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ECOLOGICAL COMPOSITES BASED ON SYNTHETIC POLYMERS AND WOODY WASTE

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Abstract : *Nowadays, the increasing of quantities of biomass waste imposes the dentification of new, clean technologies in order to reusing these biodegradable waste in a sustainable manner. The paper presents the research on recycling the pine and acacia sawdust used as fillers dispersed in the matrix of an acrylic copolymer in water dispersion, to obtain composite materials. The new, ecological composites were characterized by FTIR , optical microscopy and as biocide activity.*

Keywords: pine, acacia, sawdust, acrylic copolymer, composites.

1. INTRODUCTION

In this century, considering the needs to protect the environment and the availability of lignocellulosic biomass ((200 billion tons produced yearly) there are increasing efforts to replace fossil-based industrial products with biomass-based products [1, 2].

As renewable (through photosynthesis) raw material, biomass has a great chemical potential for production of green fuels and chemicals,clean feedstocks able to ensure a sustainable economy [3,4]. Biomaterials lignocellulosic materials consist of three main natural polymers: cellulose, hemicelluloses and lignin, having structures rich in reactive chemical functional groups, such as hydroxyl groups, phenolic hydroxyl, carboxyl, carbonyl, ether, ester groups, etc. [5, 6, 7]. These functional groups are responsible for complex chemical reactions such as: etherification, esterification, alkylation, salts formation, oxidation, polymerization, polycondensation, enabling the production of ecological products with different practical applications, such as green fuels and paints, wood adhesives and biocide compounds, biodegradable plastics, etc.

The production of composite materials based on lignocellulosic materials and synthetic polymers has become nowadays an important way for recovering, reusing and recycling biomass/wood waste as ecological coatings, with aesthetic and biocide enhanced properties, wood preservation agents, medicines. For environmental protection, biomass resources, waste/wood waste can be recycled, as secondary raw materials, for obtaining a large types of ecological composite materials [8, 9, 10].

2. EXPERIMENTAL PART

For the synthesis of the new composite materials there were selected, as matrix, an acrylic copolymer based on monomers ethyl acrylate, butyl acrylate, styrene in water dispersion, and as fillers pine and acacia sawdust. The chemical analysis of fillers pine and acacia sawdust evidenced the presence of biochemical components: *cellulose* (pine -39.5.0%, acacia-425%), *hemicelluloses* (pine-24.3%, acacia-26.4%) and *lignin* (pine-30.6%, acacia- 27.3%). The chemical functional groups from these woody biomass waste (alcoholic hydroxyl (15.20%), phenolic hydroxyl (17.20%), carbonyl (2.23%) and carboxyl (5.35%), are able to chemically react, both with each other and with the functional groups carboxyl and ester from matrix acrylic copolymer.

To obtain the new woody-waste- polymer composites, the acrylic copolymer (the matrix) was mixed, at 20^0 C with fillers (pine and acacia sawdust). The obtained composite materials are coded (a) CP1- based on acrylic copolymer and 20% pine sawdust and (b) CP2 -based on acrylic copolymer, with 20% acacia sawdust.

3. RESULTS AND DISCUSSION

The new composites based on acrylic copolymer as matrix and the fillers pine and acacia sawdust were analyzed as follows:

A. ***The morphology* of the obtained composite materials** was determined by stereo microscopy with Stereo microscope OPTIKA SZM. The images of the two composites (CP1 and CP2) are shown in Figures 1 and 2. The surface morphology shows an uniform distribution of the fillers (pine and acacia sawdust) into the polymeric matrix.

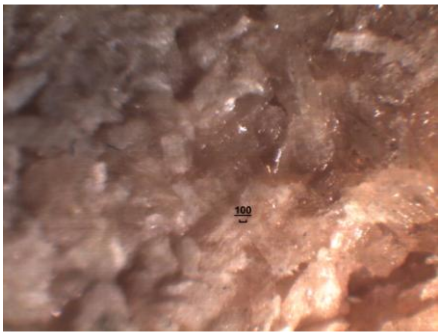

Figure 1: Image of CP1

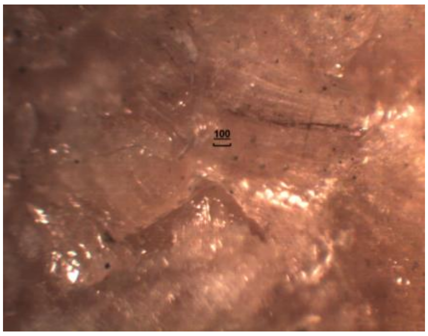

Figure 2: Image of CP2

***B. The chemical structure* of the composites** was outlined by recording their reflectance FTIR spectra using a spectrophotometer (Vertex V70, Bruker) to record the reflectance spectra, in the 600 to 4500 cm^{-1} range, after 16 scans, with 4 cm^{-1} resolutions.

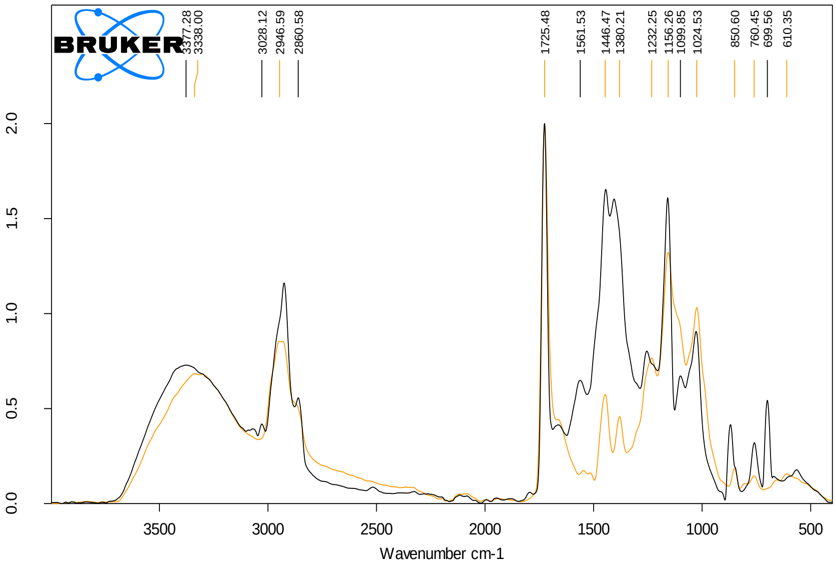

Figure 3: Reflectance FTIR Spectra of CP1 (yellow colour) and CP2 (black colour)

The FTIR spectra (Figure 3) performed on the composites CP1 and CP2, confirm the chemical interactions between the polymeric matrix (acrylic copolymer) and pine and acacia sawdust (fillers) by esterification of carboxyl groups from acrylic copolymer with alcoholic and phenolic hydroxyl groups from pine and acacia sawdust. The existing potential to esterification reaction is confirmed by peaks from 3028.12 cm^{-1} (-OH stretching vibrations of free hydroxyl alcoholic and phenolic chemical functional groups from pine and acacia sawdust. Peaks from 1725.48 cm^{-1} and from 1232.25 cm^{-1} indicate the C=O stretching vibrations from ester groups, certifying the esterification of carboxyl group specific to acrylic polymer with hydroxyl groups from pine and acacia sawdust.

The peaks at 15561.53 cm^{-1}, 850 cm^{-1}, 760.45 cm^{-1}, and 610.35 cm^{-1}correspond to C=C aromatic skeletal vibrations from pine and acacia sawdust. The peak at 1232. 25 cm^{-1} is attributed to hydroxyl phenolic groups formed as result of grafting the pine and acaia sawdust functional groups on the acrylic polymer. The presence of pine and acacia sawdust in the macromolecular matrix of acrylic copolymer is also evidenced by specific peaks at 1024. 53 cm^{-1}. 1099.85 cm^{-1} indicating the presence of new chemical etheric bonds established between hydroxyl groups from pine and acacia sawdust [2, 12].

C. Investigation of the biological durability of composites in soil (biocide activity)

The investigation of biological durability of the new composites acrylic polymer **-** wood wastes (pine and acacia sawdust) is very important in outdoor applications 11. 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 attack. The investigation of biocide activity has been performed according to *SR EN 2C1:2003* [11]. Having in view the biocide activity of acrylic copolymer and of the lignin from the fillers (pine and acacia sawdust) 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/above 50% coverage

Table 1. The results of the biological testing of the composites CP1 and CP2

Type of Sample	Degree of attack	Preservation Efficiency (SR EN 252:1995/AC1:2003)
Wood reference sample	55% of surface plenty of growth	4
Composite CP1	16% of surface, slight growth	2
Composite CP2	growth detected visually	1

4. CONCLUSIONS

Two new ecological composites based on an acrylic copolymer in aqueous dispersion (as matrix) with woody wastes pine and acacia sawdust (as fillers) were synthesized and characterized. FTIR spectra show hydroxyl and carboxyl groups in the structure of pine and acacia sawdust as anchoring points in the esterification reaction between the carboxyl groups from acrylic copolymer chains and the chemical functional groups (alcoholic hydroxyl and phenolic hydroxyl from lignocellulosic sawdust waste. The obtained composite materials present biocide activity against the microorganisms from soil and can be used as green, low cost paving materials. Taking into consideration the sustainable development and the large quantities of woody waste, the renewability and recyclability of biomass and biomass waste these results will contribute to the development of an ecological strategy in order to replace fossil-based industrial products with ecological, biomass-based products [1, 13].

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