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COMPOSITES ACRYLIC COPOLYMERS –WOOD WASTE

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Abstract: *Wood is a three dimensional polymeric composite made primarily of cellulose, hemicelluloses and lignin. Various composite wood products are now obtained, which are preferred as engineering materials, because they are economical, low in processing energy, renewable, displaying superior mechanical properties, dimensional stability, greater resistance to chemical and biological degradation, and less moisture absorption.*
Our research was focused on synthesis and characterization of new composites materials based on acrylic copolymers and wood waste sawdust and calcium lignosulfonate.
Improved properties of the new composites are obtained as the result of complex interactions, by esterification and etherification reactions, between the hydroxyl groups of wood waste sawdust and calcium lignosulfonate and the ester, carboxyl and carboxylate functional groups from the acrylic copolymer (the matrix). The chemistry behind the interactions of acrylic copolymer with lignocellulosic waste sawdust and calcium lignosulfonate was demonstrated by FT-IR analysis and AFM.
The proposed new ecological composites materials are in agreement with nowadays research in the field of recycling wood waste to obtain new ecological materials used as coatings or landscape pavers.

1. INTRODUCTION

Wood has always been an important and versatile material with many uses because of its very aesthetically pleasing character. But wood has some drawbacks such as high moisture uptake, biodegradation, and physical and mechanical property change with environmental factors [1]. These negative inherent properties of wood can be minimized by appropriate chemical treatment such as the structural modification or formation of wood polymer composites [2].
Nowadays the production of composites based on lignocellulosic materials and synthetic polymers has become an important way for recovering, reusing and recycling biomass/wood waste [3].
Lignocellulosic materials contain lignocellulosic materials, important natural renewable resources, contain polymers cellulose, hemicelluloses and lignin, which possess many active functional groups susceptible to chemical reactions, such as: primary and secondary hydroxyls, carbonyls, carboxyls, esters, ether etc. Based on the variety of functional groups, etherification, esterification, alkylation, hydroxyalkylation, graft copolymerization, crosslinking and oxidation reactions have been conducted to different lignocellulosic materials to produce a series of products with many practical applications [3, 4, 5, 6].
The composite materials based mainly on natural polymer, e.g. natural rubber latex, cellulose and starch have a much lower undesirable impact on the environment since they are made from renewable resources. Sawdust and wood flour is the most common wood filler used in wood-plastic composites and other wood-alternative material composites has made major advances in material performance. It is typically a postindustrial source consisting of wood shavings, chips, and sawdust produced by secondary wood product [7, 8].
Sawdust, obtained from wood industry is an abundant by-product which is easily available in the countryside at negligible price. It contains various organic compounds (lignin, cellulose and hemicelluloses) with polyphenolic groups that could bind heavy metal ions through different mechanisms [9, 10]. The performance and stability of sawdust-reinforced composite materials depends on the development of coherent interfacial bonding between sawdust and matrix. The general components of sawdust are cellulose, hemicelluloses, lignin, pectin, waxes, and water-soluble substances [4], [5]. Cellulose, hemicelluloses, and lignin are the main components contributed the strength, flexural, and impact properties of the composites. Moreover the bonding between sawdust and the hydrophobic matrix has effected to the mechanical properties of the composite material [9, 6].

The aim of the present work was to synthesize and characterize new ecological composites materials based on acrylic copolymers (as matrix) and wood waste sawdust and calcium lignosulfonate (as fillers). The sawdust was mixed with calcium lignosulfonate then dispersed into the acrylic copolymer.

2. EXPERIMENTAL

There are several possibilities available when considering the synthesis of wood-polymers composites. Based on some previous experiences [10] we select to mix the aqueous dispersion of the experimental acrylic copolymer with 20% of sawdust and lignin derivative-calcium lignosulfonate (5% in CPa and 10% in CPb).

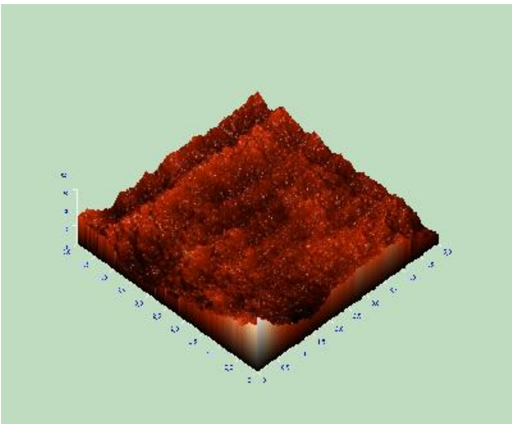
The matrix of the new composite materials consists on the water based dispersion of the acrylic copolymer obtained by copolymerization of acrylic monomers: ethyl acrylate, butyl acrylate, acrylonitrile and acrylic acid.

Calcium lignosulfonate, was obtained, as waste, from wod and paper industry and characterized in order to put into evidence its chemical reactive potential able to combine/react with natural and synthetic polymers or reagents. The complex analysis [11, 12] of the chemical structure of the calcium lignosulfonate put into evidence the presence of the functional groups: alcoholic hydroxyl (15.00 %), phenolic hydroxyl (14.75 %) carbonyl (10.50%) and carboxyl (11.25 %) in his structure [4]. The sawdust was provided by a furniture plant and has the following characteristics: 44.50% cellulose, 19.00% hemicelluloses, 27.15% lignin, 4.35% organic solvents extractives, 5.00% hot water extractives. The composites

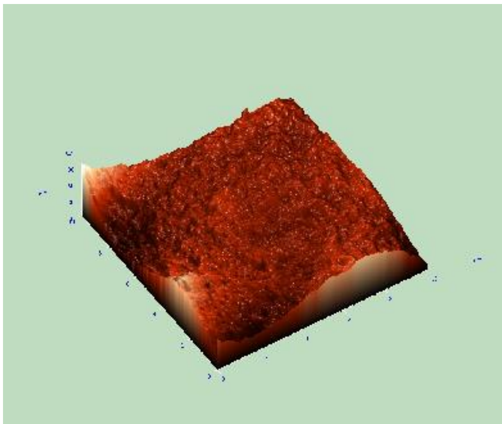
3. RESULTS AND DISCUSSIONS

The new synthesized composites based on acrylic copolymer (as matrix) and wood waste sawdust and calcium lignosulfonate (as fillers) were characterized as follows:

a. The morphology of the proposed composite materials was analysed with an AFM NT-MDT model BL 222 RNTE. The AFM images (Fig.1) detail the surface morphology showing a continuous and uniform distribution of wood waste sawdust and calcium lignosulfonate in the polymeric matrix. The acrylic copolymer –wood waste composites present a dense structure, able to assure good properties, having average roughness value 80.60 nm (CPa), respectively, average roughness value 91.20 nm (CPb).



a)



b)

Figure 1: AFM images of (a) composite CPa and (b) composite CPb

b. The interphase characterization of the composites synthesised was performed by FT-IR spectrometry with a spectrometer Spectrum BX Perkin Elmer, in reflectance mode, in the range of 500-4500 cm^{-1}, after four scans, with 4 cm^{-1} resolution.

The bonding process between the matrx - acrylic copolymer and fillers - sawdust and calcium lignosulfonate can be considered to develop mainly due to the presence of the hydroxyl groups in the structure of sawdust and calcium lignosulfonate which can participate to the esterification reaction with carboxyl groups from the acylic copolymer.

The FT-IR spectra (Fig. 2) performed on the surface of the composites CPa and CPb, confirm the interaction of the acylic copolymer segments with the sawdust and calcium lignosulfonate. Infrared absorption bands of acrylic copolymer, sawdust and lignosulfonate show specific peaks which explain the interactions between the composite matrix (acrylic copolymer) and wood waste fillers - sawdust and calcium lignosulfonate, as follows:

-The absorption bands corresponding to alcoholic hydroxyl (1020-1050 cm^{-1}) and to phenolic hydroxyl (1240-1265 $cm^{-}1$) are characteristic for lignocellulosic waste (sawdust and lignosulfonate);
-Absorption band at 1085 cm^{-1} was attributed to $–SO_3H$ group from calcium lignosulfonate bonded on the acylic copolymer structure;
-Absorption band at 1425 cm^{-1} is characteristic to methylene ($–CH_2-$) groups from lignin, respectively lignosulfonates and sawdust;
- Absorption bands at 1510-1600 cm^{-1} are characteristic to the aromatic nucleus from sawdust and lignosulfonate as lignin structure;
-Absorption band at 1580-1600 cm^{-1} is attributable to the aromatic nucleus from sawdust and lignosulfonate
-Absorption band located at 1724-1729 cm^{-1} is characteristic for carboxyl groups from carboxylic acids and esters, certifying the formation of esters by esterification of carboxyl groups present in the matrix of acrylic copolymer with hydroxyl groups from both fillers - sawdust and lignosulfonate.
-The absorption band at 2981-2958 cm^{-1} indicates the presence of metoxy group (- OCH_3) characteristic to lignin structure, respectively to sawdust and calcium lignosulfonate.

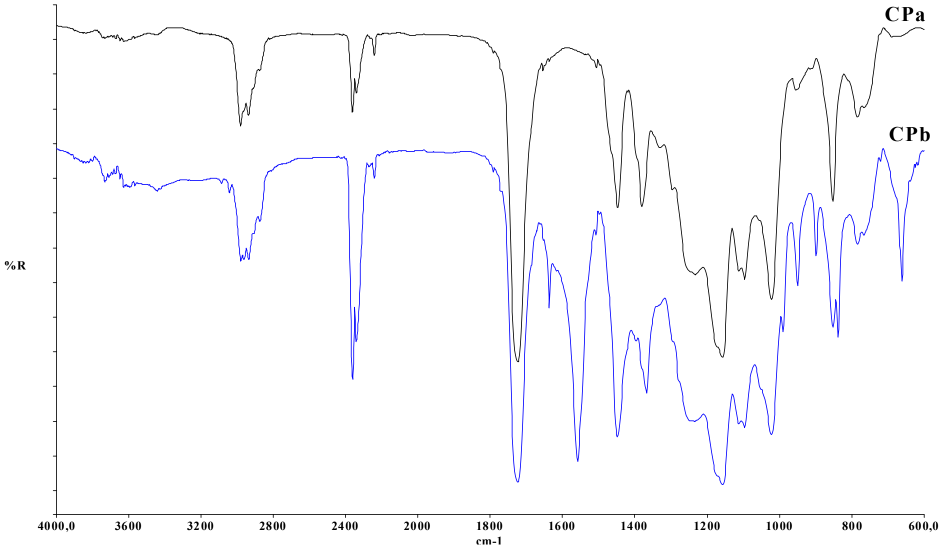


Figure 2: FTIR spectra of the acrylic copolymer-wood waste composites CPa and CPb

c. Investigation of biological durability of composites

Investigation of biological durability of composites wood-polymers is very important for outdoor applications. *The biocide activity investigation* have been performed (according to STAS 8022/91) in order to identify the composites resistance against biological attack of the microorganism from soil. Considering the biocide activity of acrylic copolymers [10] and of the component calcium lignosulfonate, the obtained composites were biologically investigated by insertion in soil for a period of 28 days. After testing, the samples were visually examined by optical microscopy in order to establish the attack level. The results of the biological testing are presented in the Table 1**.** The fungal growth was classified between 0 and 4, as following:

Table 1:. The results of the biological testing of the copolymer-wood waste composites

Treatment type	Degree of attack	Note	Preservation Efficiency
Wood reference sample	90% of surface	4	According to STAS 8022/91
Composite CPa	14% of surface	2	slight growth (good)
Composite CPb	9% of surface	2	slight growth (good)

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 total area;

3 - moderate growth or 20-50% coverage;
4 - plenty of growth or above 50% coverage.

d. Determination of the mass losses of composites
The mass losses of the composites after 28 days testing in soil was determined gravimetrically and releved that low mass losses were observed for both composites samples exposed to decay testing in soil, respectively 3.0% for composite CPa and 2.0% for composite CPb, comparing with 28% mass loss for pine sapwood control sample.

4. CONCLUSIONS

The research was focussed on synthesis and characterization of two new ecological composites based on an experimental acrylic copolymer as matrix with wood waste sawdust and calcium lignosulfonate, as fillers.
FTIR spectra show that the presence of the hydroxyl, carbonyl, carboxyl groups in the structure of both sawdust and calcium lignosulfonate represents anchoring points between the acrylic copolymer chains and lignocellulosic materials and explains the improved properties of the new composites acrylic copolymer-wood waste sawdust and calcium lignosulfonate.
The proposed composites materials submitted to the standard testing procedures for wood preservatives exhibited low moisture absorption and biocide activity against the microorganisms from soil. It was observed that increasing the proportion of calcium lignosulfonate increase also the biocide activity of composite CPb.

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