per spectrum. The Raman spectra were continuously collected in the 200-1700 cm^{-1} wavenumber region.

3. Results and Discussions

In Figure 1, the differences on color parameter for untreated and treated fir wood specimens before and after irradiation are presented.

The color of the control samples (uncoated) become darker after 60 minutes of irradiation, a change evidenced by the decrease of *L** value from 82.32 to 80.12. Also, an increase of *b** chromatic parameter from 24.75 to 25.88 after irradiation was recorded. This change highlights a higher yellowness of wood sample due to UV radiation that can depolymerize the lignin and form o- and p-quinonoid structures [6, 8].

The wood surfaces treated with SEBS-MA presented the same behavior at irradiation as the control specimens. *L** decreases with 1.91 and b* increases with 1.16 compared to the untreated wood surface. The degradation of the polymer coating occurs by chain degradation, scission and oxidation primarily at the styrene-olefin bound [2].

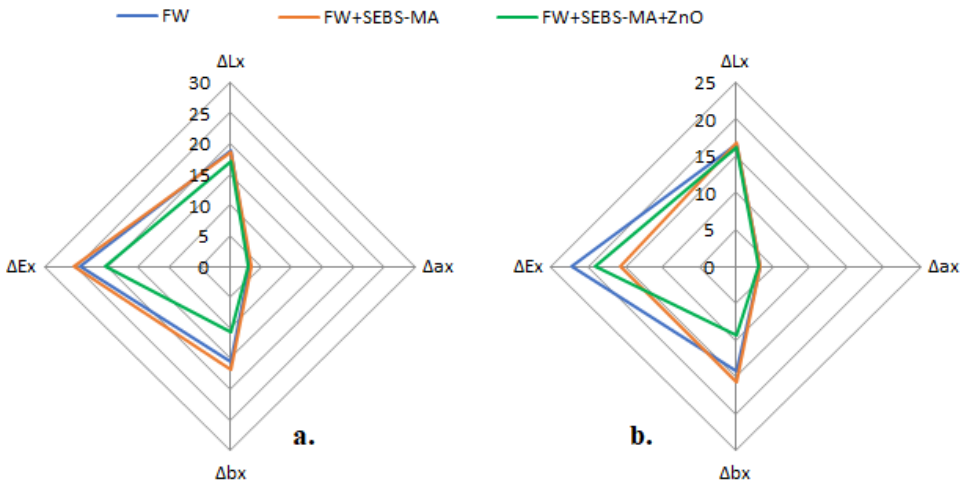

Fig. 1. *Chromatic parameter of treated wood before (a) and after irradiation (b)*

The photostability of wood can be improved by coating the surfaces with SEBS-MA and ZnO solution. As can be seen in Figure 2, the ZnO coating does not have any adverse effect on the aspect and the color of wood surface. No significant changes in lightness and yellow parameter due to light exposure are observed compared to the untreated specimen indicating the effectiveness of ZnO particles for UV protection. The overall change color Δ*E** after irradiation was 2.47 for wood, 2.25 for SEBS-MA coating and 1.55 for the sample treated with ZnO polymeric solution. These results confirm the effectiveness of ZnO particles for a better UV protection.

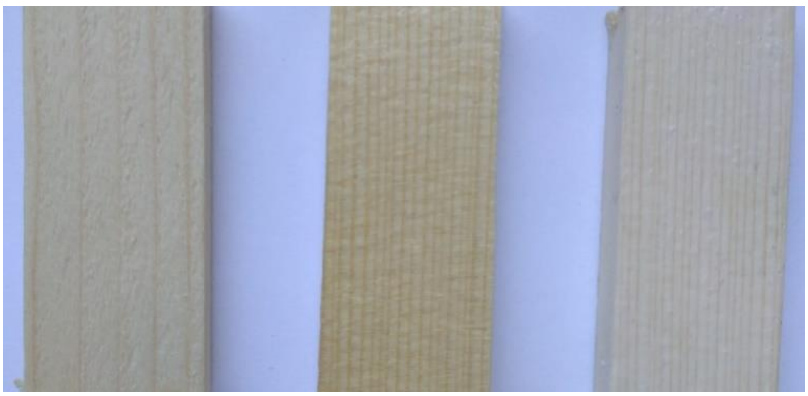

Fig. 2. *The aspect of fir wood (from left to right: fir wood, fir wood + SEBS-MA; fir wood + SEBS-MA+ZnO)*

The gloss parameters could reflect the coating quality. By irradiation, a small decrease is observed, most probably due to the polymer degradation, faster for SEBS-MA than SEBS-MA+ZnO (Figure 3).

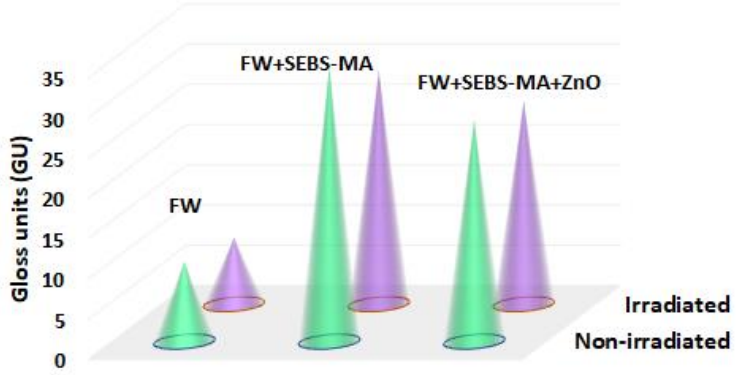

Fig. 3. *Gloss parameter of fir wood samples under different conditions*

The effect of wood humidity on the mechanical strength of specimens is presented in Figure 4. For treated and untreated samples, a decrease in strength can be observed for wet specimens. As the humidity increases in the wood cell membranes, most of the mechanical properties of wood decrease, except for elasticity which increases [7].

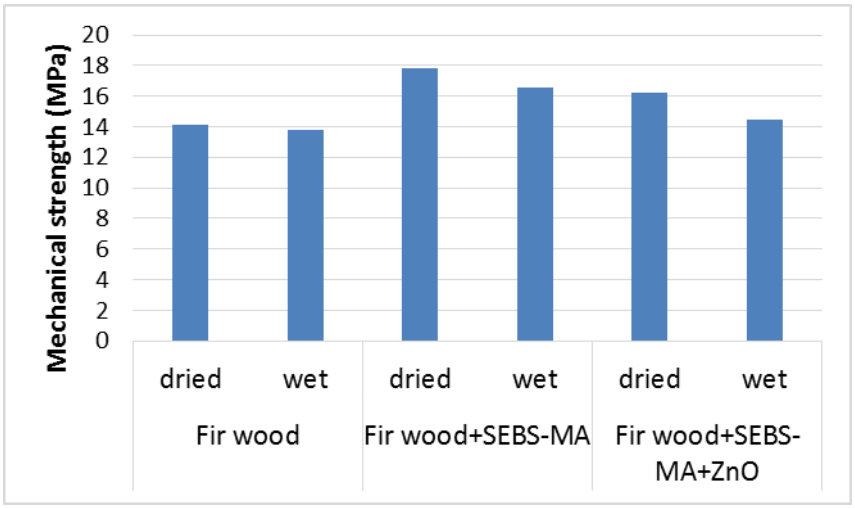

Fig. 4. *The mechanical strength of fir wood sampled dried and wet, treated and untreated*

The moisture content (w) of wood samples does not present significant changes, the smaller increase of w is observed for ZnO coated specimen (Table 1).

Moisture content determined for control and treated wood samples Table 1

Moisture content [%]	**Fir wood**	**Fir wood + SEBS-MA**	**Fir wood + SEBS-MA + ZnO**
	6.55	6.61	6.57

For the investigation of the molecular structure of the polymeric systems Fourier-transform infrared spectroscopy (FTIR) was used. Figures 5-7 show the FTIR spectra of untreated wood, wood treated with SEBS-MA and wood treated with SEBS-MA+ZnO, all of them being non-irradiated and irradiated with polychromatic light.

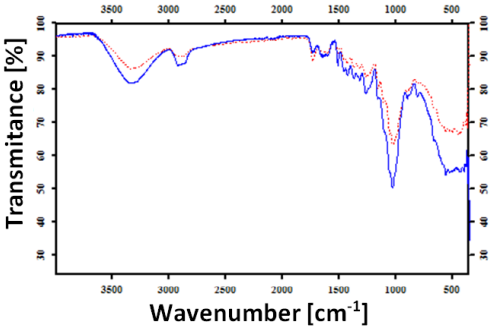

Fig. 5. *FW (continuous line) and FW(i) (dashed line)*

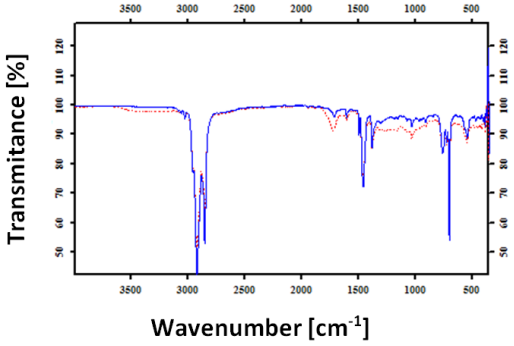

Fig. 6. *FW + SEBS-MA (continuous line) and FW + SEBS-MA(i) (dashed line)*

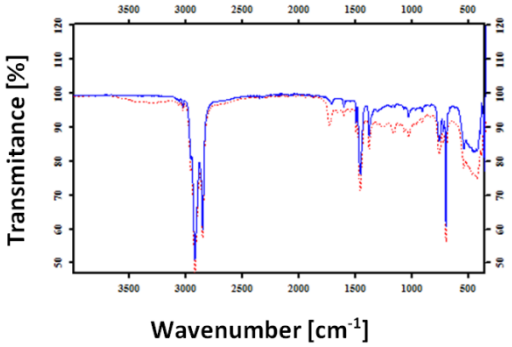

Fig. 7. *FW + SEBS-MA+ZnO (continuous line) and FW + SEBS-MA+ZnO(i) (dashed line)*

The bands from the range 1730-1750 cm^{-1} may be assigned to the C=O stretching of cyclic anhydride, from the block-copolymer functionalized with maleic anhydride. In the spectra of the wood-polymer nanocomposites (Figure 3), the bands at 1713 and 1776 cm^{-1} are detected, too, but the peak intensity at 1709 cm^{-1} seems to be considerably reduced, possibly due to the light irradiation. These observations could be checked by Raman spectra, Table 2.

Table 2

The main characteristics Raman bands of irradiated and non-irradiated wood samples

Wavenumber [cm^{-1}]	**Assignment**	**Attributed to**
877, 894	H-C-C and H-C-O bending	Cellulose
980-994	C-C and C-O strech	Cellulose
1027-1097	C-C-O strech of phenol	Cellulose
1117	Coniferaldehyde	Cellulose
1805, 1188, 1196	A phenol mode	Lignin
1251-1297	C-O group	Lignin
1328-1335	Aliphatic O-H band	Cellulose
1358	C-H band	Cellulose
1441, 1448	CH_3 bending in OCH_3	Lignin and carbohydrate
1653	C-C and C-O stretch	Lignin

Raman spectra (Figures 8 and 9) show that during irradiation, some peaks of the wood-polymer systems have lower intensity reflecting that the sample is degraded. This reduction of the peaks can be lead to by irradiation of samples. The Raman data (Table 2) comes in addition to FTIR data and supports the identified compounds.

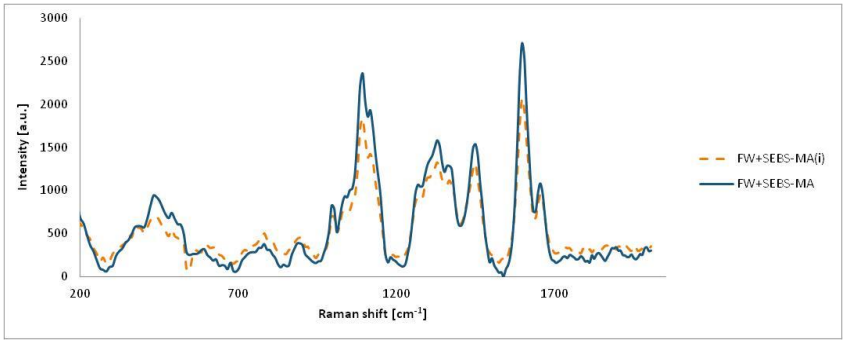

Fig. 8. *Raman spectrum for FW+SEBS-MA (continuous line) and FW+SEBS-MA(i) (dashed line)*

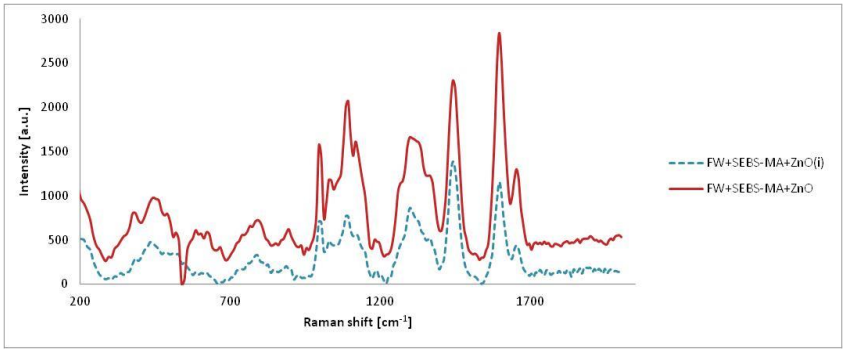

Fig. 9. *Raman spectrum for FW+SEBS-MA+ZnO (continuous line) and FW+SEBS-MA+ZnO(i) (dashed line)*

4. Conclusion

In this investigation, silver fir wood (Abies alba) samples (FW) were impregnated with some polymeric systems, as follows: (1) a block copolymer of styrene-ethylene-butylene-styrene (SEBS) grafted with maleic anhydride (MA), denoted as SEBS-MA; (2) a block copolymer of styrene-ethylene-butylene-styrene (SEBS) grafted with maleic anhydride (MA), denoted as SEBS-MA, used in combination with ZnO for the preservation of wood surfaces applied by spraying on the wood surfaces pre-treated with a suspension of ZnO in isopropyl alcohol.

The most important advantages of the investigated systems are: good permeability, temperature resistance and high mechanical strength and applicability for treating surfaces contaminated with hydrophobic substances, UV protection, no changes in the natural color of wood or its gloss. They provided a method of restoring and / or recovering a deteriorated wood surface, the present solution being related to both wood preservative compositions based on a non-toxic, hydrophobic polymeric system which prevents moisture penetration.

The treated samples before and after UV irradiation were characterized by FTIR, Raman, chromatic parameters and mechanical analysis.

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