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ECOLOGICAL WOOD COATING MATERIALS BASED ON NATURAL AND SYNTHETIC POLYMERS

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Abstract:
New water based eco-materials used as wood coatings were synthesized by emulsion copolymerization of acrylic esters comonomers (ethyl acrylate, butyl acrylate, acrylonitrile, acrylic acid) and styrene with lignin derivatives calcium and iron (III) lignosulfonates, as partial substitutes for styrene/acrylic monomers.The obtained water based, ecological coatings, were physical-chemical and by FTIR analysis characterized and submitted to the standard testing procedures for wood/furniture coatings. The research put into evidence that better properties of the coating films (tensile breaking strength, water absorption, resistance at cold liquids and dry/wet heat resistance) are obtained for the styrene-acrylic copolymer and acrylic copolymer with iron lignosulfonate as reaction partner.

Key words: *acrylic esters/styrene-acrylic esters copolymers; calcium and iron lignosulfonates; wood ecological coatings.*

INTRODUCTION

Lignocellulosic materials are the main source of renewable biomass possessing a great potential, both for fuel to heat and power production and also for chemicals and materials feedstocks (Gossling 2011, Haveren *et al.* 2008, Hill CAS 2006).

As consequence of the large availability of lignocellulosic biomass - 200 billion tons (Zhang 2008) compared to 0.3 billion tons of organic chemicals yearly produced by the chemical industry there is an increasing industrial interest for replacing petrochemical based products by bio-based ones in order to attain a sustainable economy (Bjorsvik 2002).

Lignocellulosic substances are composite materials which contain natural polymers cellulose, hemicellulose and lignin with a complex structure, both at macromolecular and micromolecular level (Hon 1996, Satyanarayana *et al.* 2007). Based on the variety of chemical functional groups (primary and secondary hydroxyls, carbonyls, carboxyls, esters, ether etc) present in these natural polymers, complex reactions of etherification, esterification, alkylation, graft copolymerization, crosslinking and oxidation have been conducted to different lignocellulosic materials to produce a range of products with different practical applications (Hon, 1996, Hon and Shiraishi 2001, Netravali and Chabba 2003, Kamel 2007, Dumitrescu *et al*. 2009, Manciulea *et al*. 2009, Ten *et al.* 2013))

Lignin products are generated in vast quantities as by-products of chemical wood pulping, when by reactions with ammonium and calcium disulphites, due to the partial degradation and introduction of sulfonic groups, lignin becomes soluble in water by forming lignosulfonates, anionic surface-active derivatives of lignin (Doherty 2011, Sarkanen 1971, Gaedda 1999).

The production of 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, (Mansour *et al.* 1998, Dumitrescu *et al*. 2009, Dumitrescu *et al*. 2012). Wood has always been an important and versatile material with many uses, but wood has some drawbacks such as high moisture uptake, biodegradation, and physical and mechanical property change with environmental factors (Hill 2006). These negative inherent properties of wood can be minimized by appropriate chemical treatment, respectively structural modification or formation of wood polymer composites (Kamden 2002).

For a better use of resources (biomass waste), and for environmental protection, the use of lignosulfonates as chemical reagents seems to be very interesting in the future. Previous research has revealed that the organic ecologic surface coatings, film-forming materials, that give biocide properties to wood surfaces and good finishing properties, can be obtained by mixing or reacting acrylic copolymers/monomers with metal complexed lignosulfonates (Dumitrescu 1999; Dumitrescu *et al.* 2012, Hon, 1996; Fengel and Wegener 1989; Shulga et al., 2007, Crestini *et al.* 2010).

The combination between synthetic copolymers and natural polymers (lignin/lignin derivatives lignosulfonates) can also improve the performances of the coatings materials and the biocide properties (Bauer *et al*. 2007, Derek, 2008, Calbo 1999, Koleske 1995, Zorll 2000, Manciulea *et al.* 2007).

OBJECTIVES

The objectives of the research were the synthesis and characterization of new coating materials based on synthetic acrylic esters/styrene-acrylic esters copolymers and natural polymers lignin/lignin derivatives lignosulfonates (waste materials, pollutants for environment). The new water based coatings represent a sustainable and ecological alternative for the former coatings, based on organic solvents, used as wood preservatives and finishing materials, from which considerable organic solvent was emitted into the atmosphere during film formation.

METHOD, MATERIALS AND EQUIPMENT

a. The calcium lignosulfonate (LSCa), from sulphite pulping), and iron (III) lignosulfonate (LSFe), obtained from the ammonium lignosulfonate and Fe $(NO_3)_3$ were analysed conforming to specific methodology for lignin (Zakis 1994).

b. For the synthesis of the new ecological coatings materials – the acrylic esters/styrene-acrylic esters comonomers were copolymerized with calcium, respectively iron (III) lignosulfonates. The monomers, the ionic and non-ionic emulsifiers system, and the initiator sodium persulphate were purchased from Merck.

Based on former research (Dumitrescu 1999; Dumitrescu *et al.* 2009), quantities of 15% from the acrylic esters/styrene and acrylic esters monomers have been substituted with calcium and, respectively iron lignosulfonates.

The copolymerization procedures have been done, using a semicontinuous technique of emulsion copolymerization, in an one litter glass reactor, equipped with a paddle type stirrer, thermometer and cooler, conforming the following standard recipe:

- Monomer composition: acrylic esters (ethyl acrylate, acrylonitrile, butyl acrylate, acrylic acid) and styrene.

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- Initiation system: sodium persulphate
- Emulsifying system: ionic emulsifier and non-ionic emulsifier
- Dispersion medium: distilled water

The acrylic esters/styrene and acrylic esters comonomers emulsion was dozed by a constant ratio, for 2.5-3 hours, under continuous stirring, into the copolymerization autoclave.

The copolymerization temperature was 80-85^{0}C. At the end of the process, the inner temperature was raised at 90^{0}C and kept for an hour, in order to finish the copolymerization. The water dispersion of styrene-acrylic copolymers, respectively acrylic copolimers were then cooled at 20^{0}C.

c. The physical-chemical characterization of the coatings (solids, pH, density, viscosity, tensile breaking strength, water absorption of the coating film) was performed by specific procedure for acrylic copolymers (Dumitrescu 1999).

The structure of obtained wood coatings based on styrene-acrylic copolymers and acrylic copolymers with calcium and iron (III) lignosulfonates was also investigated by FT-IR analysis with a spectrometer FTIR-model BX II (Perkin Elmer, 2005).

d. The evaluation of the new water-based coating materials for wood finishing and preservation was performed by brushing two coats on the surface of poplar wood samples. The successive finishing operations on the poplar wood support were: (a) application of the first coat; (b) drying 2 hours at 20^{0}C; (c) application of the second coat; (d) drying 4 hours at 20^{0}C. The coatings were also submitted to the standard testing procedures for wood/furniture coatings: (a) resistance at cold liquids, (b) dry/wet heat resistance.

RESULTS

The chemical characteristics of calcium and iron (III) lignosulfonates.used in the synthesis are presented in Table 1.

Table 1

Chemical characteristics of the calcium and iron (III) lignosulfonates.

Characteristic	LSCa	LSFe(III)
pH- value	4.00	2.75
Solids, %	36.40	35.00
Density, 20^0 C, g/cm^3	1.1450	1.1500
Viscosity at 20^0 C, cP	70.00	66.00
Ash, %	1.55	2.50
Cation (Metal), %	5.05	6.50
Functional groups: - OH phenolic, % - OH alcoholic, % - carbonyl, % - carboxyl, %	 12.25 11.00 5.80 0.65	 15.40 12.60 7.50 0.80

Where: LSCa = calcium lignosulfonate;
LSFe = iron (III) lignosulfonate

Due to the specific chemical structure (carbon-carbon double bonds and chemical functional groups phenolic and alcoholic hydroxyl and carboxyl) the calcium and iron lignosulfonates have been used as reactive comonomers in emulsion copolymerization of acrylic esters/acrylic esters-styrene comonomers.

The wood coatings based on styrene-acrylic, respectively acrylic esters copolymers with calcium and iron lignosulfonate are:

- coating P1 - styrene-acrylic copolymer with calcium lignosulfonate
- coating P2 - styrene-acrylic copolymer with iron lignosulfonate
- coating P3 - acrylic copolymer with calcium lignosulfonate
- coating P4 – acrylic copolymer with iron lignosulfonate.

The new, water- based ecological coatings present the following chemical characteristics (Table 2) and were also investigated by FT-IR analysis (Fig. 1).

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Table 2.

Characteristics of the new wood coatings based on styrene-acrylic copolymers and lignosulfonates.

Copolymer	Solids %	pH	Density g/cm3	Viscosity at 20 ^{0}C cP	Tensile breaking strength MPa	Water absorption of the coating film, %		
						1 h	24 h	48 h
P1	39.00	6.3	1.0470	69.50	2.50	3.7	16.5	37.0
P2	39.6	6.5	1.0550	75.80	2.80	3.2	14.5	35.5
P3	39.3	6.5	1.0500	51.00	2.60	3.6	15.5	36.5
P4	40.0	6.5	1.0600	80.50	3.00	3.4	14.0	35.0

Comparing the wood coatings based on acrylic copolymers and styrene-acrylic copolymers with calcium and iron lignosulfonates it can be seen that better properties of the coating films (especially tensile breaking strength and water absorption) are obtained for the styrene-acrylic copolymer (P2) and acrylic copolymer (P4) with iron lignosulfonate as reaction partner. This lignosulfonate contains a greater proportion of hydroxyl functional groups which can react, by esterification, with the carboxyl groups from the synthetic copolymers, forming crosslinked structure with better physical and chemical properties (especially tensile strengths and water absorption of the coating film).

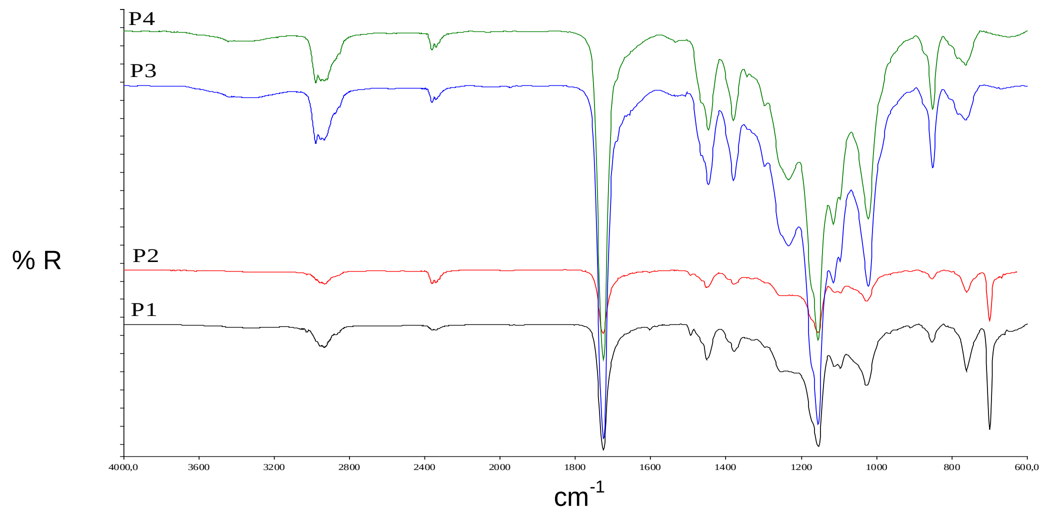

Fig. 1
IR spectra for P1, P2, P3 and P4 copolymers.

Due to the reactive chemical groups present, both in the styrene-acrylic copolymers (P1 and P2) and in acrylic copolymers (P3 and P4), with calcium and iron lignosulfonates, the two components, natural and synthetic polymers are able to react with each other to form a composite type structure in which the matrix is the synthetic copolymers and the fillers are the calcium and iron lignosulfonates.

The process of forming bioprotective and finishing coatings based on styrene-acrylic/acrylic copolymers and lignosulfonates involves a series of chemical reactions:

(a) esterification of carboxyl groups from acrylic copolymer structure with hydroxyl groups from lignosulfonates structure;

(b) calcium and iron cations reactions with hydroxyl and carboxyl groups from the structure of lignosulfonates and styrene-acrylic/acrylic copolymers.

The bonding process between the synthetic polymers and natural polymers lignin derivatives is certified by specific and common IR absorption bands corresponding to the following functional groups:

▪ Absorption band at 1723.56cm^{-1} in IR spectrum of the four copolymers coatings indicates the presence of carboxyl (-COOH) groups which may be linked to hydroxyl groups in the lignosulfonates polymer structure through esteric bonds or can be involved in reactions of salts formation with calcium and iron cations from lignosulfonates;

▪ The lignosulfonates presence in macromolecular matrix of styrene-acrylic/acrylic copolymers is evidenced by the specific absorption bands at 1021.41cm^{-1} (characteristic to $-SO_3H$ groups) and at 1447.76cm^{-1} (certifying the presence of aromatic carboxyl groups from lignosulfonates);

▪ At 1367cm^{-1} aromatic hydroxyl groups from lignosulfonates are highlighted. They can be involved in reactions of etherification or esterification with the synthetic copolymers;

▪ The absorption bands at 1240-1270cm^{-1} correspond to the functional group methoxy (–OCH_3) specific to lignin/lignosulfonates which can be transformed into a hydroxyl group through hydrolysis of the lignosulfonates able to react by esterification with the carboxyl groups from acrylic esters;

▪ The presence of the absorption bands at 1157.70cm^{-1} can be correlated with the formation of new etheric bonds, by involving hydroxyl groups from lignin derivative structure (LSCa and LSFe);

▪ The absorption bands from 700 to 900cm^{-1} certify the presence of aromatic nuclei of lignin derivatives lignosulfonates and of styrene monomer.

The ecological, water based new wood coatings, based on natural and synthetic polymers, were submitted to the standard testing procedures for wood/furniture coatings: (a) resistance at cold liquids and (b) dry/wet heat resistance. The results obtained are presented in Table 3.

Table 3

Results of testing the new wood coatings based on styrene-acrylic copolymers and lignosulfonates.

Characteristic	P1	P2	P3	P4	Standard SRN/12720/2004
Dry film aspect	good	good	good	good	
Resistance at water, 24 h	5	5	5	5	1-5
Resistance at ethanol 48%, 1 h	5	5	4	5	1-5
Resistance at ethanol 48%, 16 h	4	5	4	5	1-5
Resistance at acetic acid 44%, 1 h	4	5	5	5	1-5
Resistance at citric acid 10%, 1 h	4	5	4	5	1-5
Resistance at ammonia 10%, 1 h	5	5	5	5	1-5
Resistance at Na_2CO_3 10%, 1 h	5	5	5	5	1-5
Resistance at paraffin oil, 24 h	5	5	5	5	1-5
Resistance at coffee, 16 h	5	5	5	5	1-5
Dry heat resistance, 85 ^{0}C, 20 minutes	4	5	4	5	1-5 (SRN 12722/2004)
Wet heat resistance 85 ^{0}C, 20 minutes	4	5	4	5	1-5 (SRN 12712/2004)

CONCLUSIONS

The research was focussed on synthesis and characterization of four new wood coatings materials:

P1 - based on styrene-acrylic copolymer with 15% calcium lignosufonate;

P2 - based on styrene-acrylic copolymer with 15% iron (III) lignosufonate;

P3 - based on acrylic copolymer with15% calcium lignosufonate;

P4 - based on acrylic copolymer with 15% iron (III) lignosufonate;

From the four new ecological coating materials, submitted to the standard testing procedures for wood coatings, the coatings based on both copolymers P2 and P4 with iron lignosulfonate present better properties of the coating films (tensile breaking strength, water absorption) and higher resistance at cold liquids and dry/wet heat resistance) as coats on the poplar wood samples, comparing with the coatings based on acrylic/ styrene-acrylic copolymers with calcium lignosulfonate (P1 and P3).

This behaviour can be correlated with the presence in the coatings (P2 and P4) of the iron lignosulfonate which contain greater percentages of hydroxyl and carboxyl groups able to react with the synthetic copolymers by esterification reactions and salt formation and is certified by FT-IR analysis where the grafting process of lignosulfonates onto the synthetic copolymers chains was evidenced by specific absorptions bands for natural polymers lignosulfonates and synthetic copolymers.

Due to the biocide activity of lignin derivatives, it expects, the new eco-coating materials based on acrylic/styrene-acrylic copolymers and lignosulfonates to increase the wood biological resistance against microorganisms. Meantime, such finishing and wood preservatives, based on lignin derivatives, can provide better compatibility of chemical agents with the wood structure.

Products for wood finishing and preservation, with complex shapes and properties, can be produced by combining lignocellulosic materials/waste with synthetic materials such as acrylic polymers, to produce low VOC, more environmentally friendly coating materials, in order to improve the sustainable development.

REFERENCES

Bauer F, Flyunt R, Czihal K, Ernst H, Naumov S, Buchmeiser MR (2007) UV Curing of Nanoparticle Reinforced Acrylates, Nuclear Instruments and Methods in Physics Research, B 265, 87-91

Bjorsvik HR, Liguori L (2002) Organic processes to pharmaceutical chemicals based on fine chemicals from lignosulfonates. Org. Process. Res. Dev. 6, 279–290

Calbo L (Ed.) (1999) Handbook of Coatings Additives. New York. Marcel Dekker, 235

Derek S (2008) *Lignin as a base material for materials applications:* Chemistry, application and economics. Industrial Crops and Products, 27(2):202–207

Doherty WOS, Mousaviouna P, Fellows CM (2011) Value-adding to cellulosic ethanol: Lignin polymers. Industrial Crops and Products 33, 259–276

Dumitrescu L (1999) Research regarding the synthesis of some new wood bioprotection agents. Ph.D.Thesis., Gheorghe Asachi Technical University of Iasi, Romania

Dumitrescu L, Manciulea I (2009) New ecomaterials for wood preservation. Environmental Engineering and Management Journal, vol. 8(4):793-796

Dumitrescu L, Manciulea I, Patachia S, Perniu D (2009) Wood adhesives based on lignocellulosic materials, Annals of DAAAM for 2009, pp. 0577-0578

Dumitrescu L, Perniu D, Manciulea I (2009) Nanocomposites based on acrylic copolymers, iron lignosulfonate and ZnO nanoparticles used as wood preservatives, Solid State Phenomena, 151, pp. 139-144

Dumitrescu L, Matei A, Manciulea I (2012) Composites acylic copolymers – wood waste. Proceedings of the 4h International Conference" Advanced Composite Materials Engineering", COMAT 2012, Brasov, (Romania), DERC Publishing House, USA, pp. 323-330

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, pp. 8–22

Fengel D, Wegener G (1989) Wood – Chemistry, Ultrastructure Reaction, Walter de Gruyter, Germany

Gaedda L, Hase A, Kataya K, Leino PQ, Tuominen S, Viikari L (1999) Lignin-based adhesives for particle board manufacture, US Patent EP0953030 A1

Gosselink RJA (2011) Lignin as a renewable aromatic resource for the chemical, PhD. Thesis. Wageningen University, Holland, ISBN: 978-94-6173-100-5

Haveren JV, Scott EL, Sanders JPM (2008) Review: Bulk chemicals from biomass. Biofuels Bioproduction, Biorefinery. 2:41-57

Hill CAS. Modifying the properties of wood. (2006) In: Hill CAS, editor. Wood modification. Chemical, thermal and other processes, John Wiley & Sons Ltd., 175–90

Hon DNS, (Eds) (1996) Chemical Modification of Lignocellulosic Materials. Mark Dekker Publishers, NY. York

Hon DNS, Shiraishi N (Eds) (2001) Wood and Cellulosic Chemistry. 2nd Edition. Marcel Dekker Publishers, NY

Kamel S (2007) Nanotechnology and its applications in lignocellulosic composites, a mini review, Express Polymer Letters 1(9):546–575

Kamdem DP, Pizzi A, Jermannaud A (2002) Durability of heat treated wood, Holz als Roh-Werkstoff 60, pp. 1–6

Koleske JV (1995) Paint and Coating Testing Manual. ASTM Philadelphia

Manciulea I, Mihalevschi D, Dumitrescu L (2007) Contributions regarding the research of some new nanostructured coating materials. In: Physica Status Solidi, (c), 11:3541-3544

Mansour OY, Kamel S, Nassar MA (1998) Lignocellulosic polymer composite IV. J. Applied Polymer Science, 69:845–855

Netravali A, Chabba S (2003) Composites get greener. Material Today, 6:22-29

Sarkanen & C.H. Ludwig (eds) (1971) Lignins: Occurrence, Formation, Structure, and Reactions. New York: Wiley Interscience

Satyanarayana KG, Guimaraes JL, Wypych F (2007) Studies on lignocellulosic fibers of Brazil. Part I: Source, production, morphology, properties and applications, Composites: Part A. 38, 1694-1709

Shulga G, Betkers T, Shakels V, Neiberte B, Verovkins A, Brovkina J (2007) Effect of the modification of lignocellulosic materials with a lignin–polymer complex on their mulching properties.Bioresources, 2(4):572-582

Ten E, Vermerris W (2013) Functionalized Polymers from Lignocellulosic Biomass: State of the Art.Polymers 5, pp. 600-642

Zakis GF (1994) Functional analysis of lignins and their derivatives. TAPPI Press, Atlanta, Ga

Zang YHP (2008) Reviving the carbohydrate economy via multi-product lignocellulose biorefineries. J. Ind. Microbiol. Biotechnol. 35:367–375

Zorll U (Ed.) (2000) European Coatings Handbook. Germany. Vincentz Verlag