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**COMPOZITES ADHESIVES BASED ON SYNTHETIC AND
LIGNOCELLULOSIC MONOMERS**

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Abstract: *Important progress has been made nowadays in development of new composites engineering materials from renewable, large available lignocellulosic waste materials, as a more sustainable alternative to raw materials from fossil sources. Our research has been focused on synthesis and characterization of some new composites adhesives based on woody wastes fillers ammonium, aluminium and iron and chromium lignosulfonates, as partial substitutes for toxic synthetic monomers phenol and formaldehyde in synthesis of phenol-formaldehyde resins (matrix). The improvements achieved, by using the lignosulfonates, in the properties of the new composites resins phenol-formaldehyde-lignin derivatives consist on decrease in adhesive viscosity, better water resistance of finished boards, increasing of the pot life, resistance to biodegradation and low costs.*

Keywords: *recycling biomass waste, composites, lignosulfonates.*

1. INTRODUCTION

Lignocellulosic materials are important natural renewable resources. The processes for chemical reutilization of lignocellulosic materials offer opportunities to produce a new generation of high-performance, high quality products. As a natural product of biological origin, lignocellulosic materials are characterized by high degree of diversity and variability in their properties. Lignocellulosic materials contain natural polymers cellulose, hemicellulose and lignins which possess many active functional groups susceptible to reaction [1, 2]. Lignin, the most abundant organic polymer in the plant world, is a three dimensional aromatic polymer with a phenylpropane unit, and have in structure phenolic and alcoholic hydroxyl groups. Lignin has a complex and heterogeneous structure caused by variations in its composition, size, cross-linking and functional groups. This heterogeneity depends on the species of plant from which it is obtained, the pulping process used to separate it from cellulose, and the methods by which it is recovered from the pulping liquor [3, 4].

The presence of lignin as a waste product in pulp mills has made it an attractive raw material for adhesives. Lignin is insoluble in water, but during the technical sulphite pulping, lignin becomes soluble in water, due to the partial degradation and introduction of sulfonic groups [5,6].

At elevated temperatures, when lignosulfonate is treated with strong mineral acid, condensation reactions leading to diphenylmethanes and sulfones take place. Hydroxybenzyl alcohol groups, as well as sulfonic acid groups on the carbon alpha to the aromatic rings of the phenylpropane units of the random polymer, react with the aromatic nuclei of other phenylpropane units in the presence of the strong mineral acids. This reaction, leading to diphenylmethane, is of the same type as the formation of phenolic resins from phenol and formaldehyde. Lignin also reacts with formaldehyde and can be cross-linked by it, in the same manner of synthetic polyphenolic resins [7, 8, 9].

The production of phenol-formaldehyde (PF) resins has not undergone significant changes for decades. However, the oscillations in crude oil price have generated a great interest in development of alternatives to oil-derived binders. Thus, naturally occurring raw materials such as lignin and furfuryl alcohol offer interesting possibilities as substitutes for phenol. On the basis of its structure, lignin may be considered a type of phenolic condensate in the broadest sense of the term, making it logical to use it in the production of phenolic resins.

Moreover, the structural changes suffered by lignin during the pulping process can exert a great influence on its characteristics [10, 11, 12, 13]. Lignosulfonates represent a type of technical lignin whose utilization in polymer synthesis is still insufficiently developed. There are certain properties of lignosulfonates which make them a potential substitutes for phenol in phenol-formaldehyde resins. The most important is their macromolecular structure which allows a quick gelation process [14, 15]. Phenol-formaldehyde (PF) resins have been intensively studied to find economically and environmentally applicable natural raw materials as substituents of toxic and costly phenol and formaldehyde

Phenolic resins are considered an attractive area for commercial lignin applications because of its chemical reactivity. Lignin is available, less toxic and less expensive raw material than phenol. Due to the increase of phenol cost, research have been made to partially substitute monomer phenol with natural products, having phenolic hydroxyl groups such as lignin/lignosulfonates [16].

Our research has been focused on the obtaining of some new composites adhesives, based on metal complexed lignosulfonates (fillers), as partial substitutes for formaldehyde and phenol in the phenol-formaldehyde adhesives (the matrix of composites).

2. EXPERIMENTAL

2.1 Materials and Methods

Phenol (99%), 37% formaldehyde aqueous solution and sodium hydroxide (98%) were used. All the chemicals were supplied by Merck. The lignosulfonates were obtained by modifying ammonium lignosulfonate (LSNH₄) (from wood and paper industry) with different salts.

The aluminium lignosulfonate (LSAl) was obtained from ammonium lignosulfonate with AlCl₃ and the iron and chromium lignosulfonate (LSFe³⁺Cr) was obtained from ammonium lignosulfonate with Fe(NO₃)₃ and Na₂Cr₂O₇. The lignosulfonates were analysed conforming to the specific methodology for lignins [17, 18, 19].

In order to partially substitute the phenol and formaldehyde, ammonium, aluminum and iron and chromium lignosulfonates were used in the synthesis of the new composites adhesives phenol-formaldehyde resins. The metal complexed lignosulfonates have also been used as comonomers in the polycondensation reaction because they possess in their structure reactive functional groups: phenolic and alcoholic hydroxyl, carbonyl, carboxyl, sulfonic groups, as can be seen from the data in Table 1 and from the FT-IR spectra (Figure 1) performed with a FTIR- Spectrometer model BX II (Perkin Elmer, 2005).

Table 1. The physical-chemical characteristics of the lignosulfonates

Characteristic	LSNH ₄	LSAl	LSFeCr
pH- value	4.85	3.07	3.80
Solids, %	44.96	38.99	42,50
Density at 20 C, g/cm	1.0214	1.1400	1.1850
Viscosity at 20 C, cP	70.00	66.00	68.00
Ash, %	0.96	2.69	5.28
Cation, %	7.39	7.62	6.70 (Fe), 6.50 (Cr)
Functional groups:			
- OH phenolic, %	14.16	18.74	22.90
- OH alcoholic, %	13.74	16.50	19.40
- carbonyl, %	1.71	2.66	11.31
- carboxyl, %	0.60	0.72	3.93

The FTIR spectra of ammonium, aluminum and iron and chromium lignosulfonates show characteristic absorption bands for specific chemical functional groups, able to participate as comonomers to the polycondensation process of phenol-formaldehyde-lignosulfonates resins:

- 3039.71-3208.16 cm⁻¹ - absorption bands assigned to aliphatic and aromatic hydroxyl (-OH phenolic) groups from chemical monomer (phenol) and lignosulfonates
- 2359.77- 2363 cm⁻¹ intense aromatic C–H absorption bands from phenol and lignin structure
- 1630-1675 cm⁻¹ - absorption bands corresponding to aromatic carbonyl bonds (C=O) from lignosulfonate, which also can be involved in substitution of formaldehyde monome
- 1419.41-1507.43 cm⁻¹ - absorption bands specific for aromatic -CH₂- skeletal vibration and aromatic nuclei
- 1029.00 cm⁻¹ absorption bands specific to methoxy group (-OCH₃) from lignin and lignosulfonates

- 1109.79-1155.00 cm^{-1} - absorption bands assigned to aromatic methylene groups and to $-\text{SO}_3\text{H}$ groups from lignosulfonates

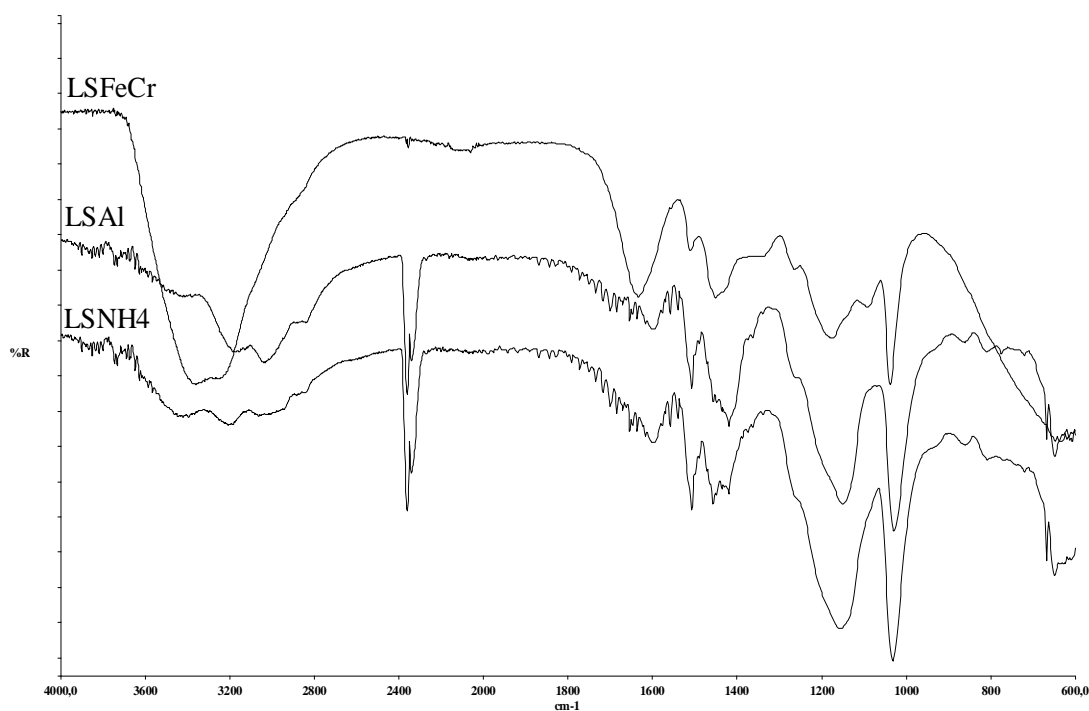


Figure. 1: The FTIR spectra of ammonium, aluminum and iron and chromium lignosulfonates

2.2 Synthesis of the composites based on phenol-formaldehyde adhesives with ammonium, aluminum and iron and chromium lignosulfonates

Phenolic resins were the first true synthetic polymers developed commercially, obtained by polycondensation of phenol with formaldehyde. The characteristic that renders these resins invaluable as adhesives is their ability to deliver, at relatively low cost, water, weather, and high-temperature resistance to the cured glue line of a joint bonded with phenolic adhesives [5,20].

Phenols condense initially with formaldehyde at pH either acid or alkaline, to form a methylol phenol or phenolic alcohol, and then, dimethylol phenol. The initial attack may be at 2-, 4-, or 6-position of the phenol molecules. The second stage of the reaction involves the reaction of the methylol groups with other phenol or methylol phenol, leading first to the formation of linear polymers and then to the formation of hard-cured, highly branched structures. Resols are obtained as a result of alkaline catalysis and an excess of formaldehyde. A resol molecule contains reactive methylol groups. Heating causes the reactive resol molecules to condense to form large molecules without the addition of a hardener [21].

A typical phenolic resin was made in a glass reactor equipped with a turbine-blade agitator, a reflux condenser and heating and cooling facilities. Molten phenol, formalin (37% formaldehyde) and water are charged into the reactor in molar proportions between: 1:1:1 under mechanical stirring.

Quantities of: 10%, 15%, 20% of ammonium, aluminium and iron and chromium lignosulfonates were also added to the mixture of above mentioned monomers.

To make a resol-type resin, such as used in wood adhesive manufacture, an alkaline catalyst, such as sodium hydroxide was added, and the reaction mixture was heated to 80-90 $^{\circ}\text{C}$ for about 2-3 hours. Since the resol can gels into the reactor, the temperature was kept below 100 $^{\circ}\text{C}$. Tests have to be done in order to determine first the degree of advancement of the resin, and second, when the batch should be discharged. Such tests consist on the measurements of the gel time/reactivity of the resin on a hot plate or at 100 $^{\circ}\text{C}$ in a water bath.

The resins are water soluble and of low molecular weight and are finished at a low temperature, usually around 40 $^{\circ}$ to 60 $^{\circ}\text{C}$. It is important that the liquid, water soluble resols, retain their ability to mix with water easily, since when they are used as wood adhesives they often require the addition of water to counterbalance the effect of the fillers added.

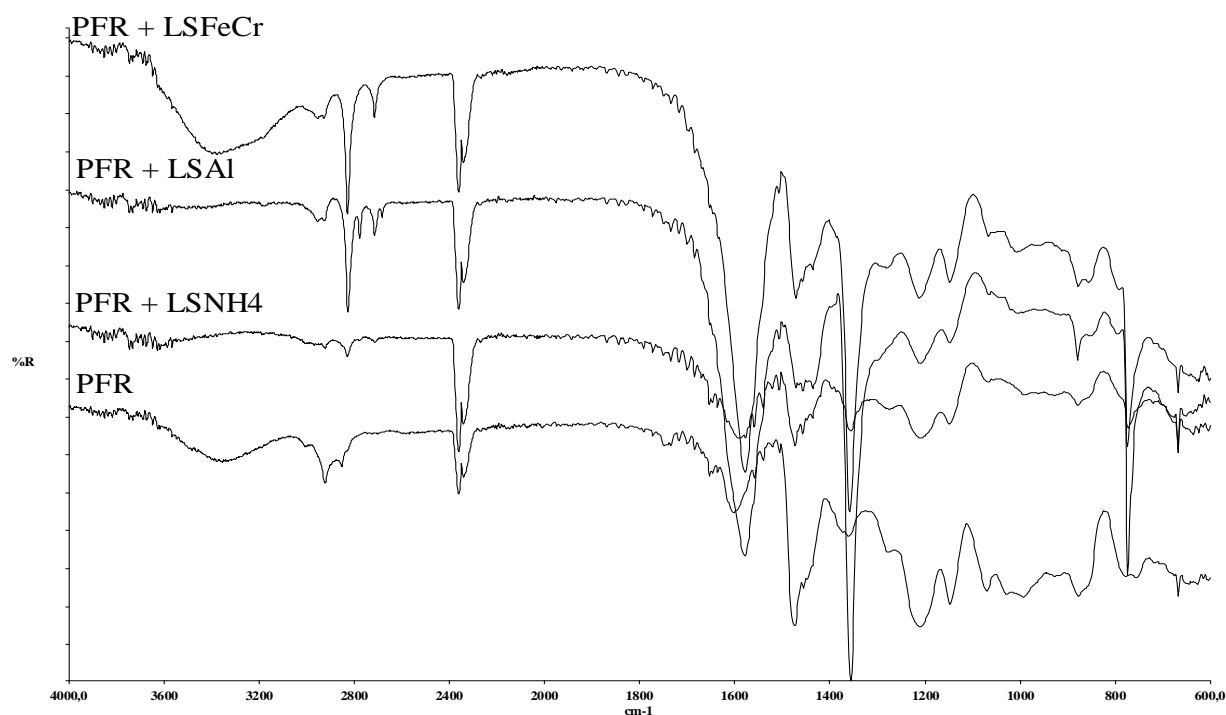
The characteristics of the new composites adhesives, based on phenol, formaldehyde (the matrix) and ammonium, aluminum and iron and chromium lignosulfonates (as fillers) are presented in Table 2.

Table 2. The characteristics of the new adhesives phenol-formaldehyde-lignosulfonates

Chemical characteristic	PF resin Standard	PF resin with LSNH ₄			PF resin with LSAI			PF resin with LSFeCr		
		10%	15%	20%	10%	15%	20%	10%	15%	20%
Aspect	White liquid	Brown liquid			Brown liquid			Brown liquid		
Density, g/cm ³	1.1700	1.13	1.16	1.19	1.10	1.15	1.20	1.15	1.18	1.20
Solids, %	45 – 50	47.0	48.0	49.0	48.3	49.0	50.0	48.5	49.5	50.0
PH-value	8 - 11	9.5	10.0	10.0	8.5	9.5	10.0	9.5	10.0	10.5
Viscosity, at 20 ^o C, cP	120 – 180	160	156	150	150	145	140	140	134	128
Miscibility with water	2 : 1	2:1	2:1	2:1	2:1	2:1	2:1	2:1	2:1	2:1
Gel time/Reactivity at 160 ^o C, s, max.	180	155	135	115	140	132	120	135	115	110

The new type of composites based on phenol-formaldehyde resin with lignosulfonates present similar physical and chemical characteristics comparing with the commercial phenol-formaldehyde resin. The improvements achieved by using the lignosulfonates as comonomers can be explained by the polyphenolic structure of lignin, respectively, the presence of carbonyl and phenolic hydroxyl groups which improve the polycondensation process. Better properties are obtained for the lignosulfonate-phenol-formaldehyde composites resins, consisting in decreased adhesive viscosity (which will insure better wettability of wood particles), better water resistance of finished boards, the decreasing of the reactivity, and the increasing of the pot life of these new composites adhesives. Due to the chemical structure richer in functional groups carbonyl and phenolic hydroxyl, the iron and chromium lignosulfonate presents an increased reactivity which conducted to superior lignosulfonate-phenol-formaldehyde resins.

The FT-IR spectra of the new ecological phenol-formaldehyde lignosulfonates composites resins (PFR) (Figure 2) were performed with a FTIR- Spectrometer model BX II (Perkin Elmer, 2005).

**Figure 2.** The FTIR spectra of the lignosulfonate-phenol-formaldehyde resins synthesized

The condensation reaction of phenol and formaldehyde with lignosulfonates is certified by characteristic absorption bands in FTIR spectra:

- The characteristic absorption bands of monomers formaldehyde (911 cm^{-1}) and phenol ($3039\text{--}3208\text{ cm}^{-1}$, 1578 cm^{-1} and 773 cm^{-1}) diminished with increasing the time of polycondensation reaction, while the absorbance bands of hydroxymethyl and methylene groups, characteristic for the new adhesives increased
- Absorption bands are registered at 1595.80 cm^{-1} and 1474.05 cm^{-1} corresponding to the C=C aromatic ring vibration
- The absorption band at 1070 cm^{-1} corresponds to single bond C-O stretching vibrations of $-\text{CH}_2\text{OH}$ groups formed in resins
- Absorption band at 1451 cm^{-1} indicates the presence of benzene ring obscured by $-\text{CH}_2-$ methylene bridge formed between chemical and lignosulfonates monomers
- In the phenol-formaldehyde resins spectra, additional characteristic signals of methylene bridge $-\text{CH}_2-$ at 1478 cm^{-1} and methylene-ether bridge C-O-C at 1116 cm^{-1} are present, certifying the reaction with lignosulfonates
- Absorption bands at 880 cm^{-1} and 762.62 cm^{-1} correspond to 1,2,4- substituted benzene ring, assigning the formation of 2,3,6-trihydroxymethylphenol, as precursor of the new adhesives [6, 7, 8, 9].
- Stretching vibration of aromatic lignosulfonates compounds can be seen in a wide absorption band at $1578.02 - 1586.36\text{ cm}^{-1}$ for all resins. The presence of these functional groups certify the polycondensation products of the reaction between phenol-lignin adduct and formaldehyde [10, 22].

3. CONCLUSION

Our research was focused on the synthesis of some new composites adhesives based on phenol-formaldehyde resins with ammonium, aluminium and iron and chromium lignosulfonates, as an ecological alternative to the existing production of commercial- phenol-formaldehyde resin.

Improved properties, respectively water resistance, decreasing of the gel time/reactivity and increasing of the pot life of the new ecological composites adhesives (especially with iron and chromium lignosulfonate) have been obtained.

The recycling of biomass wastes, lignosulfonates, had as benefits the lowering of costs, resulting from the difference in cost between chemical monomers and lignosulfonates and reducing the toxicity by partially replacing monomers phenol and formaldehyde with aqueous solutions of lignosulfonates, biomass raw materials renewed by photosynthesis.

In the future, taking into account both, the need for recycling biomass waste as chemical reactants for organic synthesis, and the environmental protection, it will be encouraging to use lignocellulosic materials to obtain ecological, low costs composites materials.

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