



**The 40<sup>th</sup> International Conference on  
Mechanics of Solids, Acoustics and Vibrations &  
The 6th International Conference on  
“Advanced Composite Materials Engineering”  
ICMSAV2016& COMAT2016  
Brasov, ROMANIA, 24-25 November 2016**

## **RECYCLING WOOD WASTE TO OBTAIN ECOLOGICAL COMPOSITES**

**Lucia Dumitrescu<sup>1</sup>**

<sup>1</sup> Transilvania University of Brasov, Research Centre Renewable Energy Systems and Recycling, Brasov, ROMANIA, lucia.d@unitbv.ro

**Abstract:** *New composite ecomaterials with biocide activity were synthesized by emulsion copolymerization of acrylic monomers (ethyl acrylate, butyl acrylate, acrylic acid) with pine and acacia bark extracts, as partial substitutes for acrylic monomers. Having in view the biocide activity both, for acrylic monomers and wood waste, the obtained composites were biologically tested and proposed as new wood ecological preservation agents.*

**Keywords:** *acrylic copolymer, bark, extracts, copolymerization, wood preservatives.*

### **1. INTRODUCTION**

Wood is among the most extensively used engineering materials, because it is renewable by photosynthesis and requires low processing costs and energy. Wood has many excellent properties that result from combination of microstructural, ultrastructural and molecular features. The main drawback is its dimensional instability in the presence of moisture, which can affect also the biological stability. Wood is a composite material formed of polymeric principal constituents cellulose, hemicelluloses and lignin, with low percentages of secondary constituents (tannins, terpenoids, starch, lipids, alkaloids, proteins, etc.). The three principal constituents make up cell walls and are responsible for most of the physical and chemical properties of wood, [1, 2]. Wood is a material susceptible to degradation by decay, insect attack, fire and weathering. Because each of these forms of degradation is essentially chemical, it can potentially be inhibited by chemical means. Wood preservation is a complex process involving a wide range of physical, chemical and biological factors, demanding much from the chemicals selected for this purpose [3]. The chemicals should react quickly with hydroxyl groups (from wood chemical structure) yielding stable chemical bonds, with no byproducts, and the modified wood must still possess the desirable properties of untreated wood. Chemicals that have been used to modify wood include anhydrides, acid chlorides, carboxylic acids, isocyanates, aldehydes, alkyl chlorides, lactones, nitriles, and epoxides. Reaction of these chemicals with wood yields a modified wood with good biological resistance and greatly improved dimensional stability. The reaction takes place in the cell wall as evidenced by increases in wood volume in proportion to the volume of chemical added, leach resistance, and infrared data. Studies on the distribution of bonded chemical show good penetration into cell wall structure. The lignin component is highly substituted while lesser amounts of bonded chemical are in the carbohydrate components [4].

Nowadays, as an alternative to the protection of wood with toxic chemicals that inhibit the activity of microorganisms, research into chemically modifying the wood substrate, in order to prevent deterioration is an important area of study. Due to the chemical modification of some polymeric components of the wood structure (cellulose, hemicelluloses, lignin), the biocatalysts enzymes will be unable to degrade them, leaving unchanged the physical and engineering properties of the wood [3, 4, 5, 6].

Based on the variety of functional groups present in cellulose, hemicelluloses and lignin (hydroxyls, methoxy, carbonyl, carboxyl etc), reactions of etherification, esterification, alkylation, hydroxyalkylation, graft copolymerization, crosslinking and oxidation can be conducted to modify the wood structure for producing eco materials with good biological resistance and improved dimensional stability, with many practical applications [3, 4, 5, 7]. The production of the **composites** 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, [8, 9, 10, 11,12].

For environmental protection and better use of biomass resources, waste/wood waste can be recycled, as secondary raw materials, for obtaining a large types of ecological composites. Previous research revealed that

film-forming composite materials, with biocide properties, used in wood finishing/bioprotection can be obtained, by reacting or mixing acrylic copolymers/monomers with different wood waste [4, 6, 9 11, 13, 14, 15.

## 2. EXPERIMENTAL

Taking into account the aspects regarding wood structure and properties, as well as the environmental protection by biorefinery lignocellulosic materials, our research were dedicated to synthesize new composites based on acrylic copolymers with extracts obtained from the bark of pine and acacia trees. The water extracts obtained from the bark of pine and acacia trees have also been used as reactive comonomers in emulsion copolymerization of acrylic monomers because they possess a reactive chemical potential, caused by the presence in their structure of lignin, cellulose and hemicelluloses having functional groups: phenolic and alcoholic hydroxyl, carbonyl, carboxyl etc [5, 13]. The chemical characteristics of the pine and acacia bark extracts used in the synthesis are presented in Table 1.

**Table 1.** The chemical characteristics of the pine and acacia bark extracts

Characteristic	Pine bark extract	Acacia bark extract
Appearance	4.50	4.80
pH- value	40.63	39.20
Solids, %	1.1250	1.1505
Density at 20 <sup>0</sup> C, g/cm <sup>3</sup>	70.50	68.70
Viscosity at 20 <sup>0</sup> C, cP	35.65	32.80
Cellulose, %	34.80	31.75
Lignin, %	15.55	14.25
Hemicelluloses	4.50	4.80

Both the acrylic copolymers and the copolymers modified with 15% pine/acacia bark extracts have been obtained using a semicontinuous technique of emulsion copolymerization, conforming the following standard recipe:

**Monomer composition:** - ethyl acrylate, acrylonitrile, butyl acrylate, acrylic acid and pine/ acacia bark extracts

**Emulsifying system:** - ionic and nonionic emulsifier

**Initiation system:** - sodium persulphate

**Dispersion medium:** - distilled water

Percentages of 15% from the acrylic comonomers have been substituted with pine and acacia bark extracts.

The acrylic monomers emulsion, with or without bark extracts, was dozed by a constant ratio, at 80<sup>0</sup> C, for 3 hours into the copolymerization autoclave. At the end of the process, the inner temperature was raised at 90<sup>0</sup> C and kept for an hour, in order to finish the copolymerization. The chemical characteristics of the new composite materials based on acrylic copolymers and tree bark extracts are presented in Table 2.

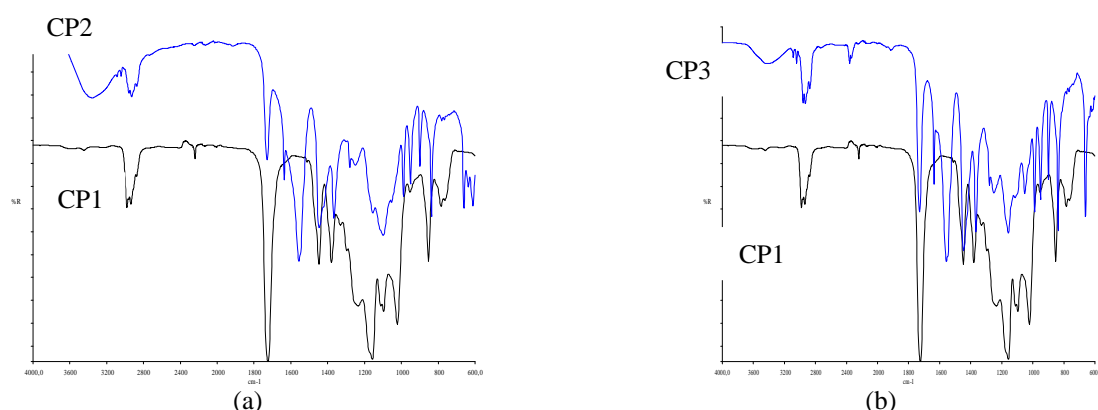
## 3. RESULTS AND DISCUSSIONS

From the data presented in Table 2 it can be observed that the composite CP2 based on acrylic copolymer and pine tree extract present better tensile breaking strength and lower water absorption of the film, comparing with composite CP3 based on acrylic copolymer with acacia tree extract and acrylic copolymer CP1 as such. This can be correlated with the higher content in lignin and cellulose of the pine extract involved in esterification reactions with acrylic copolymer.

**Table 2.** The chemical characteristics of the new composites based on acrylic copolymers and tree bark extracts

Copolymer	Viscosity at 20 <sup>0</sup> C cP	Tensile breaking strength MPa	Water absorption of the film %	
			24h	48h
CP1	36.5	2.5	17.4	37.5
CP2	38.0	3.0	15.5	35.0
CP3	41.8	3.4	14.5	30.6

The structure of the obtained composites based on acrylic copolymer as such (CP, black colour1) and with pine (CP2, blue colour) and acacia (CP3blu colour) bark extracts copolymers was also investigated by FT-IR analysis see (Figure 1).



**Figure 1:** FT-IR Spectra of CP1 with CP2 (a) and CP1 with CP3 (b)

The reaction of any reagent with a heterogeneous material as wood/tree bark extracts is very complex, taking into consideration the chemical structure of wood/wood waste. FT-IR spectra indicate the occurrence of chemical modification of wood /wood waste by reacting with acrylic copolymer in water dispersion.

Due to the reactive chemical groups present in pine/acacia tree bark extracts and in acrylic copolymer CP1, the two components, natural and synthetic polymers are able to react forming a composite type structure in which the matrix is the synthetic acrylic copolymer and the fillers are the pine/acacia tree bark extracts. The process of forming bio-protective and finishing coatings based on acrylic copolymer and pine/acacia tree bark extracts involves a series of chemical reactions from which the most important is the esterification of the carboxyl groups from acrylic copolymer structure with hydroxyl groups from pine/acacia tree bark extracts structure. The bonding process between the synthetic polymer and natural polymers (cellulose, hemicelluloses, lignin) from wood waste is certified by specific and common FT-IR absorption bands corresponding to the following functional groups [14, 15], as presented in Table 3.

Table 3. FT-IR absorption bands corresponding to the composites CP2 and CP3 and their attribution

Wavenumber [cm <sup>-1</sup> ]	Attribution
2919.89	-O-H bond vibration from alcoholic/aromatic hydroxyl groups from tree bark extracts
1734.52-1732.41	Carboxyl (COOH) from acrylic copolymer, which can be involved in esterification reaction with hydroxyl groups from cellulose and lignin from tree bark extracts
1558.3	-Aromatic nucleous vibration in lignin component of tree bark extracts
1449.50	-aromatic C=C bonds from pine and acacia trees bark extracts
1362.30	-C-H absorption specific to ester bonds between acrylic copolymer and tree bark extracts
1245. 20	- C-O bond in lignin and hemicelluloses from tree bark extracts
1098. 52	-C-C, C-O, C=O stretching in cellulose and hemicelluloses
700 to 900	Certify the presence of aromatic nuclei of lignin derivatives from tree bark extracts

Comparing the composites based on acrylic copolymer and tree bark extracts used as wood preservation agents, it can be seen that the wood coating based on acrylic copolymer and pine tree bark extract presents better properties of the coating films (especially tensile breaking strength and water absorption) comparing with the wood coating based on acrylic copolymer with acacia tree bark extract. This improved behavior can be correlated with a greater proportion of hydroxyl functional groups in pine component which can react, by esterification, with the carboxyl groups from the synthetic copolymers, forming crosslinked structure responsible for better physical and chemical properties (especially tensile strengths and water absorption of the coating film).

### Testing the coating finishes with composites CP1, CP2, CP3

The ecological water based composites used as new wood coatings with biocide activity, based on natural and synthetic polymers, were submitted to the standard testing procedures for wood/furniture coatings resistance at different chemical compounds. The results are presented in Table 4.

**Table 4.** Results of testing coating finishes with CP1, CP2, CP3 with different chemical compounds

Characteristic	CP1	CP2	CP3	Standard SRN/12720/2004
Dry film aspect	good	good	good	1-5
Resistance at water, 24 h	5	5	5	1-5
Resistance at ethanol 48%, 1 h	5	5	5	1-5
Resistance at ethanol 48%, 16 h	4	5	5	1-5
Resistance at acetic acid 44%, 1 h	4	5	5	1-5
Resistance at citric acid 10%, 1 h	5	5	5	1-5
Resistance at ammonia 10%, 1 h	5	5	5	1-5
Resistance at Na <sub>2</sub> CO <sub>3</sub> 10%, 1 h	5	5	5	1-5
Resistance at paraffin oil, 24 h	4	5	5	1-5
Resistance at coffee, 16 h	5	5	5	1-5

As can be observed from the results presented in Table 4, from the new ecological coating materials, submitted to the standard testing procedures for wood coatings, the coatings based on composites CP2 and CP3 with pine and acacia bark extracts present higher resistance at chemical compounds comparing with the coating based on acrylic copolymer.

### Testing the biocide activity of the composites CP1, CP2, CP3

Considering the biocide activity of acrylic monomers and wood waste/ tree bark extracts, the composites based on acrylic copolymer (CP1) and the acrylic copolymer with pine bark extract (CP2), and acacia bark extract (CP3) were also submitted to the biological testing.

The testing of the biocide activity of the composites, proposed as wood preservatives, consisted on treating the sapwood samples by immersion in the wood preservation agents for 30 minutes and exposing the treated samples against the attack of the microorganisms from soil. After 28 testing days, the samples were examined using an optic microscope, in order to establish the attack level of the above mentioned microorganisms.

The fungal growth was classified (according to **STAS 8022/91**) between 0 and 4, as following:

- 0 = no growth;
- 1 = trace of growth detected visually
- 2 = slight growth or 5-20% coverage of the total test area
- 3 = moderate growth or 20-50% coverage
- 4 = plenty of growth or above 50% coverage

The results of the biocide activity of the wood preservation proposed agents are presented in Table 5.

**Table 5.** The results of the biological testing of the proposed wood preservation agents

Treatment type	Degree of attack	Note
Treatment with CP1	Samples attacked in extent of 60%	4
Treatment with CP2	Samples attacked in extent of 4%	1
Treatment with CP3	Samples attacked in extent of 8%	1

### 3. CONCLUSIONS

Our research establish the presence of some functional groups (hydroxyl, carbonyl, carboxyl in the natural polymers cellulose, hemicelluloses and lignin from the chemical structure of tree bark extracts, which confer to these wood waste a specific chemical reactivity.

As consequence, bark extracts from pine and acacia trees (in amount of 15% based on the total monomer content) were used in the copolymerization of the acrylic monomers: ethyl acrylate, butyl acrylate, acrylic acid in water dispersion.

The enhanced carbonyl absorption peak at 1734.52 (for acrylic copolymer with pine tree bark extract), respectively absorption peak at 1732.41 (for acrylic copolymer with acacia tree bark extract corresponding to C=O ester, and C-H absorption at 1361,99 cm<sup>-1</sup>, C-O stretching band at 1157,93 cm<sup>-1</sup>, confirmed the formation of ester bonds between the carboxyl functional group from acrylic copolymer and hydroxyl group from

pine/acacia tree bark extract .For the copolymer CP1 (without tree bark extract) the specific peak registered at 1726,19 is less intense.

The new composites, proposed as finishing and preservation agents, present better tensile breaking strength and better water absorption of the copolymers film, essential condition for wood finishing and biocide preservation, which depends on the water content and on the accessibility of the microorganisms at the wood surface.

These aspects of the emulsion copolymerization of the acrylic monomers with extracts from the bark of pine and acacia trees, as well as the biocide activity of the copolymers increase the interest in the new research field of emulsion copolymerization of synthetic monomers with natural monomers from wood waste based derivatives and the possibility for obtaining new, ecological composites, for wood finishing and bioprotection.

## REFERENCES

- [1] Hon, D.N.S., and N. Shiraishi. *Wood and Cellulosic Chemistry*. 2nd edition. Marcel Dekker Publishers, ISBN 0824700244, New York, NY, 2001.
- [2] M. Norimoto, Viscoelastic properties of chemically modified wood, Kyoto University, in David N.-S. Hon -Technology & Engineering, 1995.
- [3] Militz, H.; Beckers, E.P.J. & Homan, W.J. Modification of solid wood: research and practical potential. IRG Document WP/97-40098 (1997).
- [4] Rowell R. M., Chemical Modification of Wood, Forest Products Abstracts, Vol. 6 No. 12, 1983
- [5] Hon, D.N.S. *Chemical Modification of Lignocellulosic Materials*. Mark Dekker, Publishers, New York, NY., 1996.
- [6] Hill CAS. Modifying the properties of wood. In: Hill CAS, editor. *Wood modification, 2006*.
- [7] Fengel, D., Wegener, G., (1989), *Wood – Chemistry, Ultrastructure Reaction*, Walter de Gruyter, Germany
- [8] Dumitrescu L., Manciualea, I., *New ecomaterials for wood preservation*. Environmental Engineering and Management Journal, vol. 8, nr. 4, pp. 793-796, 2009.
- [9] Crestini, C., Crucianelli, M. , Orlandi, M., Saladino R., (2010) *Oxidative strategies in lignin chemistry: A new environmental friendly approach for the functionalisation of lignin and lignocellulosic fibers*. Catalysis Today 156, 8–22
- [10] Dumitrescu L., Perniu D., Manciualea I. *Nanocomposites based on acrylic copolymers, iron lignosulfonate and ZnO nanoparticles used as wood preservatives*, Solid State Phenomena, vol. 151, ISSN 1012-0394, 139-144, 2009.
- [11] Kamdem DP, Pizzi A, Jermannaud A. *Durability of heat treated wood*, Holz als Roh-Werkstoff 60, 1-6, 2002.
- [12] Koleske, J.V., (1995) *Paint and Coating Testing Manual*. ASTM Philadelphia.
- [13] Zakis, G. F. (1994). *Functional analysis of lignins and their derivatives*. TAPPI Press, ISBN: 0-89852-258-7, Atlanta, US.
- [14] Bodarlan et al. 2008 Chemical modification of beech, [Bioresources3 (3), 789-800, 2008].
- [15] Mueller et al. FTIR-ATR Spectroscopic analyses, BioResources 4 (), 49-71, 2009.
- [16] Beldean, E., Timar, C. M. Laboratory test concerning the durability of wood in contact with soil. Proligno vol.6 n°4 2010.