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ECOLOGICAL COMPOSITES BASED ON SYNTHETIC AND LIGNOCELLULOSIC POLYMERS

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Abstract: *The increasing generation of biomass waste imposes nowadays to identify new procedures to better manage the reusing/ recycling this waste in a sustainable way. The paper presents the research regarding the valorisation of Salix sawdust and ammonium lignosulfonate (as fillers) and an acrylic copolymer in water dispersion (as matrix) in* ***preparation*** *of composite materials. The new, ecological composites were structurally characterized (by FT-IR and AFM analysis) and from the biological resistance against the attack of microorganisms from soil.*

Key words: *acrylic copolymer, composites, lignosulfonate, Salix sawdust.*

1. Introduction

Taking into consideration the environmental protection and the availability of lignocellulosic biomass [13], [32], in present there is an increasing effort to replace petrochemical based products with bio-based compounds. The renewable, by photosynthesis, biomass may be considered a reservoir of raw materials for production of green chemicals, fuels or materials feedstocks, to asses a sustainable economy [1], [5]. The chemical structure of lignocellulosic materials consists of three natural organic polymers: cellulose, hemicelluloses and lignin. At molecular level these macromolecules have reactive chemical functional groups: alcoholic and phenolic hydroxyl, carboxyl, carbonyl, ether, ester groups etc. [7], [14], [31] which may be involved in complex chemical reactions with other natural or synthetic polymers: etherification, esterification, oxidation, salt formation, polymerization, polycondensation, to produce ecological products such as wood preservatives and adhesives, biodegradable plastics, paints, green fuels etc. [6], [9], [10], [18], [19]. Lignin, second renewable organic material after cellulose, produced yearly in large quantities (over 50 million tons) in the pulp and paper industry [25] presents a special interest for biorefining into high value-added products. Water soluble lignin derivatives lignosulfonates are generated from chemical sulphite pulping of wood. By treating wood with ammonium disulphite, lignin partially decomposes and forms ammonium lignosulfonate which can be mixed with hot aqueous solutions of salts to get other types of lignosulfonates [11], [12], [25]. In an advanced biorefining process, lignin and lignosulfonates have to be reused as such, or after chemical modification to improve their properties

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and reactivity, in order to be used as chemical reactants in different synthesis [5], [6], [8], [15], [23].

The production of cheap composites based on biomass waste and synthetic polymers, presenting good mechanical properties and improved resistance to chemical and biological degradation, offers new perspectives both, for recycling lignocellulosic waste and for obtaining ecological, new engineering materials [18], [26], [30].

In the literature are described many types of wood-polymers composites having as matrix synthetic polymers (PET, PVC etc.) or natural polymers (cellulose, starch, natural rubber etc.) [3], [4], [17], [24].

Interesting fillers are considered the biomass waste sawdust and wood flour produced in large quantities in wood industry and from cultivation of **fast** growing willow Salix (used for pellets fabrication and as adsorbents in wastewater treatment [20], [28], [29]. The lignocellulosic waste Salix wood flour and ammonium lignosulfonate have a similar chemical structure, rich in carbohydrates polymers cellulose and hemicelluloses (with alcoholic hydroxyl groups) and aromatic polymer lignin (with alcoholic and phenolic hydroxyl groups, carboxyl, carbonyl, sulfonic groups). These chemical groups may react with functional groups from natural or synthetic polymers to form composite materials [14], [31]. Comparing with synthetic composites, these new composites made from renewable biomass waste will be recyclable, green products, friendly for environment.

2. Experimental Part

For the preparation of the new composite materials there were selected, as matrix, an acrylic copolymer based on monomers of acrylic acid and his esters (ethyl acrylate, butyl acrylate, acrylonitrile) in water dispersion and as fillers Salix wood flour and ammonium lignosulfonate. The chemical analysis of Salix wood flour (Cluster Green Energy, Romania) identified the presence biomass components: 49.50% cellulose, 18.40% hemicelluloses, 27.10% lignin, 2.53% extractives. The structural analysis of the ammonium lignosulfonate put into evidence the presence of: alcoholic hydroxyl (14.40%), phenolic hydroxyl (15.20%) carbonyl (1.24%) and carboxyl (2.35%), capable to chemically react both with the functional groups from Salix wood flour and acrylic copolymer.

To obtain the new wood-polymer composites, the acrylic copolymer (the matrix) was mixed, at 20 ^{0}C, with fillers Salix wood flour and ammonium lignosulfonate.

The water from acrylic copolymer contribute to the esterification reaction with wood polymers [2].

The obtained composite materials are coded as follows:

a) Composite CPL based on acrylic copolymer and 10% ammonium lignosulfonate;

b) Composite CPLS based on acrylic copolymer, 10% ammonium lignosulfonate and 20% Salix wood flour.

3. Results and Discussion

The new composites based on acrylic copolymer (matrix) and fillers Salix wood flour and ammonium lignosulfonate were analyzed as follows:

A. The morphology of the obtained composite materials was determined by AFM analysis with AFM NT-MDT model BL 222 RNTE). The AFM images of the two composites are shown in Figures 1 and 2.

The surface morphology shows a uniform distribution of the fillers Salix wood flour and ammonium lignosulfonate into the polymeric matrix. The acrylic copolymer - wood waste composites present a dense structure, having average roughness values of 75.50 nm (CPL), respectively of 81.30 nm (CPLS).

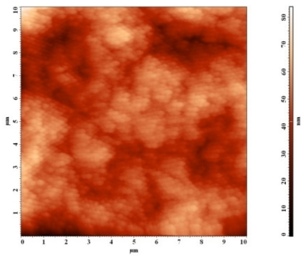

Fig. 1. *AFM analysis of the CPL thin film*

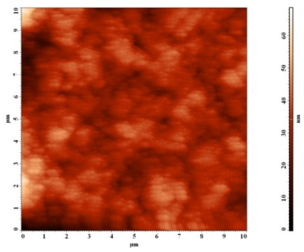

Fig. 2. *AFM analysis of the CPLS thin film*

B. The chemical structure of the composites and the interface bonds were outlined by recording their IR spectra [27]. Fourier Transform Infrared Spectroscopy (FT-IR) analysis using a spectrophotometer (Vertex V70, Bruker) was used to record the reflectance spectra, in the 600 to 4500 cm^{-1} range, after 16 scans, with 4 cm^{-1} resolutions.

The FT-IR spectra (Figure 3) performed on the composites CPL and CPLS, confirm the chemical interactions between the acrylic copolymer (matrix) and Salix wood flour and ammonium lignosulfonate (fillers), by esterification of carboxyl groups from acrylic copolymer with alcoholic and phenolic hydroxyl groups from Salix wood flour and ammonium lignosulfonate.

Comparing to the spectrum of CPL, in the spectrum of CPLS new absorption bands were evidenced, at 3606.06, 3738.44, 3850.44 cm^{-1}, due to the -OH stretching vibrations of free hydroxyl alcoholic and phenolic groups from Salix wood flour;

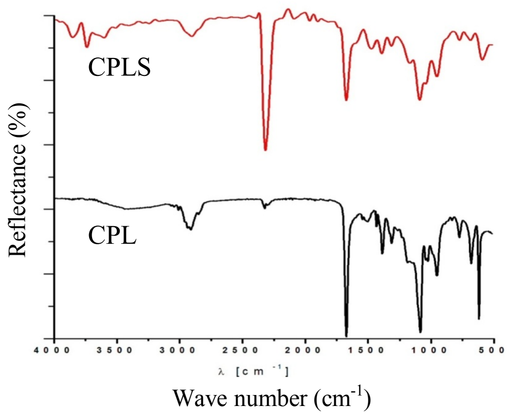

Fig. 3. *FT-IR spectra for CPL and CPLS*

Absorption bands at 1726.10 and 1726.73 cm^{-1} in FTIR spectra of the two composites indicate the C=O stretching from ester groups, certifying the esterification of carboxyl groups present in the matrix of acrylic copolymer with hydroxyl groups from Salix wood flour and lignosulfonate.

The bands from 1559.82 (in CPL) and 1532.70 (in CPLS) cm^{-1} correspond to C=C aromatic skeletal vibrations from lignosulfonate and sawdust;

The absorption band at 1237.56 cm^{-1} presented only in CPLS is attributed to hydroxyl phenolic groups formed as result of grafting the Salix wood flour components on the composite CPL based on acrylic copolymer and ammonium lignosulfonate.

The presence of lignosulfonate and Salix wood flour in the macromolecular matrix of acrylic copolymer is also evidenced by specific absorption bands at 1027.04 cm^{-1} (in CPL) and 1096.60 cm^{-1} (in CPLS) showing the presence of new chemical etheric bonds established between hydroxyl

The results of the biological testing of the composites CPL and CPLS Table 1

Treatment type	Degree of attack	Grading	Preservation Efficiency (SR EN 252:1995/AC1:2003)
Wood reference sample	75% of surface	4	plenty of growth
Composite CPL	18% of surface	2	slight growth
Composite CPLS	10% of surface	2	slight growth

groups from ammonium lignosulfonate and Salix wood flour;

The absorption band at 1237.56/2840-2921 cm^{-1} from CPLS correspond to the functional methoxy group –OCH_3) which can be transformed into a hydroxyl group through hydrolysis reactions of lignosulfonate and Salix wood flour [3], [21], [22];

The absorption bands from 766.60-900 cm^{-1} certify the presence of aromatic nuclei from ammonium lignosulfonate and Salix wood flour structures in both composites.

C. Investigation of the biological durability of composites wood waste - polymers is very important in outdoor applications. One of the most severe testing of wood products is the direct contact with the microorganisms from soil, because of permanent exposure to humidity and biological agents. The investigation of biocide activity has been performed according to *SR EN* ***2C1:2003***.

Having in view the biocide activity of acrylic copolymer and of the ammonium lignosulfonate [7] and Salix wood [16] the new composites were biologically investigated by insertion and maintaining of samples in soil for a period of 28 days. After testing, the samples were examined by optical microscopy in order to establish the attack level of microorganisms. The growth of the microorganisms 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.

The results of the biological testing are presented in the Table 1.

4. Conclusions

Two new ecological composites based on an acrylic copolymer in aqueous dispersion (as matrix) with wood waste Salix wood flour and ammonium lignosulfonate (as fillers) were prepared and tested.

FTIR spectra show that hydroxyl and carboxyl groups in the structure of both Salix wood flour and ammonium lignosulfonate were involved into esterification reactions, establishing linkage points between the matrix (acrylic copolymer) and fillers (lignocellulosic waste chains) put into evidence by the improved properties of the new composite acrylic copolymer - wood waste Salix flour and ammonium lignosulfonate.

The obtained composite materials present biocide activity against the microorganisms from soil and can be used as green, low cost paving materials.

Considering the large distribution, renewability and recyclability of biomass, these results are part of an ecological strategy for producing advanced composite materials that take advantage of the enhanced properties of all the waste materials embedded in the new products.

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