

# RECYCLED BIOMASS WASTE AS COPOLYMERIZATION PARTNERS

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**Abstract:** *Taking into account the main demand regarding the environmental protection and the need for wood preservation, our research has been focused on the developing of some new chemical agents for wood preservation, based on acrylic copolymers and lignosulfonates, biomass waste, generated as by-products of chemical wood pulping. Because the lignosulfonates posses a reactive chemical potential, evidenced by presence in their structure of some functional groups, they have been used as reactive comonomers in water emulsion copolymerization of acrylic comonomers. Having in view the biocide activity of acrylic comonomers and of lignosulfonates, the obtained copolymers were biologically investigated and proposed as ecological wood preservatives.*

**Key words:** *recycling, lignosulfonates, acrylic copolymers, ecological products.*

## 1. Introduction

Lignocellulosic materials are important natural renewable resources, containing polymers constituents such as cellulose, hemicellulose and lignins with many active functional groups susceptible to reaction [3-5]. Lignin is the second most abundant renewable organic material on planet immediately after cellulose, in wood, straw and other plant tissues. Available lignin products are generated in vast quantities as a by-product of chemical wood pulping. During the technical sulphite pulping (with ammonium and calcium disulphites), lignin becomes soluble in water, due to the partial degradation and introduction of sulfonic groups. Lignosulfonates are water soluble, anionic surface-active derivatives of lignin.

They are accompanied in the spent liquor by sugars (pentoses and hexoses) by partially degraded polysaccharides, as well as by other organic and inorganic components. Generally, the lignosulfonates from paper industry are drawn off to rivers, representing a seriously pollution sources. For a better resource utilization and environmental protection, it is very interesting to use lignosulfonates as chemical reactants [2], [6] or to chemical modify them in order to improve their properties. Wood preservation is a complex process involving a wide range of physical, chemical and biological factors, demanding much from the chemicals selected for this purpose [6]. As an alternative to the protection of wood with toxic chemicals that inhibit the activity of microorganisms,

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research regarding chemically modifying the wood substrate as a means of preventing deterioration is a current area of study. The idea of the utilization of such lignin derivatives as reaction partners into the emulsion copolymerization of acrylic comonomers is based on the observation that the third major wood component, lignin, was proved to be the major fixation site for certain wood preservation components, such as copper [4], [6].

## 2. Materials and Methods

The ammonium lignosulfonate (from wood and paper industry), iron lignosulfonate (obtained from the ammonium lignosulfonate and  $\text{Fe}(\text{NO}_3)_3$ ) and iron and chromium lignosulfonate (obtained from the ammonium lignosulfonate with  $\text{Fe}(\text{NO}_3)_3$  and  $\text{K}_2\text{Cr}_2\text{O}_7$ ) were analysed conforming to the specific methodology for lignins [8]. Both the acrylic copolymers and the copolymers modified by copper sulphate and ammonium, iron and iron and chromium lignosulfonates have been obtained using a semicontinuous technique emulsion copolymerization.

The monomers (ethyl acrylate, butyl acrylate, acrylonitrile, acrylic acid), the emulsifiers and the initiator sodium persulphate were purchased from Merck. The copolymerization reactions were carried out in a three-necked flask, equipped with a paddle type stirrer, thermometer and cooler.

Among the different polymerization processes that are generally carried out, the water emulsion copolymerization of acrylic monomers is particularly attractive, due to the colloidal nature of the process, which associates a high polymerization rate with a high average degree of polymerization. The acrylic comonomers emulsion, with or without metal complexed lignosulfonates and copper sulphate, was dozed by a constant ratio, for

2.5-3 hours into the copolymerization autoclave. The copolymerization temperature was 80-85 °C. At the end of the process, the inner temperature was raised at 90 °C and kept for an hour, in order to finish the copolymerization.

### 2.1. Results and Discussions

The chemical characteristics of the ammonium, iron and iron and chromium lignosulfonates, are presented in Table 1.

Table 1  
*Characteristics of the lignosulfonates*

Characteristic	LSNH <sub>4</sub>	LSFe	LSFeCr
pH-value	4.85	2.24	3.80
Solids, [%]	44.96	35.47	42,50
Density, 20 °C, [g/cm <sup>3</sup> ]	1.021	1.140	1.1850
Viscosity, 20 °C, [cP]	70.00	66.00	68.00
Ash, [%]	0.96	2.75	5.28
Cation, [%]	7.39	4.71	6.70, Fe 6.50, Cr
Groups, [%]:			
- OH phenol	14.16	13.35	22.90
- OH alcohol	13.74	16.06	19.40
- carbonyl	1.71	9.35	11.31
- carboxyl	0.60	0.74	1.93

where:

LSNH<sub>4</sub> = ammonium lignosulfonate;

LSFe = iron lignosulfonate;

LSFeCr = iron and chromium lignosulfonate.

For the synthesis of the new ecological wood preservation agents, the acrylic monomers (ethyl acrylate, butyl acrylate, acrylonitrile and acrylic acid) were copolymerized with ammonium, iron and iron and chromium lignosulfonates (7% from the total monomers content), which can act as reaction partners due to their functional groups hydroxyl, carbonyl and carboxyl. The chemical characteristics of the acrylic copolymers with and without the metal complexed lignosulfonates are presented into the Table 2. Comparing to

the acrylic copolymer as reference, it can be seen that the copolymers with lignin derivatives present improved properties of the acrylic latex films. The better values of the tensile breaking strength and water absorption of the film are obtained for the acrylic copolymer with iron and chromium lignosulfonate as reaction partner, which contains a higher content of functional groups hydroxyl, carboxyl, carbonyl.

These improvements of the copolymers characteristics can be correlated with the grafting process of the lignin derivatives on the acrylic copolymer macromolecules due, mainly, to the esterification reactions

between the carboxyl functional groups from the acrylic copolymers and lignin hydroxyl groups.

The structure of obtained acrylic copolymers, with and without biomass waste lignosulfonates, was also investigated by FT-IR analysis with a spectrophotometer FTIR-model BX II (Perkin Elmer, 2005).

The spectra are represented in Figure 1.

The structure of the obtained acrylic copolymers with ammonium, iron and iron and chromium lignosulfonates is certified by the presence of both specific and common absorption bands which characterize the general structure of the compounds, due to the

Table 2

*Chemical characteristics of the acrylic copolymers with/without lignosulfonates*

Copolymer	Solids, [%]	pH	Density, [g/cm <sup>3</sup> ]	Viscosity, at 20 °C, [cP]	Tensile breaking strength, [MPa]	Water absorption of the film, [%]		
						1 h	24 h	48 h
CP1	38.5	6.0	1.0400	33.00	1.96	4.2	18.4	38.0
CP2	38.8	6.5	1.0500	38.50	2.23	3.5	15.5	36.4
CP3	39.3	6.5	1.0650	42.50	2.40	3.0	14.0	33.0
CP4	40.0	6.5	1.0600	50.00	3.40	2.8	13.0	30.5

where:

CP1 = acrylic copolymer;

CP2 = acrylic copolymer with ammonium lignosulfonate;

CP3 = acrylic copolymer with iron lignosulfonate;

CP4 = acrylic copolymer with iron and chromium lignosulfonate.

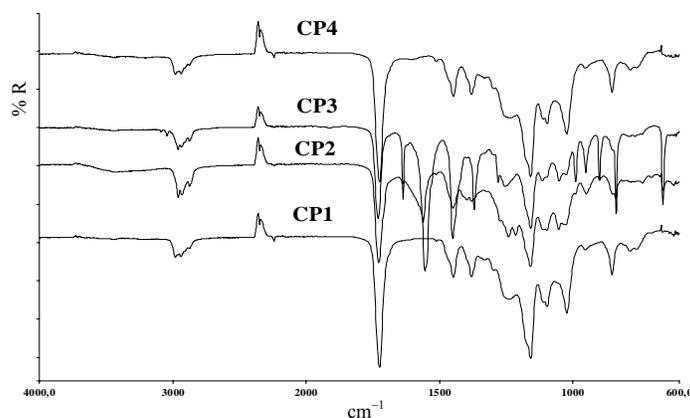


Fig. 1. FTIR spectra of the acrylic copolymers CP1, CP2, CP3, CP4

functional groups present both in acrylic copolymer CP1 and in copolymers CP2, CP3 and CP4 with lignosulfonates components having in IR absorbances corresponding to the functional groups:

- *alcoholic hydroxyl* ( $1020-1050\text{ cm}^{-1}$ ) - absorption bands characteristic to the lignocellulosic extracts;

- *phenolic hydroxyl* ( $1240-1265\text{ cm}^{-1}$ ) - absorption bands characteristic to the lignocellulosic extracts;

- *carbonyl* ( $1724-1729\text{ cm}^{-1}$ ) - absorption bands common both to the acrylic copolymer and to the lignocellulosic extracts, assigned to the valence vibration of the carbonyl group in ketone or carboxyl or ester functional groups;

- *carboxyl and ester* ( $1447-1450\text{ cm}^{-1}$ ) - absorption bands common both to the acrylic copolymer and to the lignocellulosic extracts (lignosulfonates);

- *metoxy* ( $2981-2958\text{ cm}^{-1}$ ) - absorption bands characteristic to the lignocellulosic extracts;

- *ether* ( $1157-1158\text{ cm}^{-1}$ ) - absorption bands common both, to the acrylic copolymer and to the lignosulfonates;

- *lignin aromatic catenes* ( $1554-1560\text{ cm}^{-1}$ ) - absorption bands characteristic to the lignosulfonates;

- *lignin aromatic ring* ( $1430-1550\text{ cm}^{-1}$ ) - absorption bands characteristic to the lignosulfonates.

Considering the biocide activity of acrylic monomers, copper sulphate and the major wood component lignin [1], [2], the obtained copolymers were biologically investigated and proposed as wood preservation agents. The methods consist on treating the filter paper and the sapwood samples by immersion in wood preservatives for 30 minutes and exposing the treated samples against the attack of the following microorganisms: *Chaetomium globosum* Kunze, *Paecilomyces varioti* Brainier, *Stachibotrys atra* Corda and

*Alternaria tenuis* Ness.

After 28 testing days, the samples were visually examined by optical microscope in order to establish the attack level of the above mentioned microorganisms.

The fungal growth was classified between 0 and 4, as following:

0 - no growth;

1 - trace of growth detected visually;

2 - slight growth or 5-20% coverage of the total test area;

3 - moderate growth or 20-50% coverage;

4 - plenty of growth or above 50% coverage.

The proposed wood preservation agents were as follows:

WP1 = the wood preservation agent based on the acrylic copolymer;

WP2 = the wood preservation agent based on the acrylic copolymer with 7% ammonium lignosulfonate;

WP2 = the wood preservation agent based on the acrylic copolymer with 7% iron lignosulfonate;

WP2 = the wood preservation agent based on the acrylic copolymer with 7% iron and chromium lignosulfonate.

The results of the biological testing are presented in the Table 3.

From the four proposed new wood preservation agents, the acrylic copolymer with iron and chromium lignosulfonate presented the best biocide efficiency, both on wood samples and filter paper samples. We consider that also the wood preservation agents WP3 (with iron lignosulfonate) and WP 2 (with ammonium lignosulfonate) have moderate biocide activity and can be used as wood ecological preservatives.

### 3. Conclusions

The research has established the possibility of copolymerization the acrylic comonomers with reaction partners lignin derivatives ammonium, iron and iron and chromium lignosulfonates, in amount of 7%

Table 3  
*The results of the biological testing of the wood preservation agents proposed*

Type of sample	Degree of the attack	Note	Efficiency of the preservation According to STAS 8022/91
The wood reference sample	100% from the surface	4	
The wood samples treated with WP 1	35% from the surface	3	Moderate growth
The filter paper samples treated with WP 1	40% from the surface	2	Moderate growth
The wood samples treated with WP 2	20% from the surface	2	Slight growth
The filter paper samples treated with WP 2	25% from the surface	2	Slight growth
The wood samples treated with WP 3	10% from the surface	2	Slight growth
The filter paper samples treated with WP 3	15% from the surface	2	Slight growth
The wood samples treated with WP 4	3% from the surface	1	Trace of growth detected visually
The filter paper samples treated with WP 4	5% from the surface	1	Trace of growth detected visually

based on the total monomer content. The grafting of ammonium, iron and iron and chromium lignosulfonates onto the acrylic copolymers chains is certified by the FTIR spectra, where specific absorption bands for lignin derivatives are present.

The new ecomaterials based on acrylic copolymers and biomass waste lignosulfonates will assure a better preservation action than the chemical agents as such, because they also contain lignin derivatives with biocide activity [2]. The reutilization of these new wood preservation agents based on lignin derivatives will confer a better compatibility of chemical agents with the wood structure.

The choice of lignin is justified by its biocide activity in the system of natural bioprotection of plants against the attack of microorganisms. It can be also estimated that the presence of some metal cations could accentuate the bioprotective properties into the lignin-metal-copolymer system [3].

In response to the environmental concerns, our research is dedicated to the development of some new water based preservatives formulations, in order to enhance both, product performance and environmental aspects. The processes for chemical

reutilization of lignocellulosic materials offer opportunities to produce a new generation of high-performance, high quality products [6], [7].

As the age of oil seems to change to the age of biomass, some of the chemical modifications of lignocellulosic materials will become in the future important industrial processes for producing chemical and materials.

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