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**COMPOZITES ADHESIVES BASED ON UREA-FORMALDEHYDE RESINS AND
LIGNOCELLULOSIC WASTE**

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Abstract: *In order to develop a sustainable economy and due to increasing economic and environmental issues concerning the use of petrochemicals, lignocellulosic materials, as natural, abundant and renewable resources, will be extensively used in the future, as raw materials, for the production of chemicals, fuels and composite materials.*

Our research has been focused on synthesis and characterization of some new, ecological composite adhesives based on woody wastes fillers ammonium, calcium and iron lignosulfonates and Salix wood aqueous extract, as partial substituents for toxic, synthetic monomers urea and formaldehyde in the synthesis of urea-formaldehyde adhesives (matrix). The improvements achieved, by using the lignosulfonates and Salix wood extract, in the properties of the new composite adhesives urea-formaldehyde-lignosulfonate-Salix extract consist on decreasing of the gel time and the content on free formaldehyde, increasing the water resistance, the pot life, the resistance to biodegradation and low costs.

1. INTRODUCTION

The growing environmental pressure caused by the synthesis of petroleum based plastics have determined the development of new, biodegradable, environmentally friendly engineering materials [1, 2]. Biodegradable polymeric materials derived from natural, renewable sources such as proteins, poly carbohydrates (cellulose, hemicelluloses, starch), lipids etc., have been regarded as alternative ecological materials, and considered as very promising materials because their availability and cost effectiveness. [3,4]. The renewable, by photosynthesis, biomass has a great chemical potential for production of green chemicals for a sustainable economy. From the chemical point of view the lignocellulosic biomass consists of natural polymers: cellulose (50-55%), hemicelluloses (15-25%) and 20-30% lignin (20-30%), along with minor content of other organic and mineral secondary compounds. Cellulose, hemicelluloses and lignin are complex polymer structures rich in chemical functional groups, sensitive to reactions, such as alcoholic and phenolic hydroxyl groups, carboxyl, carbonyl, ether, ester groups, etc. [5, 6]. These functional groups can participate to chemical reactions of etherification, esterification, alkylation, salts formation, oxidation, polymerization, polycondensation, to produce new, ecological engineering materials, such as polymers, paints, green fuels, wood preservatives and adhesives, etc., [7, 8, 9, 10, 11]. The research in the field of recycling lignocellulosic waste to obtain new ecological, environmental friendly materials are in agreement with the sustainable development of society and environmental protection. Meantime, the production of new composites materials based on natural and synthetic polymers becomes an important way for reusing/recycling biomass/wood waste [12, 13, 14]. The major wood component lignin obtained as waste product in the paper industry is an attractive raw material for resin based adhesives. Native lignin is neither hygroscopic nor soluble in water, but, during the technical sulphite pulping of wood, lignin becomes soluble in water, due to the partial degradation and introduction of sulfonic groups [15]. The natural polymer lignin is composed of phenylpropane units linked together by carbon-to-carbon and carbon-to-oxygen ether bonds. When lignosulfonate is treated with strong mineral acid at elevated temperatures, condensation reactions leading to diphenylmethanes and sulfones take place. The reaction are 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. Urea-formaldehyde resins are the most used class of amino resins adhesives in wood industry. These copolymers present many advantages such as low water absorption, high tensile strength, hardness, non-inflammability and adaptability to a variety of curing conditions. They are widely

used for the production of wood-based composite panels, such as particleboards, fiberboards and plywood [16]. The greatest disadvantage of the amino resins is their bond deterioration, caused by water and moisture, due to the hydrolysis of the amino methylene bonds. Amino resins produced from urea are synthesized by polycondensation reaction, when urea is reacted with formaldehyde, to form the addition products, such as methylol compounds. By further reactions of water elimination, the formation of low-molecular-weight condensates (that are still soluble) is promoted. Higher-molecular-weight products (which are insoluble and infusible) are obtained by further condensing the low-molecular-weight condensates. The cured resin consists in both linear and branched polymers, as well as tridimensional networks [17, 18].

2. EXPERIMENTAL

2.1. Synthesis and characterization of urea-formaldehyde composite resins with ammonium, calcium, iron lignosulfonates and Salix wood aqueous extract

a. Analysis of ammonium, calcium and iron lignosulfonates and Salix wood extract

Our research has been focused on the obtaining of new composite adhesives, based on metal complexed lignosulfonates and Salix wood aqueous extract, as partial substituents for formaldehyde in the urea-formaldehyde adhesives. The calcium lignosulfonate (LSCa), from sulphite pulping), and iron (III) lignosulfonate (LSFe), obtained from the ammonium lignosulfonate and $\text{Fe NO}_3)_3$ were analysed conforming to specific methodology for lignin [5, 6]. The chemical characteristics of the ammonium, calcium and iron lignosulfonates are presented in the Table 1.

Table 1. Chemical characteristics of the metal complexed lignosulfonates.

Characteristic	Ammonium lignosulfonate	Calcium lignosulfonate	Iron lignosulfonate
Appearance	brown liquid	brown liquid	Brown liquid
pH- value	4.25	5.70	2.24
Solids, %	38.64	36.00	35.47
Density at 20 ⁰ C, g/cm ³	1.14	1.15	1.15
Viscosity at 20 ⁰ C, cP	66	70	68
Ash, %	1.09	2.75	2.57
Cation, %	7.10	5.50	4.71
Functional groups:			
- OH phenolic, %	14.16	11.22	16.06
- OH alcoholic, %	13.74	14.20	13.35
- carbonyl, %	1.71	1.35	9.35
- carboxyl, %	0.60	0.56	0.74

The Salix wood was provided by Salix Cluster Green Energy (Sf. Gheorghe, Romania). As lignocellulosic material, Salix aqueous extract has the same type of chemical functional groups as ammonium, calcium and iron lignosulfonates, present into the polymeric structures with the following characteristics: 49.50% cellulose, 18.40% hemicelluloses, 27.10% lignin.

b. Synthesis and characterization of urea-formaldehyde resins with ammonium, calcium and iron lignosulfonates and Salix aqueous extract

The reaction between urea and formaldehyde are two stages. The first is an alkaline condensation to form mono-, di-, and trimethylureas compounds. The second stage is the acid condensation of the methylolureas, first to soluble, and then to insoluble cross-linked resins.

At the alkaline pH, the reaction of urea and formaldehyde, at room temperature, leads to the formation of methylolureas compounds. At acid pH, the products precipitated from the aqueous solutions of urea and formaldehyde, or from methylolureas, are low-molecular-weight methyleneureas. Due to the methylol groups, the reaction is possible to continue, to harden the resin. Generally, an initial urea/formaldehyde molar ratio of 1:2.0 was used. Methylation was carried out by maintaining the mixture under reflux, at temperatures of 90-95 °C. The temperature raised after 10 to 30 minutes, when methylolureas compounds formed. The reaction was completed by decreasing the pH at 5.0 to initiate the polymer-building stage. As soon as the right viscosity was reached, the pH was increased to stop polymer building and the resin solution is cooled to about 25 °C. More second urea was added

to consume the excess of the formaldehyde, until the molar ratio of urea to formaldehyde was in the range of 1:1.1 to 1:1.7. The resin was left to react at 25⁰C for 24 hours. The excess of water was eliminated by vacuum distillation until a solid concentration of 65% is reached, and the pH was adjusted to achieve suitable storage life. The main strategy to reduce the formaldehyde emission of UF resins has been the change its formulation by decreasing the molar ratio of formaldehyde to urea. However, the reduction weakens the mechanical properties of particleboard and moreover it increases the time required for hardening under the action of current hardeners (latent acids) [14]. Hence it is necessary to optimize the synthesis of UF resins by changing the production process. In order to substitute the toxic monomer formaldehyde and to decrease both, formaldehyde emission and the gel time of the urea-formaldehyde adhesives, the quantities of 5%, 10% and 15% of ammonium, calcium and iron (III) lignosulfonates together with 5% Salix aqueous extract were used in the synthesis of the composite resins (see characteristics of the new composite adhesives in Table 2).

Table 2. Chemical characteristics of the urea-formaldehyde resin modified with ammonium, calcium, iron lignosulfonates and Salix wood extract

Chemical characteristic	UF resin Standard	UF resin with LSNH ₄			UF resin with LSCa			UF resin with LSFe		
		5%	10%	15%	5%	10%	15%	5%	10%	15%
Aspect	White liquid	Brown liquid			Brown liquid			Brown liquid		
Density, g/cm ³	1.28± 0.05	1.30	1.31	1.32	1.28	1.30	1.31	1.29	1.31	1.32
Solids,%	65 ± 0,2	64.8	65.0	65.4	65.0	65.3	65.5	64.6	65.2	65.3
PH-value	7,5 ± 0,5	7.6	7.6	7.6	7.6	7.7	7.8	7.6	7.5	7.5
Viscosity, Ford cup 4, s	16 – 60	15	17	18	16	17	19	17	18	20
Free CH ₂ O % ,max	0.90	0.60	0.56	0.50	0.70	0.68	0.62	0.55	0.50	0.47
Gel time, 100 ⁰ C, s	60	48	44	40	51	46	43	36	33	28

Where:

LSNH₄ = ammonium lignosulfonate

LSCa = calcium lignosulfonate

LSFe = iron (III) lignosulfonate

The chemical structure of the composites and the interface bonds between lignosulfonate, Salix wood extract and urea formaldehyde resin were outlined by recording their FTIR spectra with a spectrophotometer (Vertex V70, Bruker) used to record the reflectance spectra, in the 600 to 4500 cm⁻¹ range, after 16 scans, with 4 cm⁻¹ resolutions. In the Figure 1. are presented the FTIR spectra for the standard UF resin and for the UF resin modified with iron lignosulfonate and aqueous extract of Salix wood (UF+LSFe).

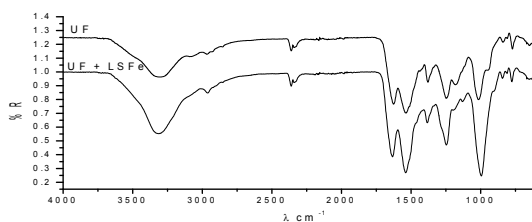


Figure: The FTIR spectra of the UF and UF+LSFe resins

In both spectra of UF and UF+LSFe resins, the broad absorption bands at 3300 cm⁻¹ can be attributed to the O-H functional groups of methylol urea, the absorption band at 2900 cm⁻¹ is assigned to the N-H functional group, the band at 1446 cm⁻¹ represent the functional group -CH₂ from methylene bridge and the band at 1086 cm⁻¹ was attributed to the functional group C-O-C of ether linkage [19, 20]. It can be seen that the FTIR spectra of standard UF resin and UF+LSFe composite resins present both two strong bands at 1500 and 1650cm⁻¹, which can be assigned to the formation of amide II and amide I compounds. Also, two more medium intensity bands at the 1150-1250cm⁻¹ attributed to the lignosulfonate chemical structure are present in the FTIR spectrum of UF+LSFe composite. The band at 1350cm⁻¹, correlated with the formation of methylol groups becomes more distinct and

decreases as methylol groups decrease due to the condensation reaction of UF resin with LSF_e and Salix aqueous extract. All the described basic structural peaks of UF also appear in the spectrum of the new UF + LSF_e composite resin, confirming the same basic chemical structure of these two amino resins. Meanwhile, the higher intensities of the peaks of the UF + LSF_e resin compared with those of the standard UE resin certified the formation of chemical interactions between UF and iron lignosulfonate to form UF + LSF_e composite resin.

It can be also seen that better properties (especially the gel time, and the content on free formaldehyde (CH₂O) for the new adhesives based on urea, formaldehyde, metal complexed lignosulfonates and Salix wood extract are obtained for the lignin derivative LSF_e with iron (III) cation as reaction partner. The gel time of urea-formaldehyde resins is essential to the establishment of effective processing parameters for applying these polymers in wood based-composites engineering. The main advantage of the new urea-formaldehyde-lignosulfonate-Salix extract resins composites is the lowering of the gel time, especially for UE resin with iron lignosulfonate and Salix extract.

Due to the content in lignin derivatives lignosulfonates and Salix wood extract, the new wood adhesives present resistance to water/weather and a lower emission of formaldehyde (the two principal disadvantages of the standard urea-formaldehyde resin).

3. CONCLUSIONS

Our research focused on the synthesis of some new composite adhesives based on urea-formaldehyde resins with lignin derivatives- ammonium, calcium and iron lignosulfonates and Salix wood aqueous extract, as ecological alternative to the existing production of commercial- urea-formaldehyde resins. The improved properties of the new composite adhesives, such as better water resistance, lower gel time and higher pot life were achieved by the contribution of the lignosulfonates and Salix extract in the polycondensation process. Due to their content on carbonyl groups, (especially for LSF_e (9.35%) and to their acidic pH (especially for LSF_e=2.24) the lignosulfonates and Salix aqueous extract actually participate as comonomers in the synthesis of the new urea-formaldehyde-lignosulfonate-Salix composite resins.

The reason for their application has to be seen also in the lowering of toxicity and costs, resulting from the difference in cost between monomer formaldehyde and the biomass waste lignosulfonates and Salix extract. Having in view the biocide activity of lignin it can be also expected an improvement of their resistance against the attack of the microorganisms.

The possibility of obtaining ecological, new type of wood adhesives based on lignin derivatives lignosulfonates and Salix extract presents a great interest in the future, taking into account the need for using lignocellulosic materials as non-polluting reactants for organic synthesis.

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