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# COMPOSITES BASED ON SYNTHETIC POLYMERS AND WOOD WASTE

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***Abstract***

*The paper presents the results of the research dedicated to synthesis and characterization of some new, ecological composite materials based on an acrylic copolymer, lignin derivative iron and chromium lignosulfonate and Salix wood sawdust. The FT-IR analysis put into evidence the complex interactions, by esterification and etherification reactions, between the organic functional hydroxyl groups of lignosulfonate and Salix sawdust (the fillers) with the organic functional groups (carboxyl, ester) from the structure of acrylic copolymer (the matrix) and explain the improved properties of the new composites. The proposed new composites are in agreement with the research in the field of recycling lignocellulosic waste to obtain new ecological, environmental friendly materials.*

***Key words:*** *acrylic copolymer; iron and chromium lignosulfonate; Salix sawdust; composites.*

## INTRODUCTION

The Council of the European Union proposes, in 2007 as target, a contribution of 20% of biomass in the energy production. Nowadays, due to the fossil fuels depletion, new composite materials based on woody biomass are obtained and used because they are renewable, low cost and present dimensional stability and good resistance to chemical and biological degradation.

The deficit of wood as industrial raw material could be supplied by using both, lignocellulosic biomass /woody biomass waste and perennial plants such as Salix with short vegetation period (Doczekalska et al. 2010; Wroblewska et al. 2009). Woody biomass, as lignocellulosic materials, important natural renewable resources, contain polymers cellulose, hemicelluloses and lignin, which possess many active organic functional groups susceptible to chemical reactions, such as: primary and secondary hydroxyl, carbonyl, carboxyl, ester, ether etc (Hon 1996). Based on this 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 interesting products with many practical applications (Zakis 1994; Dumitrescu 1999; Crestini et al. 2010; Derek 2008). 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 (Bodarlau et al. 2009; Dumitrescu et al. 2009). Wood is one of the oldest construction material with many uses due to its complex chemical structure and excellent properties which also present as disadvantages in use the changing of physical and mechanical properties with environmental factors and biodegradability (Hill 2006)**.** Nowadays, these drawbacks can be minimized by both structural modification of wood and synthesis of wood polymer composites (Kamdem et al. 2002; Dumitrescu et al. 2012).

The matrix of these new wood-plastic composite materials are based mainly on natural polymers (natural rubber latex, cellulose, starch) or synthetic polymers (PET, PVC, PE etc.). Wood waste as shavings, chips, sawdust and wood flour are the most common wood fillers used in wood-plastic composites and other wood-alternative material composites (Winandy et al. 2004; Wang et al. 2011). The composites based on natural and synthetic polymers have a lower undesirable impact on the environment since they are made from renewable resources (Prompunjai et al. 2010).

Especially fast growing biomass species, like willows species such Salix Viminalis, have been intensively cultivated because they produce high biomass yields and are metal tolerant species, useful as ecological adsorbents in wastewater treatment (Szafranek et al. 2008; Zupancic, 2010; Mleczek et al. 2010; Robinson et al. 2015).

Sawdust is a low cost, abundant by-product obtained from wood industry. It contains various organic compounds (lignin, cellulose and hemicelluloses) with polyphenolic groups that could bind heavy metal ions through different mechanisms (Li et al. 2007). The performance and stability of sawdust-reinforced composite materials depends on the development of coherent interfacial bonding between the filler sawdust and matrix. The chemical components of sawdust are cellulose, hemicelluloses, lignin, pectin, waxes, and water-soluble substances (Mosadeghzada 2009; Kord 2011). Cellulose, hemicelluloses, and lignin are the main components contributed to the strength, flexural, and impact properties of the composites. The bonding process between sawdust and the hydrophobic matrix improves the mechanical properties of the composite material (Wang 2004).

The combination between synthetic copolymers and natural polymers (lignin derivatives lignosulfonates) also can improve the performances of the composite materials, especially the biocide properties (Kamel *et al*. 2007; Manciulea et al. 2007; Vermerris, 2013).

## OBJECTIVE

The main objective of the present work was to synthesize and characterize new ecological composite materials based on synthetic, acrylic copolymers in water dispersion (as matrix) and natural polymers represented by wood waste Salix sawdust and iron (II) and chromium lignosulfonate (as fillers).

## MATERIAL, METHOD, EQUIPMENT

Like any other lignocellulosic materials, Salix sawdust and iron and chromium lignosulfonate contain a significant amount of natural polymers cellulose, hemicelluloses, and lignin and consequently, the same type of chemical functional groups (alcoholic and phenolic hydroxyl, carboxyl, carbonyl) able to chemically react with acrylic copolymers in water dispersion.

*The Salix sawdust***,** provided by Salix Cluster Green Energy (Sf. Gheorghe, Romania) is structurally composed of: 46.50% cellulose, 25.10% lignin 19.20% hemicelluloses, 5.50% organic solvents extractives, 4.20% hot water extractives.

*Iron (II) and chromium lignosulfonate* (aqueous solution 45%) was obtained by reacting ammonium lignosulfonate (from sulphite pulping process) with iron (II) nitrate and sodium dichromate ($Na_2Cr_2O_7$). He was analysed conforming to specific methodology for lignin (Zakis, 1994) and presents in his structure the functional groups: alcoholic hydroxyl (15.02%), phenolic hydroxyl (21.73%) carbonyl (9.38%) and carboxyl (1.00%) (Dumitrescu 1999).

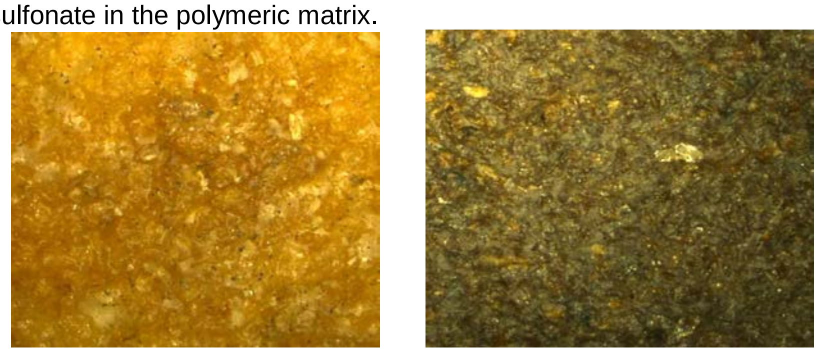
From the several possibilities to synthesize wood-polymer composites (Wang et al. 2011; Muller et al. 2009) and based on some previous experiences (Dumitrescu et al. 2012) we select to mix, at ambient temperature, the aqueous dispersion of an acrylic copolymer (the matrix, obtained by copolymerization in aqueous dispersion of acrylic monomers ethyl acrylate, butyl acrylate and acrylic acid) with the fillers iron (II) and chromium lignosulfonate and Salix sawdust. The obtained composite materials are:

- Composite C1 based on acrylic copolymer and 10% iron and chromium lignosulfonate and 10% Salix sawdust;
- Composite C2 based on acrylic copolymer, 20% iron and chromium lignosulfonate and 20% Salix sawdust.

## RESULTS AND DISCUSSION

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

**a. The morphology** of the proposed composite materials was analyzed with a digital microscope Keyence VHX-600 type, with objective magnification of 500x. Fig. 1 (a and b) details the surface morphology showing a continuous and uniform distribution of Salix wood waste sawdust and iron and chromium lignosulfonate in the polymeric matrix.



*(a)* *(b)*

***Fig. 1.***

***Microscope images of (a) composite CP1 and (b) composite CP2***

**b. The interphase characterization** of the composites **synthesized** was performed by FT-IR spectrometry with a spectrometer Spectrum BX Perkin Elmer, in reflectance mode, in the range of 500-4500cm$^{-1}$, after four scans, with 4cm$^{-1}$ resolution. The bonding process between the matrix (acrylic copolymer) and fillers (sawdust and iron and chromium lignosulfonate) can be considered to develop mainly due to the presence of the hydroxyl groups (alcoholic an phenolic) from the structure of sawdust and iron and chromium lignosulfonate able to participate to the esterification reactions with carboxyl/carbpxylate groups from the acrylic copolymer. The FT-IR spectra (Fig. 2) performed on the surface of the composites CP1 and CP2, confirm the interaction of the acrylic copolymer segments with the sawdust and iron and chromium lignosulfonate. Infrared absorption bands of acrylic copolymer, sawdust and lignosulfonate show specific peaks which explain the interactions established between the composite matrix (acrylic copolymer) and wood waste fillers – Salix sawdust and iron and chromium lignosulfonate, as follows:

- The absorption bands from 628 - 820cm$^{-1}$ certify the presence of aromatic nuclei from lignosulfonate and sawdust structures in both composites.
- The presence of lignosulfonate and sawdust in the macromolecular matrix of acrylic copolymer is evidenced by specific absorption bands at 1020cm$^{-1}$ (in C1) and 1080cm$^{-1}$ (in C2) showing the presence of new chemical etheric bonds established between hydroxyl groups from lignosulfonate and sawdust.
- The absorption bands corresponding to alcoholic hydroxyl (1150 - 1170cm$^{-1}$) and to phenolic hydroxyl (1240 - 1265cm$^{-1}$) are characteristic for lignocellulosic waste (Salix sawdust and iron chromium lignosulfonate and assure the posibility of chemically bonding the natural polymers with synthetic acrylic copolymer.
- Absorption bands at 1100 - 1080cm$^{-1}$ was attributed to $–SO_3H$ group from iron and chromium lignosulfonate bonded on the macromolecules of natural polymers.
- Absorption bands at 1480 - 1450cm$^{-1}$ are characteristic both, to hydroxil (-OH) from carboxyl functional group from acrylic copolymer, lignosulfonate and sawdust and to methylene ($–CH_2$-) groups from aromatic nuclei from lignosulfonate and sawdust.
- Absorption bands at 1510 - 1600cm$^{-1}$ are characteristic to the aromatic nuclei from sawdust and lignosulfonate as lignin structure.
- Absorption bands located at 1770 - 1775cm$^{-1}$ are characteristic for carbonyl (>C=O) groups from carboxylic acids and esters, certifying the formation of esters between carboxyl groups present in the matrix of acrylic copolymer and hydroxyl groups from both fillers - sawdust and iron and chromium lignosulfonate.
- The absorption bands at 2970 - 2920cm$^{-1}$ indicate the presence of metoxy group ($-OCH_3$) characteristic to lignin structure, respectively to sawdust and iron and chromium lignosulfonate. Metoxy groups can be transformed into new phenolic hydroxyl group through hydrolysis reactions of natural polymers Salix sawdust and lignosulfonate, able to be anchored on the macromolecules of acrylic copolymer through esterification reactions.

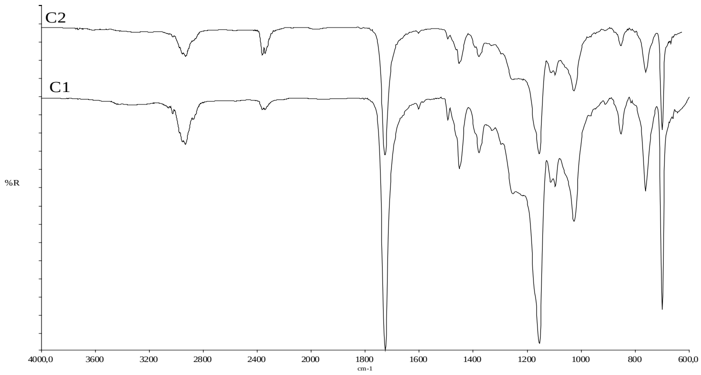



***Fig. 2.***
***FTIR spectra of the composites C1 and C2***

**c. Investigation of biological durability of the composites**

Investigation of biological durability of the new composites wood waste-polymers is very important for outdoor applications. The investigation of the biocide activity have been performed (according to SR EN 252:1995/AC1:2003 in order to put in evidence the resistance of the composites against biological attack of the microorganisms from soil. Considering the biocide activity of acrylic copolymers and of the component iron and chromium 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 degree of resistance to microbial attack. The results of the biological testing are presented in the Table 1**.** 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.

***Table 1***

***The results of the biological testing of the acrylic copolymer-wood waste composites***

| Treatment type | Degree of attack | Grading | Preservation Efficiency (SR EN 252:1995/AC1:2003) |
|---|---|---|---|
| Wood reference sample | 85% of surface | 4 | plenty of growth |
| Composite C1 | 10% of surface | 2 | slight growth |
| Composite C2 | 8% of surface | 2 | slight growth |

**d. Determination of the water absorption of the wood waste-polymer composites**

Analysis of the water absorption in wood - plastic composites is very important in order to develop solutions to decrease the water absorption, enabling new applications of this type of composite materials. Water uptake tests were carried out according to ASTM D-7031-04 specification. Five specimens of each composites were selected and dried in an oven for 24 hours at 102±3°C. The weight of dried specimen was measured to a precision of 0.001g. The specimens were then placed in distilled water and kept at room temperature. For each measurement, specimens were removed from the water and the surface water was wiped off using blotting paper. Weight of the specimens was measured after 1, 2, 3, 4, 5, 6, 7 days. The values of the water absorption in percentage (presented in Fig. 3) were calculated using the following equation (1):

$$WA(t) = \frac{W(t) - W_0}{W_0} x\,100 \quad (1)$$

where: WA(t) is the water absorption at time t, $W_o$ is the initial weight and W(t) is the weight of specimen at a given immersion time t.

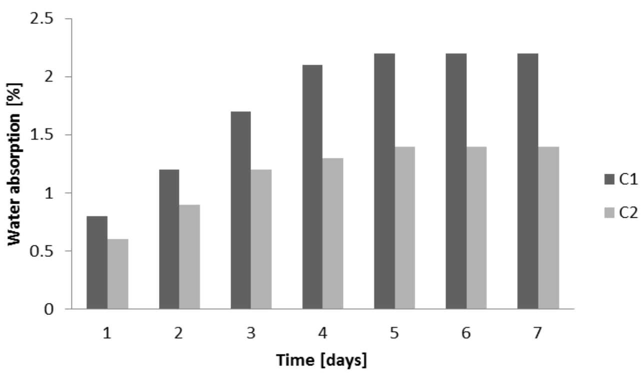



***Fig. 3.***
***Water absorption of the composites C1 and C2***

## CONCLUSIONS

The research was focussed on synthesis and characterization of two new ecological composites based on an experimental acrylic copolymer, in water dispersion, as matrix, with Salix wood sawdust and iron and chromium lignosulfonate, as fillers.

FTIR spectra show that the hydroxyl, carbonyl, carboxyl functional groups in the structure of both Salix sawdust and iron and chromium lignosulfonate are anchoring points between the acrylic copolymer chains and lignocellulosic waste materials. The proposed composites materials were submitted to some standard testing procedures for polymer-wood composites (water absorption and biocide activity). The low levels of moisture sorption in the composites based on acrylic copolymers and wood waste iron and chromium lignosulfonate and Salix sawdust suggests that decay of these materials will be retarded. The biological investigation of the two composites by insertion in soil for a period of 28 days reveals a good biocide activity mainly for the composite C2 with increased proportion of the fillers Salix sawdust and iron and chromium lignosulfonate.

This behavior can also be correlated, by FT-IR analysis, with the reduction of water sensitive hydroxyl groups from the chemical components of fillers wood waste (cellulose, hemicelluloses and lignin) by implication in esterification and etherification reactions with the matrix of the acrylic copolymer. The research enables the development of new applications of wood-polymer composites with economical and ecological advantages for the polymers based engineering materials.

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