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Ecological Fire Retardant for Wood Impregnation

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ABSTRACT
In this research, it was study Pinus elliottii wood impregnated with 5 and 10% whey proteins suspensions to improve its behavior against fire action.
The good results obtained either in Thermogravimetric Analysis, in "Intermittent flame of a Bunsen burner test" and in Oxigen Index test allowed concluding that treated wood showed increased fire resistance. This would be based on the fact that the water adsorbed by the proteins could partially dissipate during combustion and, in addition, dilute the volatile products generated forming an oxygen-poor atmosphere, near the material. In addition, the thermal energy released during conflagration takes longer to reach the substrate due to more char is formed in the impregnated wood, acting as thermal insulator.
Keywords: *Wood; Protein; Impregnation; Fire*

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I. INTRODUCTION

The use of soft wood has been increasing over last years but, due to its fire performance, it needs to be treated with fire retardants. These products can be applicated as coatings or by impregnation using a vacuum-pressure technique (e.g. Bethell method) and, although innovatives technologies (such as plasma treatments) are being investigated [1-4], coatings continue to be the most popular protecting method [5-8] and impregnation is widely used because of it does not usually alter the visual characteristics of wood.

Even though there are many products that improved fire performance of wood, they are dangerous for the environment. Phosphorus based compounds are some of the best known fire retardant treatments [9, 10] but it is well-known that they worsen the physico-mechanical properties of wood and wood products (e.g. monoammonium phosphate, MAP). The use of nitrogen compounds is widespread because they do not have negative environmental impacts; nevertheless, the combinations of phosphorus and nitrogen compounds are preferred due to their synergic effect (the fire retardation performance of the individual components is enhances) [11-13]. On the other hand, impregnation with boron compounds are used all over the world but, nowadays, many end-users and regulators recognise the hazards that they present (toxicity, smoke and corrosivity of fire retardant compounds); thus, there is a need to move away from boron based fire retardants [14, 15]. Finally, the silicon based compounds are continually under improvement [16-18] and new products and technologies for fires retardants on plastics and fabrics have not been used on wood [19, 20].

In this research, it has been evaluated the behavior of *Pinus elliottii* wood impregnated with whey proteins in different concentrations, trying to find an ecological fire retardant [21-23]. To make this, the samples were characterized by SEM and FTIR and were performed thermogravimetric analyzes (TGA) and a flammability tests (Oxygen Index, OI and Resistance to Intermittent flame of a Bunsen-burner, RIB). Moreover, a test of contact angle was performed to assess water absorption characteristics of surface [24].

II. MATERIALS AND METHODS

2.1 Wood

Pinus Elliottii wood was used because it is a very forested wood in the region, which is easily obtained and has a density that makes it very suitable for its treatment by impregnation (490 $g.cm^{-1}$).
The specimens were cut according to the dimensions required for the different tests and kept in laboratory for two months for their conditioning (25 ± 2 ºC and 65 ± 3% relative humidity).

2.2 Whey proteins

Whey protein powder was used; its chemical characteristics were: 79.2% protein; 8.7% carbohydrate; 7.9% fat and less than 1% of potassium, phosphorus and sodium. The amount of each amino acid per gram of protein is described in Table 1.

Table 1. Amino-acids profile of proteins

AMINO-ACIDS PROFILE (mg / g of protein)	
Alanine	53
Arginine	26
Aspartic acid	103
Cysteine	22
Glutamic acid	174
Glycine	18
Histidine	18
Isoluene	62
Leucine	103
Lysine	88
Methionine	21
Phenylalanine	29
Proline	60
Serina	56
Threonine	66
Tryptophan	25
Valine	60
Total = 98,4%	

2.3 Impregnation

For the impregnation two formulations were designed in 5% and 10% w/w. For this, the corresponding amount of whey protein powder was suspended in distilled water by mechanical stirring at 700 rpm during approximately half an hour. Then, wood samples were added and placed at room temperature (25 ± 2 °C) in a desiccator connected to a vacuum pump for 4 hours. After that, samples were removed from the desiccator and left for 24 hours submerged in the protein suspension. Finally, the specimens were left under laboratory conditions until constant weight to ensure drying up to equilibrium moisture.

The impregnant retentions were calculated using the equation:

$$R\% = \frac{W_f - W_i}{W_i} x100$$

In which Wf is the weight of impregnated specimen and Wi is the weight of the same specimen without impregnation (both weights were calculated when the equilibrium moisture was reached, ie when at least two consecutive equal weights were obtained), Table 2.

2.4 Scanning Electron Microscopy, SEM

The characterization of the treated and untreated surfaces was performed using a scanning electron microscope, FEI model Quanta 200, installed in the Laboratory of Investigations of Physical Metallurgy "Ing. Gregorio Cusminsky" (LIMF, UNLP), for which 10 x 10 x 10 mm samples were previously metalized with gold.

2.5 Fourier Transform Infrared Spectroscopy, FTIR

The samples were analyzed by Fourier Transform Infrared Spectroscopy (FTIR) in a PERKIN ELMER (CIDEPINT, CONICET) equipment using the single rebound Attenuated Total Reflectance (ATR) method because these type of samples can not be placed in the usual supports for the transmission method and since this technique does not require a previous samples preparation.

2.6 Contact Angle

In order to see if the treatment modifies the surface characteristics in terms of its hydrophobicity, a contact angle test was carried out on 10 x 10 x 150 mm specimens. For this, a Ramé-Hart model 500 goniometer (INIFTA, UNLP) was used and the images were analyzed with "DROP image Advanced v2.2" software. The sample was placed on the platform, where a drop of distilled water was deposited. The equipment consists in a light spot located at one end, while at the other, is located the video camera. The image obtained corresponds to a black or dark image corresponding to the drop with white background. The software marks the points of contact of the right and left angles θ of the baseline of the drop and registers them. Each contact angle data is the result of the average of 13 measurements of static contact angles in both the right and left zones of the drop

formed on the surface under study. The contact angles were determined at room temperature. The test were performed in quadruplicate for an untreated sample and for a sample impregnated with dispersion of 10% whey proteins.

2.7 Thermogravimetric Analysis, TGA

For determination of the thermal behavior of the materials, there were performed thermogravimetric analysis (TGA) of the whey proteins and sawdust of wood (obtained from the untreated and treated with the proteins in 5% and 10% suspensions). For this, it was used a TG-Shimadzu 50 equipment in the Laboratory of Techniques of Thermal Analysis (LATAT) located at the Institute of Physics La Plata, UNLP. The test was carried out under a nitrogen atmosphere until reaching a temperature of 700 °C and a heating rate of 10 °C/minute.

2.8 Resistance to intermittent flame of a Bunsen burner, RIB

This test uses a UL 94 Flame Chamber camera, whose dimensions are 1130 mm high, 1200 mm wide and 510 mm long. The chamber is connected to the outside by a chimney extractor of fumes and toxic gases. On its front face has a glass window which allows positioning the samples and the lighter. It also has two metal gates. On the left side are the controls for the ignition of the equipment, the opening and closing of the gas line, the pressure and gas flow regulator, the ignition of the interior light and the extractor hood. On the side are the time controls or timers. Inside it has a lighter adjustable in position and inclination angle (45 °, 20 ° or 0 °).

Table 2. Amino-acids profile of proteins

Sample identification	W_i, g	W_f, g	$W_f - W_i$, g	Retention, %	Average R, %
P5-1	4.9645	5.4411	0.4766	9.60	**10.29±2.24**
P5-2	6.3167	6.8459	0.5292	8.38	
P5-3	7.5840	8.3345	0.7505	9.90	
P5-4	6.5689	7.0905	0.5216	7,94	
P5-5	7.6655	8.3868	0.7213	9.41	
P5-6	7.5683	8.0668	0.4985	6.59	
P5-7	6.2161	6.8396	0.6235	10.03	
P5-8	6.0990	6.6210	0.5220	8.56	
P5-9	5.1335	5.6632	0.5297	10.32	
P5-10	7.3482	7.8889	0.5407	7.36	
P5-11	7.6344	8.3467	0.7123	9.33	
P5-12	5.6639	6.1654	0.5015	8.85	
P5-13	0.4928	0.5464	0.0536	10.88	
P5-14	0.4397	0.4938	0.0541	12.30	
P5-15	0.4798	0.5327	0.0529	11.03	
P5-16	0.4465	0.5022	0.0557	12.47	
P5-17	0.4208	0.4664	0.0456	10.84	
P5-18	0.4619	0.5165	0.0546	11.82	
P10-1	4.7672	5.2913	0.5241	10.99	**10.99±2.24**
P10-2	7.5123	8.1489	0.6366	8.47	
P10-3	5.7062	6.2191	0.5129	8.99	
P10-4	6.7158	7.3469	0.6311	9.40	
P10-5	6.5310	7.2721	0.7411	11.35	
P10-6	7.1954	7.8852	0.6898	9.59	
P10-7	7.6130	8.4058	0.7928	10.41	
P10-8	7.6385	8,1881	0.5496	7.20	
P10-9	5.7521	6.4306	0.6785	11.80	
P10-10	7.7848	8.3863	0.6015	7.73	
P10-11	8.4873	9.3492	0.8619	10.16	
P10-12	5.8724	6.5097	0.6373	10.85	
P10-13	0.5068	0.5699	0.0631	12.45	
P10-14	0.4222	0.4775	0.0553	13.10	
P10-15	0.5455	0.6138	0.0683	12.52	
P10-16	0.4446	0.5081	0.0635	14.28	
P10-17	0.4684	0.5293	0.0609	13.00	
P10-18	0.4896	0.5654	0.0758	15.48	

The specimens of 10 x 10 x 150 mm are handled from the upper end in such a way that their longitudinal axis has an inclination of 45 ° with respect to the support plane.

The test was carried out in the cabin to avoid drafts. It consisted in subjecting the lower front of the specimen to the intermittent action of the flame of a Bunsen burner. The flame was adjusted to reach 10 mm in height of the blue cone and the outlet of the burner was placed 15 mm from the surface under examination. Then, they were

subjected to the action of the flame for 20 s, with rest periods of 10 s. The fire / resting cycle was repeated until the flame self-extinguished within 5 s of removal of the lighter or the carbonized zone did not exceed 8 cm^2.

2.9 Oxygen Index Test, OI

This test determines the minimum oxygen concentration in a nitrogen/oxygen mixture that supports material combustion under equilibrium conditions as candle-like burning. The determination of OI index was carried out with a flow rate of 3.2 $cm.s^{-1}$ by using specimens, free of defects, prepared with size of 150 x 10 x 10 mm. The importance of determining OI lies in measuring the ease of combustion of substrates to compare results.

It is important to mention that although this method is not representative of the real behavior of a material in contact with fire, it is one of the preferred methods in the development of fire retardant treatments because it allows obtaining reproducible numerical values.

III. RESULTS AND DISCUSSION

3.1 Characterization of the wood surface with and without treatment

The average retention level reached by the specimens was 10.3% and 11.0% for the samples treated with 5% and 10% proteins, respectively, Table 2.

SEMs captures are presented in Figure 1 for differents magnifications and, in them, it is possible to observe how the proteins form a film that covers a large part of the wood surface and even try to cover the edges of the traqueids but they are not able to enter inside them because there is a steric hindrance.

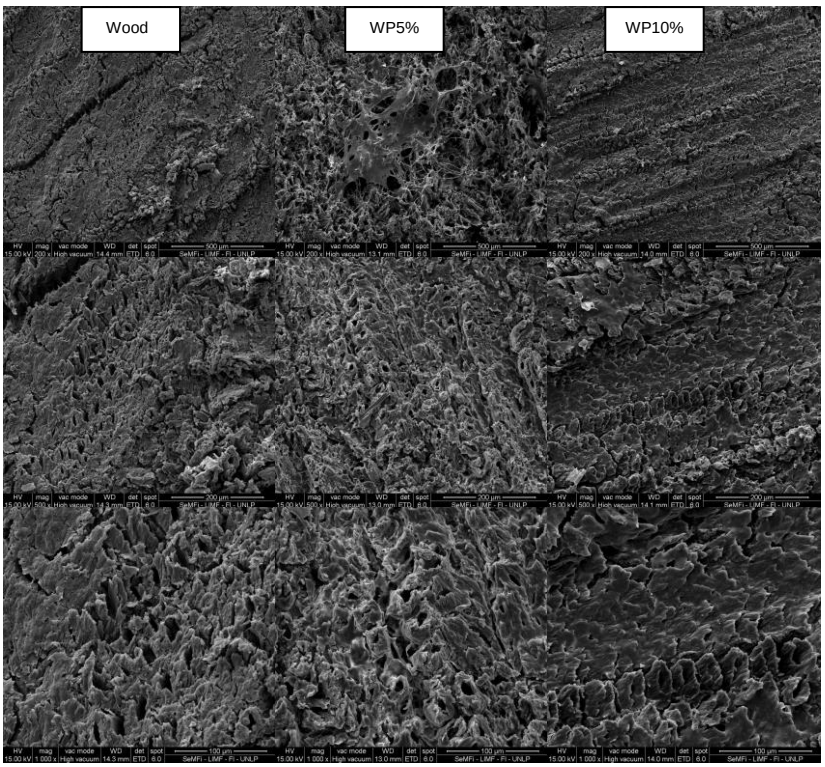

Figure 1. SEM micrographs of untreated and treated wood (200x, up; 500x, medium and 1000x, below)

On the other hand, Figure 2 shows the FTIR spectra of untreated and treated wood with 10% dispersion, in which the effectiveness of the deposition of the whey proteins on the wood can be visualized. In the spectrum of untreated wood, they are observed the typical vibration modes of cellulose: -OH at 3400, at 1650 and at 1300 cm^{-1}; -CH_2 at 2900 and at 1425 cm^{-1}; -CH at 1370 cm^{-1} and C-C at 1020 cm^{-1}. In the case of impregnated wood, they are observed vibration modes of the amides of the protein at 1650 and 1533 cm^{-1}, but the cellulose peaks (less pronounced) are still observed [19, 20].

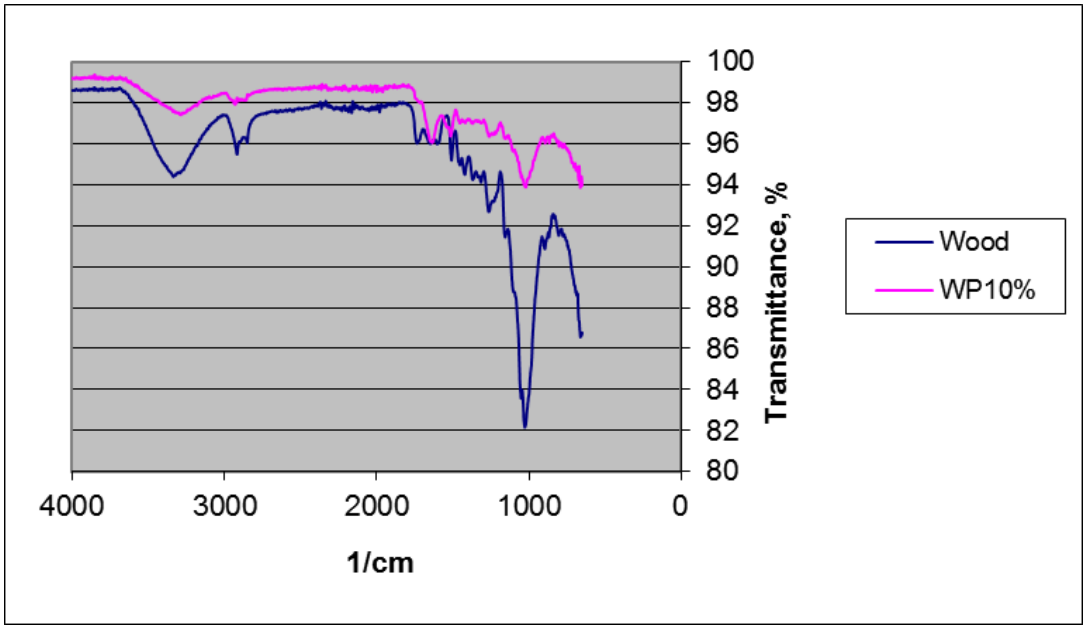

Figure 2. FTIR of untreated and treated wood

In Figure 3 a "Drop Shape Image Analysis" is shown and in Figure 4 the corresponding photographs of contact angle test. A slight decrease in the average mean contact angle from 105.3 ° to 92.5 ° is found; this decrease is possible due to the fact that the proteins adsorb water to an equilibrium and the surface becomes more hydrophilic, Table 3.

Drop Shape Image Analysis

Drop phase : Water Density : 0.9987
Extern.phase : Air Density : 0.0013

No.	Time	Theta(R)	Theta(L)	Mean	Dev.	Height	Width	Area	Volume
1	0.0	97.00	100.10	98.55	1.55	1.826	3.127	18.46	10.45
2	0.9	98.87	97.40	98.14	0.73	1.824	3.152	18.51	10.50
3	1.9	98.68	97.26	97.97	0.71	1.821	3.153	18.47	10.47
4	2.9	98.39	97.14	97.76	0.62	1.816	3.154	18.43	10.44
5	3.9	98.49	96.77	97.63	0.86	1.809	3.153	18.34	10.36
6	4.9	98.38	96.60	97.49	0.89	1.805	3.154	18.29	10.33
7	5.9	98.34	96.45	97.39	0.94	1.803	3.153	18.26	10.30
8	6.9	98.37	96.32	97.34	1.03	1.800	3.153	18.22	10.27
9	7.9	98.62	96.32	97.47	1.15	1.798	3.154	18.22	10.27
10	8.9	98.49	96.31	97.40	1.09	1.796	3.154	18.21	10.26
11	9.9	98.44	96.20	97.32	1.12	1.795	3.154	18.19	10.24
12	10.9	98.49	96.17	97.33	1.16	1.794	3.154	18.17	10.23
13	11.9	98.68	96.15	97.42	1.26	1.793	3.154	18.16	10.22
Mean:		98.40	96.86	97.63	1.01	1.806	3.152	18.30	10.33
Stand.dev.:		0.12	0.29	0.10	0.07	0.003	0.002	0.04	0.03

Figure 3. Test result in Goniometer

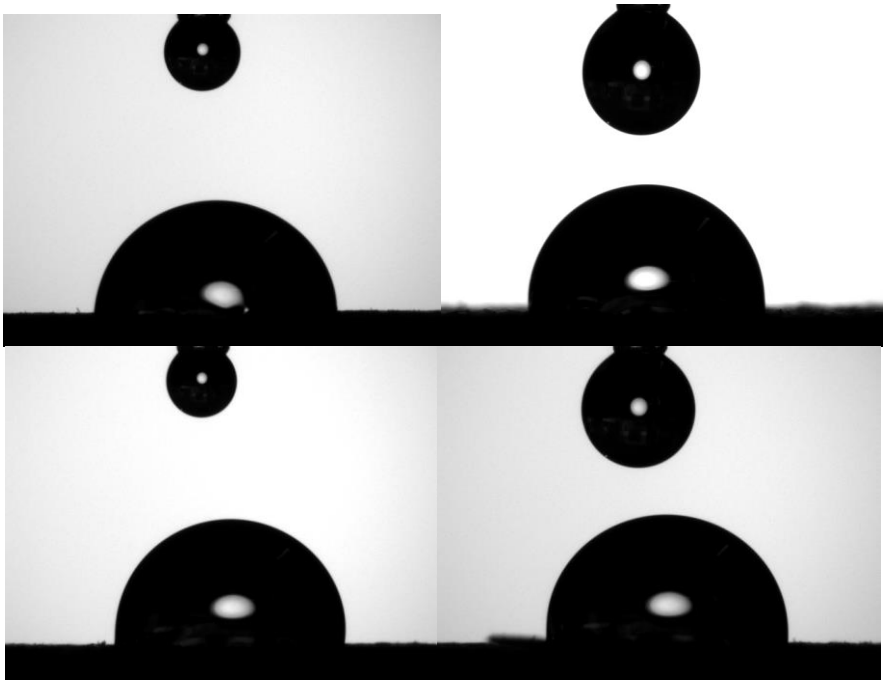

Figure 4. Goniometer photographs

3.2 Fire performance tests of wood with and without treatment

Figure 5 shows the Thermogravimetric Analysis results of whey proteins of untreated and treated wood. In the curve of the pure proteins, a more pronounced fall is observed at 100 °C due to the loss of the water adsorbed by them. During the cellulose decomposition, which occurs at approximately 300 °C, a greater amount of carbonaceous residue is observed in the untreated wood (less loss of mass). However, during the second phase of cellulose decomposition, it is observed the formation of more thermally stable products when there are proteins in the system (synergistic effect); that is why the curves are inverted and in the case of wood treated with 10% whey proteins suspension, remains 3% more of the desirable carbonaceous residue.

The Resistance to Intermittent flame of a Bunsen burner test (RIB) showed that, in all cases, untreated wood does not support one cycle. On the other hand, the treated wood resists two or three cycles although no differences are observed between the concentrations. In addition, it can be seen in Figure 6 that in the untreated samples (4 and 9) there is a greater flame spread than in the treated ones (12, with 5% suspension and 1 with 10% suspension).

Finally, for the Oxygen Index test it was found that untreated wood presents an average of 22% oxygen in the mixture while in the wood treated with 5% proteins showed a value of 28% and those treated with 10% a value of 30%.

IV. CONCLUSIONS

The studies allowed concluding that the wood treated with whey proteins showed a better behavior against fire action. Thus, good results were obtained either in the TGA, in the RIB and in the OI tests.

This better behavior against fire action is because the water adsorbed by the proteins could partially dissipated heat during combustion and diluted the volatile products that were generated, forming an oxygen-poor atmosphere, near the material. Also, this higher water amount, allowed to maintain the substrate at 100 ºC for longer and delayed the combustion process.

Another fact that improves the behavior is that as more char was formed in the impregnated wood, the energy released during the conflagration took longer to reach the substrate, since it acted as a thermal insulator.

New studies with pure protein (Casein) and with amino acids will allow, as expected, to improve the behavior even more because the commercial proteins used as nutritional supplement have numerous impurities.

Table 3. Results of contact angle test

Sample	Identification	Mean contact angle	Average
Untreated	B-1	109.24	**105.85±3.87**
	B-2	103.99	
	B-3	100.57	
	B-4	107.61	

Treated	P-1	96.25	**92.52±3.59**
	P-2	88.02	
	P-3	94.36	
	P-4	91.47	

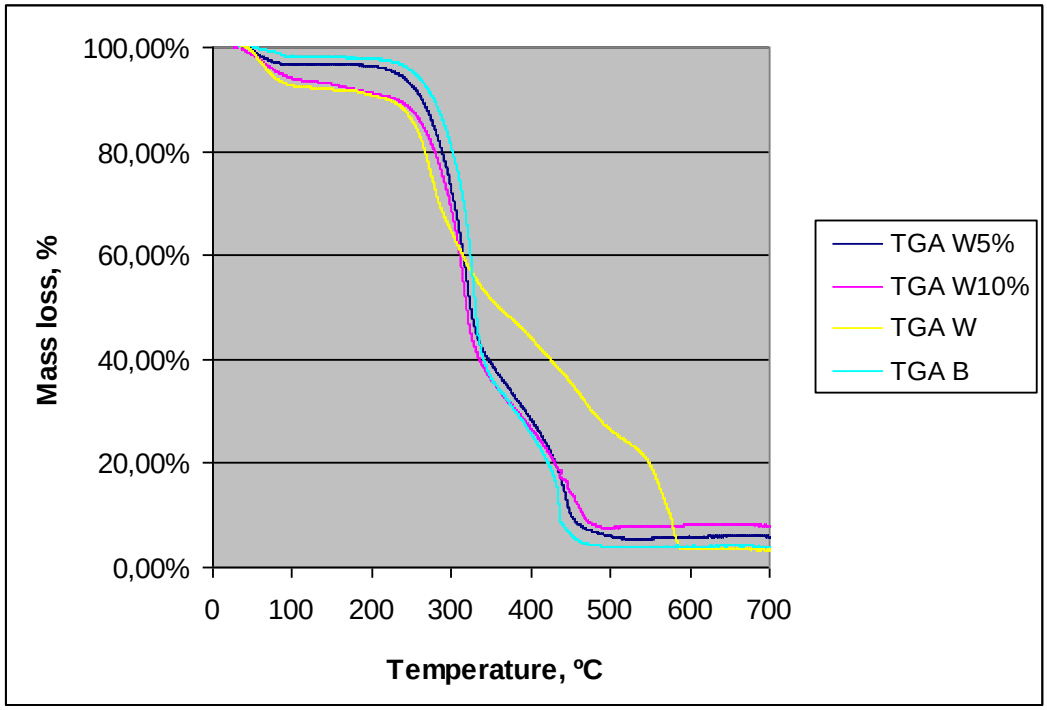

Figure 5. TGA of untreated and treated wood

Figure 6. Untreated (up) and treated wood (down) after RIB test

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