Nanocomposite Ecomaterials Based on Polymers and Alumina Nanoparticles for Wood Preservation

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Abstract: - The synergistic combination of polymers and inorganic compounds via sol-gel process has attracted great attention, by manipulating structure at molecular level, for developing new materials with desired properties. These new hybrid materials could have a controllable combination of the benefits of polymers (flexibility, toughness, ease of processing) and those of ceramics or glasses (hardness, durability, thermal stability). The microstructures and the properties of hybrid materials depend on the particle size of inorganic phase, the uniform distribution of inorganic phase within the organic phase and the interfacial force between the two phases.
The paper presents research concerning the obtaining of composite coating nanomaterials consisting of an organic component (functionalized acrylic copolymers in water dispersion and iron and chromium lignosulfonate) and inorganic component nano aluminium oxide. The formation of a crosslinked nanometric network of inorganic and organic domains was evidenced by AFM analysis.The interphase characterization of the nanostructured materials was performed using FT-IR analysis.

Key words: nanocomposites, acrylic copolymers, alumina nanoparticles.

1.   Introduction

The synergistic combination of polymers and inorganic compounds via sol-gel process has attracted great attention, by manipulating structure at molecular level, for developing new materials with desired properties. These new hybrid materials could have a controllable combination of the benefits of polymers (flexibility, toughness, ease of processing) and those of ceramics or glasses (hardness, durability, thermal stability) [7], [14]. The microstructures and the properties of hybrid materials depend on the particle size of inorganic phase, the uniform distribution of inorganic phase within the organic phase and the interfacial force between the two phases. Therefore, nanocomposite materials have successfully been applied in many fields such as plastic processing, medicine, optics, electrics, textile [12], [3], [2], etc. As the nano-scale morphology plays an important role in achieving desired macroscopic properties, the characterization of the interaction between the intrinsically immiscible phases is necessary [6].

The stability of the hybrid materials requires that the inorganic can be easily dispersed in polymer and form strong chemical bonds with the organic moieties [10]. Therefore, the dispersion of the particles in polymer could be improved by the method of surface modification, so that the interfacial binding force between particles and the polymer could be increased.

Long-term antimicrobial activity can also be imparted in many coating formulations through the incorporation of nanomaterials. The desire for permanent coatings to impart long-term antimicrobial or bacteria-stat properties to coated products has been expressed in a variety of industries, including healthcare, industrial and institutional cleaning, food processing, food service, and general paints and coatings. Due to the small size of the nanomaterials, penetration into a porous surface rather than simple surface adhesion can be achieved. With the discontinuation of wood preservation materials based on toxic components, such as arsenium, for residential uses, the wood industry is searching for

cost-effective long-lasting antimicrobial products that will allow wood to perform well in outdoor applications [4], [8], [14].

Lignocellulosic materials, important natural renewable resources, contain polymers cellulose, hemicellulose and lignins which posses many active functional groups susceptible to reaction [9] such as: primary and secondary hydroxyls, carbonyls, carboxyls, esters, ether etc. Based on the variety of functional groups, etherification, esterification, alkylation, hydroxyalkylation, crosslinking, graft copolymerization and oxidation have been conducted to different lignocellulosic materials to produce a series of products with many practical applications [9], [13]. Lignin is the second most abundant renewable organic material on planet after cellulose in wood and other plant tissues. Available lignin products are generated in vast quantities as a by-product of chemical wood pulping. During the technical sulphite pulping, with ammonium and calcium disulphites, lignin becomes soluble in water, due to the partial degradation and introduction of sulfonic groups. Lignosulfonates are water soluble, anionic surface-active derivatives of lignin. For a better resource utilization and environmental protection, it is very interesting to use lignosulfonates as chemical reactants [3, 4] or to chemical modify them in order to improve their properties.

Introduction of functional groups onto the surface of the alumina inorganic component can promote more easily chemical bonding between the inorganic particles and the organic.

The presence of a polymer bearing suitable reactive groups induces an increased force between the two parts, increased stability of the nanocomposites [9].

2. Experimental

There are several possibilities available when considering a change from an established coating system without nanoparticles to a coating system that contains nanoparticles. The easiest way is to use a nanoparticle concentrate as additive for existing coating systems [1], [4], [5], [15].

The objective of this study is testing the performance of alumina nanoparticles (inorganic phase) used as additive for the organic phase (acrylic copolymers) in wood coating system.

A. *The organic phase* of the nanomaterials consisted on:

(a) acrylic copolymer (CP1) obtained by water emulsion copolymerization of the acrylic monomers (ethyl acrylate, butyl acrylate, acrylonitrile, acrylic acid) and copper sulphate; (b) acrylic copolymer (CP2) obtained by water emulsion copolymerization

of the acrylic monomers (ethyl acrylate, butyl acrylate, acrylonitrile, acrylic acid), with iron and chromium lignosulfonate and copper sulphate.

B. *The inorganic phase* consisting on alumina sol-gel was obtained by mixing aqueous solution of $AlCl_3$, ethanol and ammonium polyacrylate (Aldrich) with ammonium solution 25% and stirred 3 hours at 20^0C, until the sol was formed. Afterwards, the mixture was stirred 3 hours at 50^0C until a translucent alumina gel was formed. The obtained nanocomposites materials were:

(a) nanocomposite NC1 - based on the acrylic copolymer CP1 and 3% alumina nanoparticles;

(b) nanocomposite NC2 - based on the acrylic copolymer CP2 with iron and chromium lignosulfonate and 3% alumina nanoparticles.

3. Results and discussion

The surface morphology of the proposed coating materials was analyzed with an AFM NT-MDT model BL 222 RNTE.

The AFM images (Fig.1 and Fig.2) detail the surface morphology showing a continuous and uniform distribution of alumina nanoparticles both in the polymeric matrix of the acrylic copolymer as such (CP1) and acrylic copolymer which contains iron and chromium lignosulfonate (CP2).
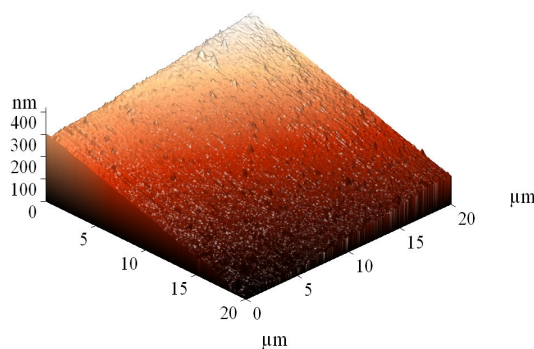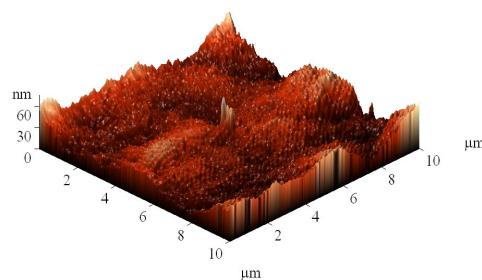

Fig.1. The AFM image of NC1

Fig.2. The AFM image of NC2

The nanocomposites present a dense structure, able to assure good coating properties, having average roughness value 88.00 nm (NC1), respectively, average roughness value 100.05 nm (NC2).

The interphase characterization of the nanostructured materials synthesized was performed using a Spectrometer FTIR-model BX II (Perkin Elmer, 2005) were done in reflectance mode, in the range of 500-4500 cm^{-1}, after four scans, with 4 cm^{-1} resolution. The bonding process between acrylic copolymer, respectively iron and chromium lignosulfonate based acrylic copolymer and the alumina nanoparticles perform as follows. The aluminium oxide nanoparticles surface molecules react with atmospheric water vapour creating oxyhydroxide surface groups:

$$Al_2O_3 + H_2O \rightleftharpoons 2AlO(OH)$$
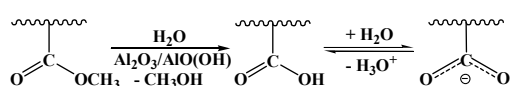
The presence of the OH group on the nanoparticles surface of the copolymers CP1 and CP2 facilitates hydrolysis of the acrylic ester group to produce a conjugate carboxylate base (COO⁻) [3], [4].

This will directly interact with the positively charged Al atoms to generate a bond between the polymers segment and the aluminium oxide nanoparticles surface [3], [8]. The hydration reaction has been proven to occur with several metal oxides, including Al, Cr, Co, and Cu [3].

The FT-IR spectra (Figure 3) performed on the thin films of nanocomposites NC1 and NC2, confirm the interaction of polymer segments with the alumina nanoparticles. Infrared absorption bands of acrylic copolymers with alumina nanoparticles show specific peaks which explain the interactions between organic and inorganic components of the synthesized nanomaterials. The band located at 1723.56 cm^{-1} in the IR spectrum, both for the nanocomposites NC1 (with alumina nanoparticles) and NC2 (with iron and chromium lignosulfonate and alumina nanoparticles) indicates the formation of carboxyl groups (COOH) which can bond alumina cations or can form some new ester groups, also trapping inorganic alumina nanoparticles in their structure.

The presence of the peaks at 1021.97 cm^{-1} and 1157.70 cm^{-1} (for both NC1 and NC2) can be correlated to the formation of some ether groups by implication of OH groups from the alumina nanoparticles surface.

In the same time, the FT-IR analysis put into evidence the grafting process of lignosulfonate in the macromolecular chain of CN2 by specific peaks at 1558.13 cm^{-1}, 1021.41 cm^{-1}, 1447.76 cm^{-1} (certifying the presence of lignin aromatic cycle), at 700-900 cm^{-1} (aromatic rings from lignin derivatives), the peak at 1367 cm^{-1} (aromatic OH from lignin), the peak at 3383.97 cm^{-1} (aliphatic and aromatic OH from lignin), peaks at 1240-1265 cm^{-1} (methoxy functional group from lignin) and the peaks at 1044.23 – 1242.16 specific for Ar-COO⁻ components of lignin, which also can bind the alumina nanoparticles.

Figure 3: The FT-IR spectra performed on the thin films of nanocomposites NC1 and NC2
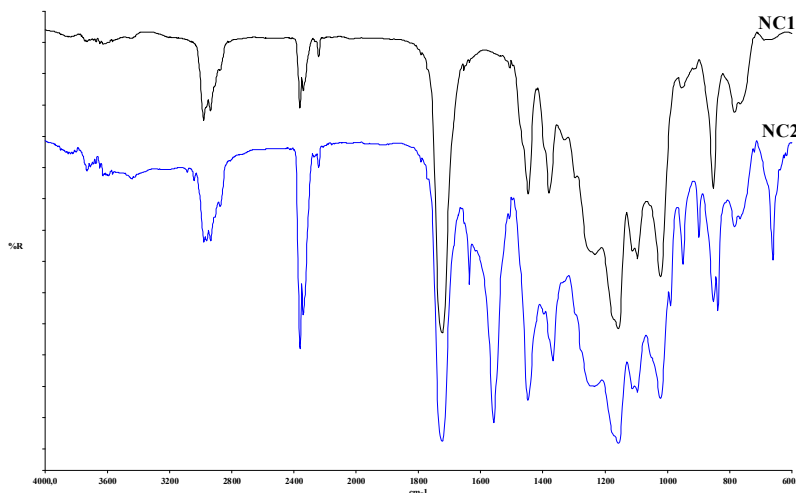
The application of new coating materials based on acrylic copolymer (NC1) and on the acrylic copolymer with 3% alumina nanoparticles (NC2) on the wood surface was performed by spraying two coats of lacquer (110-120 g/m2/coat).

The successive finishing operations on the wood support PAL veneered with beech were:
(a) application of the first coat of acrylic copolymers with TiO2 nanoparticles; (b) drying 1-2 hours at 20^0 C(c) sanding with abrasive paper; (d) dust cleaning; (e) application of the second coat of acrylic polymers with alumina nanoparticles; (f) drying 4-6 hours at 20^0 C.

The coatings were submitted to the standard testing procedures for wood/furniture coatings: (a) resistance at cold liquids, (b) dry/wet heat resistance, (c) scratch resistance (by lead).

The scratch resistance of the coatings was ranked visually, on a scale from 5 (no scratches, excellent scratch resistance) to 1 (highly scratched surface, poor scratch resistance).

The results obtained are presented in Table 1.

Table 1. *The characteristics of the new nanostructured coating materials*

Characteristic	NCP1	NCP2	Standard SRN/12720/2004
Dry film aspect	5	5	good
Resistance at water, 24 h	5	5	1-5
Resistance at ethanol 48%, 1 h	5	5	1-5
Resistance at ethanol 48%, 16 h	4	5	1-5
Resistance at acetic acid 44%, 1 h	4	5	1-5
Resistance at citric acid 10%, 1 h	5	5	1-5
Resistance at ammonia 10%, 1 h	5	5	1-5
Resistance at Na2CO3 10%, 1 h	5	5	1-5
Resistance at paraffin oil, 24 h	5	5	1-5
Resistance at coffee, 16 h	5	5	1-5
Dry heat resistance, 85^0 C, 20 minutes	4	5	1-5 (SRN 12722/2004
Wet heat resistance, 85^0 C, 20 minutes	4	5	1-5 (SRN 12712/2004
Scratch resistance (by lead)	H	2H	STAS 6000-7/1986

The biocide activity investigation have been performed in order to identify the wood preservation potential, against biological attack, of these water based ecological nano-composite materials.

Considering the biocide activity of acrylic monomers, copper sulphate and the major wood component lignin [12], the obtained composites NC1 and NC2 were biologically investigated and proposed as wood preservation agents.

The proposed wood preservation agents were as follows:
- The wood preservation agent based on the acrylic copolymer itself, CP1;
- The wood preservation agent based on nanocomposite NC1 (acrylic copolymer CP1 with 3% alumina nanoparticles);
- The wood preservation agent based on nanocomposite NC2 (acrylic copolymer with iron and chromium lignosulfonate CP2 and 3% alumina nanoparticles).

The methods consist on treating the the sapwood samples by immersion in wood preservatives for 30 minutes and exposing the treated samples against the attack of the following microorganisms: *Chaetomium globosum Kunze, Paecilomyces varioti Brainier, Stachibotrys atra Corda, Alternaria tennuis Ness, Trichoderma viridae Person ex. Fries, Alternaria humicola (Qud)*.

After 28 testing days, the samples were visually examined by optical microscope in order to establish the attack level of the above mentioned microorganisms.

The results of the biological testing are presented in the Table 2.

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 2. The results of the biological testing

Treatment type	Degree of attack	Note	Preservation Efficiency
Wood reference sample	85% of surface	4	According to STAS 8022/91
Wood with CP1	16% of surface	2	Moderate
Wood with NC1	4% of surface	1	Good
Wood with NC2	2% of surface	1	Good

4. Conclusions

The research was focussed on synthesis and characterization of new coating nanocomposites materials based on acrylic copolymer and alumina nanoparticles (NC1) and acrylic copolymer with iron and chromium lignosulfonate (NC2) as organic phase and alumina nanoparticles, obtained by sol-gel method, as inorganic phase. The research established the importance nanoparticles have on improving the properties of the wood coating materials, both for furniture finishing and improving its biocide activity.

When used as wood coating, the acrylic copolymer with iron and chromium lignosulfonate and alumina nanoparticles showed better surface coating properties (resistance at ethanol 48%, 16 h, resistance at acetic acid 44%, 1 h, dry and wet heat resistance at 85^0C, for 20 minutes and enhanced scratch resistance) comparing with the acrylic copolymer as such.

This behaviour can be correlated with the presence of more functional groups (hydroxyl, carbonyl, carboxyl) into the structure of lignin derivative - iron and chromium lignosulfonate, able to contribute to increasing the anchoring points between the organic copolymer and inorganic alumina nanoparticles.

The chemistry behind the interaction of acrylic copolymer with/without iron and chromium lignosulfonate and nano-aluminium oxide surface was demonstrated by FT-IR analysis.

Improved properties are obtained as the result of complex interactions, by esterification, etherification, salt formation reactions, between the hydroxyl groups or nanostructured aluminium oxide (inorganic phase) and the acrylic ester groups, carboxyl and carboxylate groups from the acrylic copolymers (organic phase).

The compatibility between alumina nanoparticles and acrylic copolymers explains the stability and the improved properties of the new wood coating nanomaterials [12], [9], [11]. This bonded segment represents an anchoring point for the acrylic copolymers chain on the alumina nanoparticles surface and explains the improved properties of the new wood coating nanomaterials.

The proposed ecological water based wood preservation agents are in agreement with nowadays research in the field of wood coatings, who is looking for new opportunities to replace toxic chemical treatments with benign alternatives aiming the reduction of volatile organic emissions.

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