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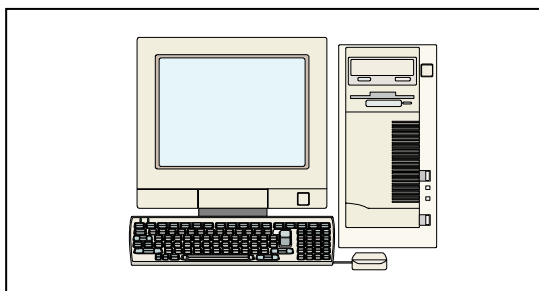
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POLYOXOMETALATE CATALYSTS FOR DELIGNIFICATION OF WOOD PULP AND NATURAL FIBERS

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Abstract

Although polyoxometalates have been studied extensively, however, were not sufficiently tested as catalysts in the pulp bleaching processes. The idea of using them came because of their ability to react selectively with lignin and to regenerate with oxygen from different sources, but not at the last and thanks to stability in the range of pH and temperature fields. As can be seen from the experimental results shown in this material, while traditional methods have failed bleaching pulp grades no more than maximum of 65% brightness, using new generations of polyoxometalates gave better results, becoming a brightness up to 85% in just two steps. Simple method of bleaching under atmospheric conditions and average temperatures of up to 70 °C, as well as advanced and selective degradation of lignin, make polyoxometalates a new class of agents with a huge potential in green technology for pulp bleaching.

Key words: *Polyoxometalats, Bleaching, Chemical Pulp, Environmental Impact*

Rezumat

Although polyoxometalates have been studied extensively, however, were not sufficiently tested as catalysts in the pulp bleaching processes. The idea of using them came because of their ability to react selectively with lignin and to regenerate with oxygen from different sources, but not at the last and thanks to stability in the range of pH and temperature fields. As can be seen from the experimental results shown in this material, while traditional methods have failed bleaching pulp grades no more than maximum of 65% brightness, using new generations of polyoxometalates gave better results, becoming a brightness up to 85% in just two steps. Simple method of bleaching under atmospheric conditions and average temperatures of up to 70 °C, as well as advanced and selective degradation of lignin, make polyoxometalates a new class of agents with a huge potential in green technology for pulp bleaching.

Key words: *Polyoxometalats, Bleaching, Chemical Pulp, Environmental Impact*

INTRODUCTION

The oxidation of organic substrates by aqueous hydrogen peroxide is very attractive for a synthetic and industrial viewpoint since this reagent is relatively inexpensive, of low equivalent weight, environmentally clean and

easy to handle. The help of metal catalysts are often required and a considerable effort has been devoted to the search for new efficient metal derivatives suited to the purpose [1-6].

Soluble transition metal-based catalysts such as molybdenum and tungsten have been developed for the oxidation with an aqueous

H₂O₂. Great effort has been devoted to searching for efficient catalysts that can active but not decompose H₂O₂.

Polyoxo – and polyperoxo – metalates are currently of considerable interest as catalysts for a variety of organic oxidations with the environmentally acceptable H₂O₂ as co – oxidant. Dioxo complexes of group 6 transition elements have been known long time ago, the chemistry of peroxo compounds of the transition elements was thoroughly reviewed [7-8]

Mo (VI) and W (VI) form an enormous variety of polyoxoanions (isopoly and heteropoly species). Addition of H₂O₂ to aqueous solution of Mo (IV) and W (IV) anions generally leads to the formation of the simple monomeric or dimeric complexes. If the concentration of H₂O₂ is kept fairly low, polynuclear peroxo complexes can be isolated.

The chemistry of transition metal peroxo – complexes has received special attention due to their importance in a variety of industrial, pharmacological and biological studies. They are widely used in stoichiometric as well as catalytic oxidation in organic, biochemistry and have been applied also in bleaching process [9-16].

Polyoxometalates (POMs) were originally proposed as activating agents for oxygen delignification of wood pulp and have been vividly investigated since [17-26]. The starting point in POM bleaching research was originally to produce a biomimetic way of lignin decomposition. The activity of POMs is based on the idea that they react selectively with phenolic lignin structures in cellulose fiber and that they can often be regenerated with O₂. Moreover, POMs are remarkably stable at wide pH and temperature ranges. Although, POMs have been widely investigated, they have not been applied in the wood pulp industry; this is most probably due to inefficiency and/or complexity of the processes presented.

The selective bleaching of wood pulp in conjunction with paper manufacture, one of the largest industries worldwide – wide, has been associated with significant environmental impact. The industry has moved away from traditional Cl₂ based delignification process because of the potential environmental impact of chloroaromatic by – products. The most attractive alternatives to Cl₂ based technology are O₂ and H₂O₂, both with respect to environment and economy [27].

Oxygen delignification can be considered as an intermediate step between kraft pulping and bleaching since up to about 50% of the residual lignin in kraft pulp can be removed by this stage. Extending a conventional O₂

delignification stage beyond its currently limits would decrease bleach chemical demand with serious environmental benefits and significant increases on return on investment. Oxygen, while effective at depolymerizing and solubilizing lignin, is not sufficiently selective to fully delignify kraft pulps without extensive cellulose degradation [28-30]. If its oxidative capacity could be adequately, oxygen, the least expensive alternative to chlorine, would be a very attractive choice. One way to control the reactivity of O₂ is by using transition – metal based oxidants reversible to mediate in the transfer of electron from lignin to oxygen.

Ozone, while very effective at removing lignin, reacts rapidly with cellulose that high process selectivity is difficult to achieve on an industrial scale [31].

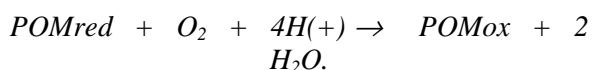
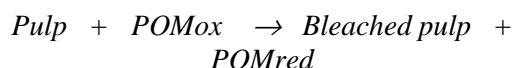
Polyoxometalates

Polyoxometalates are a large and rapidly growing class of inexpensive, minimally or non – toxic complex compounds whose molecular properties are extensively modifiable through either traditional or thermodynamic (one – pot) synthetic. They are comprised of early – transition metals, usually in their d electronic configuration (e.g. Mo(VI), W(VI), V(V), Nb(V),...) bridged by oxygen. The principal building blocks of POMs are MO₄ polyhedra or MO₆ octahedra that are linked by one, two or occasionally three oxygen atoms. There are two classes of POMs: the isopolyanions, which contain only the d metal cations and oxide anions and heteropolyanions, which contain one or more d or p heteroatom cations, X⁽ⁿ⁺⁾, in addition to the metal cations and oxide anions.

All the physicochemical properties of POMs that impact their applications in catalysis, material science, biology and medicine, including but not limited to redox potentials, acidities, polarities, solubilities, sizes, shapes and charges, can be readily and systematically altered. This versatility follows directly from the element compositions and structures of the POMs, from the easy by which these can be modified.

POMs are readily accessible synthetically because most of the p -, d – and f – block elements can function as the central “heteroatom”, X⁽ⁿ⁺⁾, in the general formula XM₁₂O₄₀⁽⁸⁻ⁿ⁾⁻, Xⁿ⁺ is located at the center of the tetrahedron inside the Keggin structure), Many of d -, f – block metals can be substituted for one or more of the main metals, M, in the structure to give “mixed addenda anions”.

The process cycle delignification starts with the reaction of fully oxidized POM complexes under anaerobic conditions. At this stage, the POMs are reduced and oxidized lignin fragments are dissolved in the bleaching liquor. After the bleaching, the reduced POM liquor can be reoxidized in a separate stage using O₂. During the regeneration of the POM complexes, the dissolved lignin fragments are converted to CO₂ and H₂O.



The second generation of POMs has been developed. The first generation of POMs was able to operate only at acidic pH; the second generation of POMs is stable at pH level neutral. In this respect, the hydrolysis of cellulose is significantly reduced. Polyoxometalate Na₆SiW₁₀V₂O₄₀ was effective in reducing the kappa number of unbleached kraft pulp from about 30 to below 10 with limited losses in viscosity.

The third generation of POMs operates under aerobic conditions. In this respect, the possibility of oxygenating wood pulp is mixture of organic solvents with water in a single stage [28-30]. The oxidation of lignin under an oxygen atmosphere occurs via its reaction with POM while at the same stage the re-oxidation of a reduced form of POM by O₂ takes place. The presence of such a redox cycle could conceivably offer good process efficiency.

Peroxo – polyoxometalates

Peroxo – polyoxometalates (POMs) are a special class of POMs, which are widely used as catalysts in different process. A major use is in the catalytic epoxidation of olefins, alcohols, epoxides, sulfides, [31-36].

The delignification of kraft pulp with H₂O₂ catalyzed by transition metals was proposed and patented [37]. An acidic peroxide delignification stage was shown to be improved by the addition of transition metals selected from the group of W, Mo, Cr, Os and Se. Transition metal oxides under acidic conditions reacted with peroxide to form transition metal peroxo – complexes which are stronger oxidants than peroxide itself.

The ability of molybdate metal oxides to catalyze the acidic peroxide delignification of

kraft pulp was confirmed. The catalytic effect of molybdate was attributed to its ability to form under acidic conditions reactive diperoxo complexes with H₂O₂ [38-40]. Under acidic conditions silicomolybdenic acid activate peroxide bleaching, such anion, under optimal conditions are anticipated to be selective delignifying agent [41, 42]. Unfortunately, silicomolybdenic acids do not react with H₂O₂ to form peroxo – silicomolybdenic acid [4, 8].

We try to develop new family of catalysts based on peroxo – polyoxometalates for selective oxidation of lignin from wood pulp and especially natural fibers (hemp, flax and nettle).

EXPERIMENTAL

Materials and methods

Na₂MoO₄ · 2H₂O, NaWO₄ · 2H₂O, WO₃, MoO₃, NaOH and 30% H₂O₂ were used without further purification. POMs and PPOMs : K₅H₄PMo₆V₆O₄₀ · 10H₂O, Na₂H₃PMo₁₀V₂O₄₀ · 2H₂O, K₂(MoO(O₂)₂(C₂O₄)), K₂(W₂O₃(O₂)₄(H₂O)₂) · 2H₂O, Na₂(Mo₂O₃(O₂)₄(H₂O)₂) · 2H₂O and (NH₄)₈(Mo₁₀O₂₂(O₂)₁₂) · 16H₂O were prepared according to known or little improved preparation [4, 40, 42-46].

The compounds were characterized by elemental analysis, thermogravimetry, FTIR and Raman spectroscopy, UV – VIS and Raman spectra.

The bleaching of Eucalyptus pulp and hemp pulp were performed in two stages:

- *Stage 1:* in a plastic bag 100 gr. Pulp was suspended in 950 ml. water solution containing 0.01 gr. peroxo – catalysts, 1.5 – 2.0 gr. H₂O₂, the suspension was heated 2 hrs. at 90 °C in a thermostat water bath without stirring. The suspension was cooled at room temperature, the pulp was filtered off, washed with small portions of water and the filtrate which contains catalysts was keeping for the regeneration of catalysts. For the mixed addenda catalysts, the concentration of the catalyst in aqueous solution was 0.05 M.
- *Stage 2:* in a plastic bag, the pulp from stage 1 was suspended in 1 l. 0.1 N NaOH aqueous solution which contain 1.5 gr. H₂O₂ and 4 gr. Na₂SiO₃. The plastic bag with mixture was heated 1 hr. at 80 °C in thermostat water bath. After cooling at room temperature, the pulp was filtered off, washed with water at pH = 5-6 and dry at room temperature.

The bleaching of natural fibers (flax, hemp) with POMs and PPOMs were performed in two stages:

- *Stage 1:* in a plastic bag, 100 gr. natural fiber was suspended in an aqueous solution [1.2 l.] which contains 0.1 gr. peroxy – catalyst, 2 – 3 gr. H₂O₂, the plastic bag was heated 21 hr. at 90 °C in a thermostat water bath. After cooled at room temperature, the natural fiber was filtered off, washed with small portions of water and the filtrate contain catalyst was reactivated and reused again.
- *Stage 2:* in a plastic bag, the natural fiber from stage 1 was suspended in 1.2 liter 0.1 N NaOH aqueous solution contains 2.0 – 2.5 gr. H₂O₂ and 4 gr. Na₂SiO₃. The plastic bag was heated 1 hr. at 80 °C in a thermostat water bath. After cooling at room temperature, the natural fiber was filtered off, washed with water till pH = 6.0 and dry in the air at room temperature.

RESULTS AND DISCUSSIONS

Catalysts:	Kappa	Viscosity(mL/g)	Brightness(%)
O ₂ delignification	10.9	1075	64.9
K ₂ [MoO(O ₂) ₂ (C ₂ O ₄)]	2.26	769	81.4
K ₂ [W ₂ O ₃ (O ₂) ₄ (H ₂ O) ₂]	1.69	811	84.8
Na ₂ [Mo ₂ O ₃ (O ₂) ₄ (H ₂ O) ₂]	1.66	806	85.0
(NH ₄) ₈ [Mo ₁₀ O ₂₂ (O ₂) ₁₂]	1.49	807	85.4
K ₅ H ₄ PMo ₆ V ₆ O ₄₀	8.50	805	72.4
Na ₂ H ₃ PMo ₁₀ V ₂ O ₄₀	8.24	778	73.5



The experimental results are presented in tables 1 – 3 of bellow.

Table 1 Bleaching of eucalyptus pulp

Fig.1 Left: bleached hardwood using POM-E-POM; Right: unbleached initial hardwood

Table 2 Bleaching of hemp pulp

Catalysts	Kappa	Viscosity / mL/g	Brightness / %
Unbleached pulp	12.2	987	38.8
K ₂ [MoO(O ₂) ₂ (C ₂ O ₄)]	1.4	814	83.7
K ₂ [W ₂ O ₃ (O ₂) ₄ (H ₂ O) ₂]	1.3	810	84.2
Na ₂ [Mo ₂ O ₃ (O ₂) ₄ (H ₂ O) ₂]	1.2	794	84.9
(NH ₄) ₈ [Mo ₁₀ O ₂₂ (O ₂) ₁₂]	1.1	802	85.2
K ₅ H ₄ PMo ₆ V ₆ O ₄₀	9.6	720	62.2
Na ₂ H ₃ PMo ₁₀ V ₂ O ₄₀	9.3	734	65.5



Fig.2 Left: unbleached hemp; Middle: bleached hemp (using POM catalysts); Right: bleached hemp following alkali extraction.

Table 3 Bleaching of natural fibers

Catalysts:	Brightness (%)	
	flax	hemp
Unbleached fibers	38.4	40.2
K ₂ [MoO(O ₂) ₂ (C ₂ O ₄)]	78.2	78.8
K ₂ [W ₂ O ₃ (O ₂) ₄ (H ₂ O) ₂]	78.7	79.2
Na ₂ [Mo ₂ O ₃ (O ₂) ₄ (H ₂ O) ₂]	79.5	80.6
(NH ₄) ₈ [Mo ₁₀ O ₂₂ (O ₂) ₁₂]	80.8	81.4
K ₅ H ₄ PMo ₆ V ₆ O ₄₀	65.2	64.1
Na ₂ H ₃ PMo ₁₀ V ₂ O ₄₀	70.0	71.3



Fig.3 Left: unbleached flax; Middle: bleached flax (using POM catalysts); Right: bleached flax following alkali extraction.

CONCLUSIONS

Peroxometalates activated hydrogen peroxide, they can be considered as efficient and selective catalysts for oxidation of lignin from wood pulp and natural fibers. The mechanism of selective oxidation reaction of lignin is quite different than of polyoxometalats with Keggin structures.

The peroxotransition-metal complexes / hydrogen peroxide system efficiently generate molecular oxygen at room temperature. This catalytic system was need for the first time in our research team for the bleaching of hemp pulp and natural fibers with good experimental results.

There is a possibility to achieve brightness over 80% for the pulp from wood and from hemp using peroxometalates of Mo (VI) and of W (VI) as catalysts at a level of specific consumption of 1 kg / to_{BDT}. This can be achieved in 2 stages without a significant decrease of bleached pulp viscosity.

In the bleaching process of hemp and flax natural fibers using catalysts from Mo (VI) and W (VI) peroxometalates class, the achieving brightness over 80% depends a lot of the presence of the mechanical impurities (sand, soil) within the unbleached fibers. Therefore it is necessary the pretreatment of the unbleached fibers before of the bleached process.

The peroxometalates of Mo (VI) and of W (VI) presents in the filtrate of the first stage of unbleached pulp treatment, together with the dissolved lignin fragments can be easily regenerated by H₂O₂ treatment at a temperature of 70 – 80 °C. The lignin fragments are finally oxidized at CO₂ and H₂O.

In the process of bleaching of pulp and natural fibers were used peroxometalates isolated in solid phase, respectively peroxometalates directly synthesized in aqueous solution.

Because of the economic reasons, in the pilot pulp and natural fibers bleaching trials (samples of 20-30 kg of natural fibers was used) were used peroxometalates directly synthesized in aqueous solutions.

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ASSESSING THE COMPATIBILITY OF COMPOSITE STRUCTURES BASED ON LIGNOCELLULOSIC FIBERS WITH THE DEVELOPMENT PROCESS OF PLANT SEEDLINGS

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Abstract

This paper studies the physical, chemical and microbiological characteristics of nutritive biodegradable pots based on cellulose fibers and peat, in the context of their use in production of vegetable seedling. Following the use of different compositional versions of nutritive biodegradable pots to produce the tomatoes and lettuce seedling, results revealed that these nutritive pots are a *resilient support* for a variable duration depending on the cultivated plant, but also a particular form of *biological active material* that by successive destruction in soil give it the biostimulative effects. Therefore, the technological parameters related to biological stability were met, the retention capacity and dismissal of key nutrients, based on microbiological activity of rhizosphere, there are at a high level. Regarding the morphological characteristics of plants, was established that the tested nutritive pots have a positive influence on the plants growth and are able to ensure the normal growth regime.

Key words: Biodegradable nutritive pots, Soil, Seedling, Plants, Biodegradability

Rezumat

În lucrare se evaluează caracteristicile fizice, chimice și microbiologice ale suporturilor nutritive biodegradabile pe bază de fibre celulozice și turbă, în contextul utilizării lor în procesul de producție a răsadurilor de legume. În urma utilizării unor variante compoziționale diferite de suporturi nutritive biodegradabile la producerea răsadurilor de tomate și salată, rezultatele obținute au scos în evidență faptul că aceste suporturi reprezintă în primul rând un suport rezilient al răsadului dar și o formă particulară de îngrășământ organo-mineral complex care prin destrucție succesivă în sol conferă efecte biostimulative. Prin urmare, parametrii tehnologici cu privire la stabilitatea biologică au fost la un nivel ridicat (capacitatea de retenție și capacitatea de eliberare a elementelor nutritive). Cu privire la caracteristicile morfologice ale plantelor, s-a constatat că suporturile nutritive testate au o influență pozitivă asupra plantelor, fiind capabile să asigure un regim normal de creștere și dezvoltare.

Cuvinte cheie: Suporturi nutritive biodegradabile, Sol, Răsad, Plante, Biodegradare

INTRODUCTION

In the recent years, there has been an enhancement of introduction lignocellulosic fibers as substrate to achieve the nutritive biodegradable pots for vegetable production. This is a modern solution to reduce environmental pollution generated by plastics from agricultural sources and to restore the flow of ecosystem recycling of important organic matter sources, respectively,

wastes from agricultural products processing and recovered papers and paperboards. [1]

Physical, chemical and microbiological properties of these composite structures are strongly influenced by the properties of component materials, the distribution and interactions that occur between them, having direct implications on the plants development process and their morphological parameters. [2]

Lignocelluloses fibrous materials represent the main raw material for biodegradable nutritive pots, and have a key role in composite structure forming, strength properties development, as well as in the pots' biodegradability. Under these circumstances, the most used fibrous materials are: Kraft pulps to achieve the needed strength of the structure; recycled pulp fibers, obtained from different waste used paper products that mainly function as consolidation material in structure forming; and peat consisting of vegetal material, including wood fibers in various degradation stages, that provides the porosity, adsorption and water retention capability of composite structure, as well as nutritive properties. [1,2]

Assessing the compatibility of such composite structures based on lignocellulosic fibers with plant seedlings development was based on the results obtained within two directions of investigation: 1. assessment of physical and biological strength characteristics during variable time period depending on plant cultivation; 2. evaluation of morphological characteristics of seedling.

EXPERIMENTAL

Materials

Recycled fibers

Secondary fibre pulp, obtained by slushing, sorting and cleaning of old corrugated containers (OCC).

Peat

Oligotrophic red peat, consisting of sediments containing hygrophite plants and moss, decomposed in an anaerobic environment for long terms.

Additives

Within the experimental program, the following types of chemical additives were used:

- *mineral salts* as source of various chemical elements [4]: *urea and dibasic ammonium phosphate* – to release nitrogen and phosphorus; *borax and ammonium molybdate* – to release microelements as boron and molybdenum; *zinc sulphate and*

- copper sulphate* for zinc and copper; and *potassium nitrate* to release potassium;
- *chitosan* – natural polymer derived from chitin, polysaccharide consists of β (1-4)-2-amino-2-deoxy-D-glucose units or D-glucosamine, with high molecular weight and linear structure, which contains amine functional groups and primary and secondary hydroxyl, added to control of the biodegradation capacity, as an inhibitor of pathogenic fungi, as incentive germinating and to increase of plants resistance to infection;
- *waste from grape processing* (bunching and peeling wastes) that were dried and crushed as powder - as a biochemical aid and partial substitute for the fibrous material;
- *wet-strength resin* - in order to improve the wet strength of the composite fibrous structure, a polyamide epichlorhidric resin (Kymene 611, Hercules GmbH) was used.

Methods

Obtaining composite materials

Four compositional versions of biodegradable nutritive pots dedicated to producing the seedling material were obtained, as follows:

- **S1 version:** mixture of peat + cellulosic fibers (100%) and chemical aid charge;
- **S2 version:** mixture of peat +cellulosic fibers (85%) and residue from grape processing;
- **S3 version:** mixture of peat and cellulosic fibers (100%); a charge of 6% wet strength resin (Kymene 611) was used in these three compositional versions;
- **S4 version:** mixture of peat cellulose fibers (100%) + chemical aids, in this composition a half of the wet strength resin charge was replaced with chitosan.

The nutritive pots were made as a conoid (H = 6 cm, D = 6.5 cm, d = 4.2 cm) of 5.1 – 9.0 g weight by means of a pilot plant that operates based on the formation and dewatering system through die molding, following the stages illustrated in Figure 1. The obtained nutritive supports were dried in an oven at a temperature of 105°C. [2]

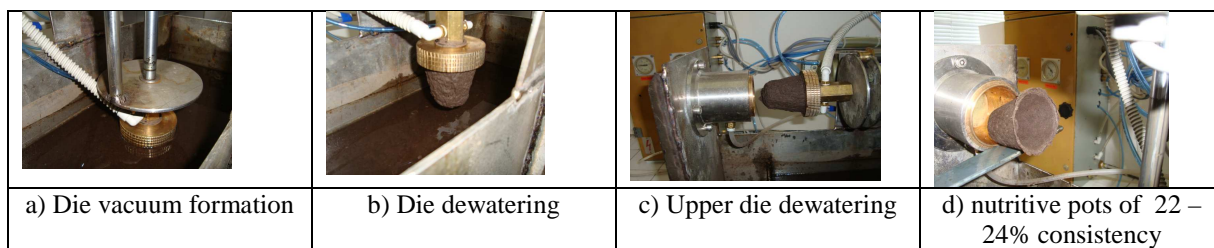


Fig.1 Formation and dewatering of biodegradable nutritive pots

The mechanical strength properties are some of the most important for a composite structure, since regardless their specific application, they should meet certain characteristics as regards shape, hardness, and strength. A specific device for strength evaluation was developed in order to simulate the specific form and individual stresses that biodegradable nutritive pots are subjected to. (figure 2).[3] The principle consists of the plunger penetration moved with constant speed through the upper clamp of Instron testing device inside of biodegradable pot and measuring of the resistance opposed to plunger advance by a sensor-transducer installed on the upper clamp of device. It is registered the maximum load resisting to penetration.

Strength tests of the pots were carried out both on samples conditioned in the standard atmosphere (23°C, moisture 50% RH) and wetted by water immersion at 23°C for 15 minutes.



Fig. 2 The testing device of nutritive pot strength

Biodegradability testing

The biodegradability of nutritive pots was evaluated through the determination of the cellulosic degradation rate (Ștefanic 1999), using the following procedure: from the handsheets of composite materials was prepared the nutritive pots pot samples that were dried at 105°C and then incubated in a Terracult nutritive substrate

used in producing seedlings. During incubation, tested nutritive pots were introduced in a previously weighted synthetic bag, in order to recover totally the fibrous material contained in it. During the entire experimenting period, the effective substrate moisture wherein pots were introduced was maintained in the range of 60 to 65% relative humidity, and temperature in the range 24 to 28°C. Testing samples were regularly obtained by following method: the bag containing the sample was taken out of the substrate, flushed thoroughly, dried in the oven at 105°C for 4 hours, and then weighed. The biodegradation rate (degradation degree) was calculated as follows:

$$\% \text{ decomposed cellulosic material} = \frac{Gi - Gf}{Gi - Gs} \times 100 \quad (1)$$

Gi – sample weight + bag weight before being introduced in the pot

Gf – sample weight + bag weight after taken out of pot

Gs – bag weight

Another indicator emphasizing the substrate biological activity is the *capability to create a favorable environment for developing a typical microflora for soil and culture substrates*. This indicator has been evaluated by microflora respiration intensity, having in view that microflora are involved in cellulosic material degradation (Szegi 1988). The experiments have been carried out on both experimental nutritive pots and the current process for the production of lettuce (*Lactuca sativa*, var. Capitata) and tomatoes (*Lycopersicum esculentum*) seedlings.

RESULTS AND DISCUSSION

The results obtained after strength testing are presented in Figure 3.

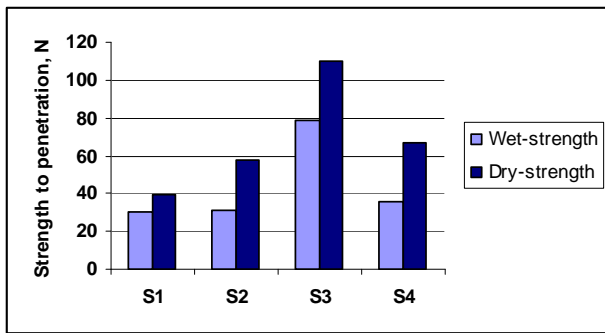


Fig. 3 Strength to penetration (dry and wet) of tested nutritive pots

Mechanical strength of composite material structure (regarding how it can support the traction and pressure loads) should be evaluated for both, in dry and wet state when the structure is saturated with water. The optimization of this parameter is difficult for the following reasons: the strength of composite material influence both, the manufacturing processes of nutritive pots using die dewatering, and their behavior in applications for germination, growth and transplantation of seedlings into the soil. The difficulty arises from the fact that some strength requirements are somewhat opposite: to obtain the composite material as nutritive pot using the die forming are required relatively high resistance, while when it is used in the seedlings production, in the first stage the resistance must have an appropriate level, especially in wet state (composite material will work in wet conditions), and after a period, strength of

penetration should be low enough to allow roots to penetrate the composite material structure.

Given these considerations, it can be seen easily from the in Figure 3 that the best properties of strength, both to test the dry and wet testing of nutritive pots were presented by the S3 version. It seems that in case of S1 version, the addition of nutrients as salts has adversely effect on the resin retention and cross-linking, known that the resin adsorption onto fibers decreases substantially with increasing valences of metal ions and their concentration in the pulp [4]. In case of S2 version, the addition of waste from grape processing fragments the fibrous network continuity and enter the fine and colloidal material with anionic charge. It is very interesting the behavior of the S4 version where it is noted that a combined of additives charge, consisting of Kymene resin and chitosan, leads to the similar values of wet and dry resistance with those that can be achieved with Kymene only (S1 and S2 versions). Effects of chitosan on the dry and wet strength of nutritive pots, lead to the hypothesis that it interacts faster with anionic colloidal material than resin Kymene, thus contributing to improving of wet strength and better resin retention. The direct contribution of chitosan to improve of nutritive pots dry strength could be explained by the affinity of polymer to lignocellulosic compounds and by its cationic charge that leads to heterocoagulation of fine and colloidal material on fibers surface. [5] This mechanism could explain the slight increase structure porosity of material, which leads easily to walls penetration by plant roots. (Figure 4)

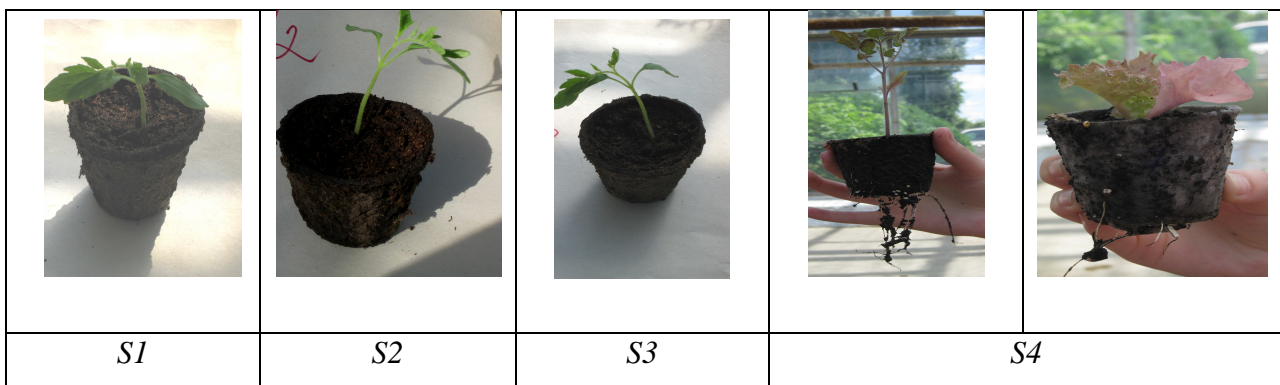


Fig.4 Nutritive pots behavior during plant seedling

Regarding to the degradation potential and biological activity of microorganisms, can be seen in the graphs from Figures 5 and 6 that, unlike the other compositional versions, S4 version without plant has a daily rate of biodegradation much higher than S1 version. On

the one hand, this aspect can be attributed reducing the addition of wet strength resin, even if the value of this parameter is higher compared with S1 version, and on the other hand, the presence of chitosan leads to a more porous structures easily accessible to microorganisms

that are involved in biodegradation. During operating conditions, can be noted that the plants, by rizosphere effect, causes a decrease of daily degradation rate in case of pots obtained with version S4. This aspect can be explained by the fact that the plants, for growth and development, consumes a lot of nutrients,

competing for food the microorganisms involved in biodegradation. This behavior of S4 version compared with S1, S2 and S3 can be attributed, also, to chitosan from composition that can acts as incentive germinative and regulator of biodegradation capacity.

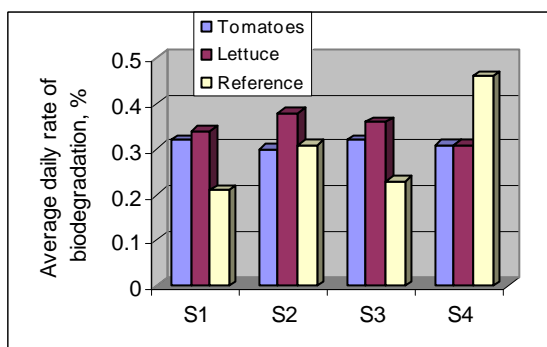


Fig.5 Development of daily average biodegradation rate of nutritive pots cultivated on seedlings

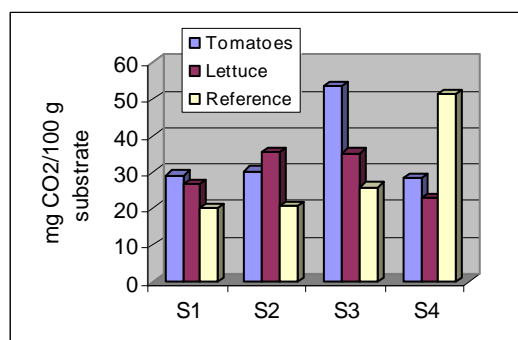


Fig.6 Respiratory potential (mg CO₂/100 g substrate) of substrate in rhizosphere of lettuce and tomatoes

Table 1 presents the morphological characteristics of plants, where it can be seen that for all versions studied, growth indicators have values which allow their classification to the acceptance limits and in accordance with the literature. Although the absolute values obtained

for growth parameters, S4 version is lower compared to S1 and S3, a good penetration of walls by the plants roots were not physiologically stressed, and to be within a normal regime of growth.

Table 1 Morphological characteristics of the seedlings planted in biodegradable nutritive pots

Plant characteristics	S1	S3	S4
Tomatoes			
Height, cm	20,8	18,8	14,9
Roots length, cm	20,1	19,2	11,5
Number of leaves	6	5	5,6
Roots volume, cm ³	3,5	2,3	0,86
Penetration capacity of pot walls	High	Very high	Low
Lettuce			
Height, cm	15,1	16,8	4,6
Roots length, cm	15,4	15,8	9,6
Number of leaves	8,0	7,8	4,6
Roots volume, cm ³	2,6	2,1	1,06
Penetration capacity of pot walls	High	Very high	Low

CONCLUSIONS

1. Biodegradable nutritive pots based on lignocellulosic materials used in the production of vegetables constitute an organic material reserve for soil; such applications are aligned with the European Directives concerning to reduce of environmental pollution with plastics from agricultural sources by re-introducing in the eco-systemic cycle some important recyclable resources of organic matter: recovered paper and board, as well as residues from grape processing;
2. The mechanical strength properties and biodegradation capacity of tested nutritive pots prove that these composite structures are able to maintain their structural integrity until the roots of seedling are high dispersed in the substrate walls;
3. Obtained results for the compositional versions containing chitosan have shown that these structures have, besides to an appropriate level of wet and dry mechanical strength, a good capacity of walls

penetration by plant roots, which leading to a more appropriate development without physiological stress.

ACKNOWLEDGEMENTS

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STUDY CONCERNING THERMAL STABILITY OF SOME HYDROXYMETHYLATED LIGNINS

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Abstract

The aim of the research was to characterize through thermal analysis in dynamical conditions, of five types of lignins : L1 (lignin of wheat straw), L2 (lignin of grass) and Pb1000, Pb2000, Pb3000 (comercial products), offered by GRANIT company, modified through hydroxymethylation reaction in different conditions of temperature and pH, to obtain some information referring to thermostability and degradation mechanism. With this end in view the thermal dynamic analysis (TG, DTG) has been applied and kinetic processing of thermogravimetric data using STARE software. The results shows that degradation take place in two or three steps after an complex mechanism. For each step the kinetic parameters and thermogravimetric characteristics have been evaluated.

Cuvinte cheie: Lignină, Hidroximetilare, Termogravimetrie, Parametri cinetici, degradare.

Rezumat

S-a efectuat un studiu privind caracterizarea prin analiză termică în condiții dinamice, a cinci tipuri de lignină L1 (lignină din paie de grâu), L2 (lignină din iarbă) și Pb1000, Pb2000, Pb3000 (produse comerciale), oferite de firma Granit, modificate prin reacția de hidroximetilare în diferite condiții de temperatură și pH, în vederea obținerii unor informații referitoare la stabilitatea lor termică și la mecanismul de degradare. În acest scop s-a folosit analiza termică dinamică (TG, DTG) și prelucrarea cinetică a datelor termogravimetrice utilizând softul STARE. Rezultatele evidențiază ca procesul de degradare decurge în două sau trei etape după un mecanism complex. Pentru fiecare etapă s-au evaluat parametrii cinetici și caracteristicile termogravimetrice.

Keywords: Lignin, Hydroxymethylation, Thermogravimetry, Kinetic parameters, Degradation.

INTRODUCTION

Lignin is a natural macromolecular compound more chemically active than cellulose or other natural polymers due to the functional groups contained in its structure. Being the main aromatic component of plant tissues, representing 20-40% of higher plants mass lignin is located in the cellular wall and in intercellular spaces [1, 2]. It is the second most abundant polymer on the Earth, following cellulose, about 50 million tons of lignin being produced annually as a residue of pulp production. However, due to its numerous

functional groups and bio-properties, lignin offers new important possibilities in the preparation of ecological adhesives, in water treatment and agriculture. Based on these considerations, chemical modifications are performed to adjust the functional properties for specific applications.

The condensation reaction of the non-modified lignin with the formaldehyde will result in a three-dimensional structure with a limited number of branching points and it will therefore be a more fragile resin than a phenol-formaldehyde [3-6]. The research tendencies are related to the chemical reactions as well as to the

biochemical one applied for residual lignocelluloses complex, which consequently increase its functionality and reactivity [7-9]. Initial lignin characteristics and those of its derivatives can be investigated through chemical and spectral methods, and thermogravimetry [10, 11]. In this way we can highlight functional groups and thermal properties, which provide very useful information in order to predict the behavior of lignin derivatives and the applications and properties of the products to be made. In this context, the results presented in this paper refer to the hydroxymethylation of lignin's separated from annual plants (wheat straw and Sarkanda grass) and the characterization of synthesized derivatives through thermogravimetry (TG, DTG) methods.

In this context, the results presented in this paper refer to the hydroxymethylation of lignin's separated from annual plants (wheat straw and Sarkanda grass) and the characterization of synthesized derivatives through thermogravimetry (TG, DTG) methods.

EXPERIMENTAL

1. Materials

In this study the following materials have been used: lignin from wheat straw (L1), lignin of Sarkanda grass (L2), resulted from alkaline delignification process and three commercial products: Protobind 1000 (Pb1000) Protobind 2000 (Pb2000) Protobind 3000 (Pb3000), offered by the Granit company SA Recherche Development Lausanne, Switzerland. The five types of lignin studied were chemically modified by hydroxymethylation reaction [3, 4, 11].

2. Method

Lignin hydroxymethylation

37 g lignin a.d. were gradually dissolved in 130 mL NaOH solution of concentration 3 %, at room temperature under mechanical stirring for one hour. The pH of the solution thus obtained was checked and corrected till 10.5 using a solution of 3N NaOH. Then 24.1 mL solution of formaldehyde (37 %) was added and the stirring was continued at a temperature of 90 °C, for three hours. Periodically, at each hour, samples were taken from the reactor to determine the reacted formaldehyde. After three hours, the reaction mixture was cooled and treated with a solution of HCl 1N to obtain a pH 2. The hydroxymethyl derivatives were separated through centrifugation at 2500 rpm for 10 minutes and the precipitate was washed with distilled water and dried [3,11].

RESULTS AND DISCUSSION

The modification of lignin through *hydroxymethylation* is known for a long time and consists in the introduction of hydroxymethyl groups in the aromatic ring.

The hydroxymethylation reaction has been applied both for lignins separated from the two annual plants and commercial products offered by the producer under the name of Protobind. The lignin reactivity depends on its structure taking in consideration that the hydroxymethyl groups are introduced in the guaiacyl structural units. In the following discussion, the reaction products of hydroxymethylation were symbolized as L1H, L2H, Pb1000H, Pb2000H and Pb3000H, and their functional characteristics are presented in Tables 1 [3, 5, 8, 11]:

Table 1 The functional groups of hydroxymethylated lignins obtained in optimum reaction conditions

Sample	OH total groups	Ar-OH groups	OCH ₃ groups	Ak/Ar ratio	C=O groups	S/G ratio
L1	1.06	0.93	0.94	0.72	0.80	0.82
L1H	1.16	0.98	1.13	1.20	0.93	0.97
L2	1.05	0.91	0.96	0.88	0.88	0.82
L2H	1.34	0.95	1.10	1.11	0.92	0.85
Protobind 1000	1.10	0.89	1.05	1.17	0.89	0.83
Pb1000H	1.15	0.98	1.13	1.20	0.91	0.96
Protobind 2000	1.12	0.90	1.05	0.71	0.78	0.73
Pb2000H	1.18	0.97	1.11	0.72	0.8	0.75
Protobind 3000	1.14	0.91	1.09	0.73	0.68	0.79
Pb3000H	1.19	0.99	1.14	0.75	0.81	0.99

The content of functional groups was determined according to the methods presented by different research groups. The determination of total hydroxyl groups was done by the comparison of UV-VIS spectra of the samples before and after chemical modification with acetic anhydride in pyridine medium, in the same manner, the phenolic OH group's content was established using UV-VIS method; in addition the determination of total hydroxyl groups was performed using FTIR spectra [11]. The other methods applied for chemical characterization were: the determination of carboxylic groups and methoxyl groups, aromatic hydroxyl groups, the calculation of the phenolic groups/aliphatic groups' ratio, as well as, the determination of syringyl/guaiacyl unit's ratio. The behind chemical analysis the characterization by thermogravimetry of these products unmodified and modified by reaction of hydroxymethylation [3, 11] was performed.

Thermal stability

A structural characterization of the initial and hydroxymethylated lignins provides the information referred to thermal stability of the compounds. The thermogravimetric analysis is known as a thermoanalytic method that is used to determine the rate for the chemical reactions which take place under the action of temperature necessary to assess the thermal stability of a product, an important characteristic for certain applications. The recorded data show that the thermal decomposition of the lignin from wheat straw (L1), grass lignin (L2) or the

commercial products Pb2000, Pb3000, as well as the thermal decomposition of the chemically modified lignin by reaction of hydroxymethylation are not complete one and generate a quantity of approximately 40-50% residue.

The thermal degradation of lignin from wheat straw (L1) and grass (L2) occurs in two stages (figure 1). In the first stage the humidity from the sample is diminished to approximately 4.8% and during the second stage the thermal decomposition takes place.

In the case of commercial Protobind samples and hydroxymethylated derivatives the degradation process consists of three stages (figure 2), the most significant mass loss being registered in the last stage. The lignins modified by hydroxymethylation reaction in different conditions of temperature and pH are thermally degraded in two or three steps. During the last stage of the samples degradation the temperature characteristic for the highest degradation rate ($\approx 370^\circ\text{C}$) is approximately the same for all analyzed samples. Additional information concerning the mechanism of thermal degradation of lignin can be obtained from the kinetic processing of the thermogravimetric data. (The METTLER TOLEDO device is equipped with STARE SW 9.10 software). In this way, there were determined the kinetic parameters by applying the method Freeman-Carroll and the obtained values are presented in Table 2 [11].

Table 2 The kinetic parameters of the lignin thermal degradation

Sample	Degradation stage	ln A	Ea (KJ/mol)	n
L1	II	4.83±1.67	56.48±1.67	1.08±0.005
L1H_90_pH=10.5	II	2.48±0.21	38.55±0.85	0.59±0.0029
	III	8.98±0.26	78.11±1.34	1.78±0.0024
L2	II	4.21±0.3	52.49±1.42	1.25±0.0045
L2H_90_pH=10.5	II	9.30±0.19	79.39±0.56	1.89±0.00225
Pb1000	II	3.81±0.18	43.85±0.75	0.76±0.0024
	III	16.76±0.25	117.43±1.27	1.52±0.016
Pb1000H_90_pH=10.5	II	1.54±0.24	35.54±1	0.52±0.003
	III	8.80±0.39	77.54±2.03	1.74±0.0034
Pb2000	II	5.38±0.17	47.27±1.15	1.07±37.65
	III	6.31±0.14	63.31±0.73	0.83±10.39
Pb2000H_90_pH=10.5	II	5.30±0.17	47.02±0.68	0.63±16.79
	III	10.87±0.40	87.11±2.07	1.75±33.92
Pb3000	II	1.81±0.61	29.73±2.27	0.64±65.99
	III	2.85±0.21	45.17±1.02	0.98±24.88
Pb3000H_90_pH=10.5	II	5.63±0.26	50.62±1.09	0.66±22.95
	III	2.03±0.34	41.41±1.76	1.00±25.63

(A - preexponential factor, Ea - apparent activation energy, n - reaction order)

To process these data, Freeman-Carroll method based on the following equation was applied [11, 12]:

$$\frac{\Delta \ln \frac{d\alpha}{dT}}{\Delta \ln(1-\alpha)} = n - \frac{Ea}{R} \times \frac{\Delta \left(\frac{1}{T}\right)}{\Delta \ln(1-\alpha)}$$

and the kinetic characteristics are shown in Table 2. Drawing graph dependency of $\Delta \ln (d\alpha / dt) / \Delta \ln (1-\alpha)$ by $\Delta (1 / T) / \Delta \ln (1-\alpha)$, the activation energy (Ea) and order of reaction (n) can be calculated. Preexponential factor was obtained by using the following equation:

$$\frac{d\alpha}{dT} = \frac{1}{a} A \exp\left(\frac{-Ea}{RT}\right) f(\alpha)$$

Different values of the reaction order may be explained by supposing a radicalic mechanism for the thermal degradation of the studied compounds.

Analyzing the apparent activation energies of the last thermal degradation stage of the samples modified by hydroxymethylation, the values around of 70-80 kJ / mol are comparable with those recorded in the case of unmodified lignin. The activation energy and the order of the reaction have lower values.

The exceptions appear in the case of Pb1000 and Pb2000H samples when the activation energy presents the highest values registered among all the lignins characterized by thermal analysis. The kinetic parameters of Pb1000 may be correlated with its higher content of carbonyl groups in comparison with those of other types of lignin and with a high ratio of aromatic and aliphatic groups (Ak/Ar) as well as with a higher ratio of syringyl and guaiacyl units (S/G).

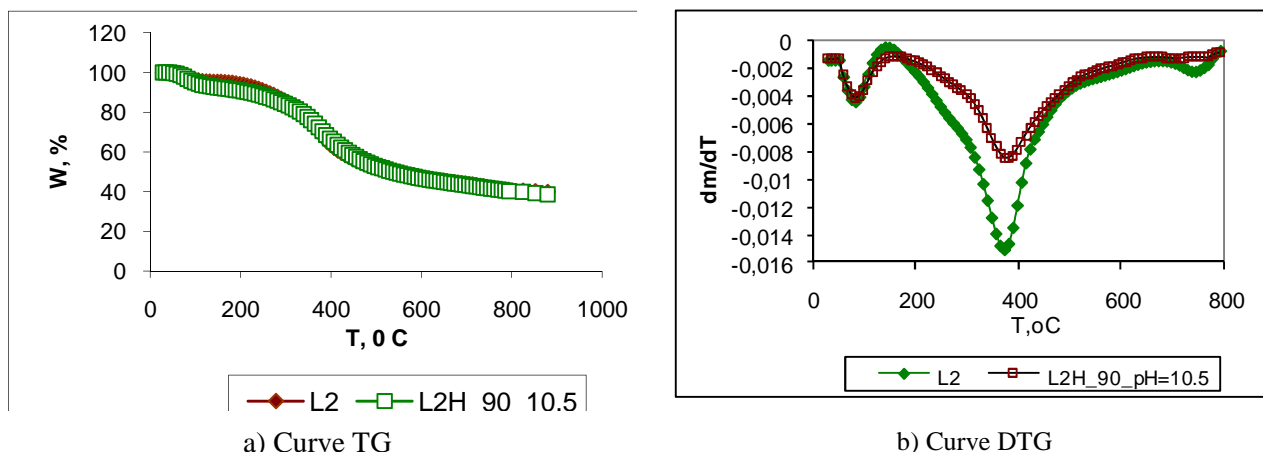


Fig. 1 The thermogravimetric curves for L2 (lignin of lignin from the grass) and for hydroxymethylated samples L2H_90_10.5

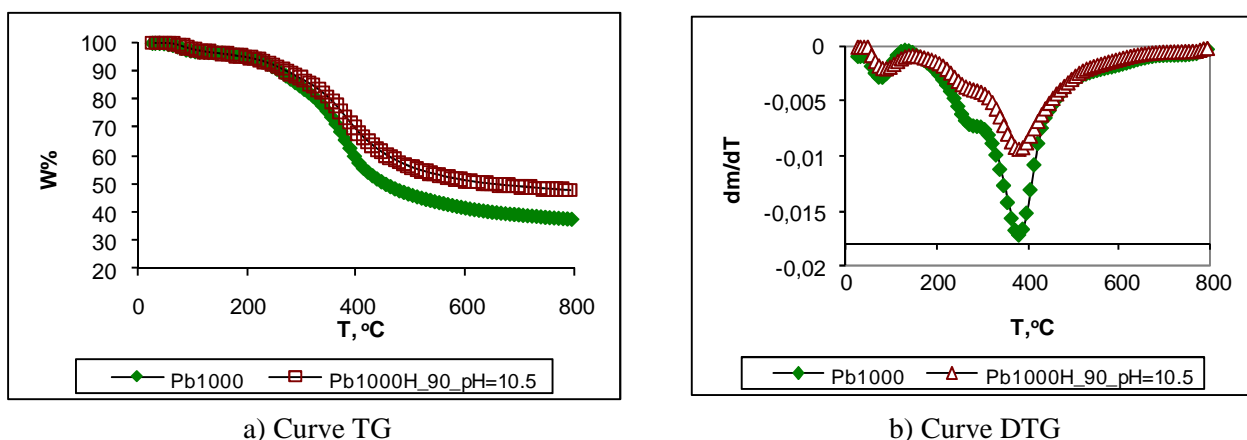


Fig. 2 The thermogravimetric curves for Pb1000 and hydroxymethylated sample Pb1000H_90_10.5

Table 3 The characteristics of thermal degradation process of lignins and their and derivatives

Samples	Degradation stage	T _i (°C)	T _{max} (°C)	T _f (°C)	Mass losses (%)
L1	I	56	78	110	4.75
	II	204	376	584	55.25
L1H_90_pH=10.5	I	62	72	111	5.71
	II	237	264	336	14.26
	III	336	376	563	34.97
L2	I	59	80	111	4.85
	II	222	373	467	54.69
L2H_90_pH=10.5	I	58	84	117	8.94
	II	265	371	540	51.35
Pb1000	I	52	77	106	3.31
	II	229	267	330	17.05
	III	330	383	532	42.47
Pb1000H_90_pH=10.5	I	64	83	122	4.71
	II	244	264	341	14.03
	III	341	379	523	34.28
Pb2000	I	63	75	110	1.86
	II	205	234	326	22.78
	III	326	381	496	39.23
Pb2000H_90_pH=10.5	I	56	79	115	5.06
	II	216	248	328	12.90
	III	329	3374	580	36.37
Pb3000	I	54	72	88	2.18
	II	147	196	267	11.01
	III	267	369	479	46.73
Pb3000H_90_pH=10.5	I	54	77	116	6.53
	II	241	257	330	13.50
	III	330	379	570	31.49

(T_i- initial temperature at which degradation begins, T_{max}- temperature corresponding to maximum rate of degradation, T_f- final temperature and W - mass losses percentage).

The most important thermogravimetric characteristics are presented in table 3. Thermal degradation of commercial products offered by the company Protobind Granite and those modified by hydroxymethylation reaction take place in three stages with the most significant mass loss percentage in the last stage. Lignins modified by hydroxymethylation reaction in different conditions of temperature and pH, are degraded in two or three stages. The moisture content of these samples is approximately 5.7%. The most significant degradation temperature values were achieved in case of Protobind modified commercial samples, exceeding the value of final temperature of 500 °C [11]. In the last stage of degradation of the samples the temperature at which maximum rate of degradation is achieved, has about the same value for all analyzed samples - T_{max} ≈ 370 °C.

If worst neglect the first stage in which the moisture from the sample was removed,

analyzing the second stage T_i it can be observed that the thermostability was modified by hydroxymethylation, being increased by about 10-30 °C.

CONCLUSIONS

1. The unmodified and hydroxymethylated lignins samples were characterized using chemical and spectral analysis), the techniques bring off the possibility to distinguish the functional modification appeared in lignin derivatives after hydroxymethylation.

2. The lignin samples modified by hydroxymethylation are characterized by a different thermal stability appreciated by activation energy and reaction order. The apparent activation energies calculated from the last stage of thermal degradation of the lignin samples modified by hydroxymethylation have values about 70-80 kJ / mol. In the case of

Pb1000, Pb1000H and Pb2000H samples the activation energy has much higher values in comparison with the other samples submitted to thermal analysis.

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ON THE POTENTIAL USES OF VEGETAL FIBERS IN ENVIRONMENTALLY FRIENDLY BUILDING MATERIALS

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Abstract

The current paper reviews the potential applications of vegetal fibers as reinforcements in cement fiber composites. Some considerations regarding manufacturing processes and factors affecting mechanical properties of composites are presented. Some aspects regarding the environmental impact and life cycle of the vegetal fiber composites are also discussed.

Keywords: *vegetal fiber, cement matrix, environmentally friendliness*

Rezumat

Lucrarea de față este o trecere în revistă asupra potențialelor aplicații ale fibrelor vegetale ca materiale de ranforsare în compozitele pe bază de ciment. Sunt prezentate unele considerații cu privire la procedeele de fabricare și factorii care afectează rezistența mecanică. De asemenea sunt discutate și unele aspecte privind impactul ecologic și ciclul de viață ale compozitelor cu ciment ce includ fibre vegetale.

Cuvinte cheie: *fibre vegetale, matrice de ciment, compatibilitate cu mediul ambiant.*

INTRODUCTION

Over the last decade there has been a continuous debate on the potential of integrating vegetal fibers into new and environmentally friendly building composite materials. Vegetal fibers have an enormous potential of replacing classical energy intensive materials, considered responsible for global climate change. The environmentally friendliness of vegetal fibers resides on their economicity (low cost and low resource consumption for their production) renewability, low density, recyclability, biodegradability and carbon sequestration. These advantages make vegetal fibers a potential replacement for glass fibers and other synthetic fibers in composite materials. Mechanical properties of vegetal fibers, especially flax, hemp, jute and sisal, are very good and may compete with glass fiber in specific strength and modulus [1-3]. Typical examples of vegetal fibers used for the production of composites include jute, hemp,

cotton, kenaf and last but not least wood fibers, wood pulp and recovered paper. Agricultural residues such as straws, rapeseed plant residues and others [4] have lately drawn the attention as potential new vegetal fiber resources.

Several widely cited disadvantages of the vegetal fibers uses in field applications may include: high level of moisture absorption capacity, dimension instability, susceptibility to microbial attack and rotting, restricted processing temperature due to low decomposition temperature of cellulose, insufficient adhesion with matrix and aging [5]. However despite the mentioned disadvantages the vegetal fibers have been extensively investigated as possible substitutes for the synthetic fibers [6].

The aim of this article is to review the potential applications of vegetal fibers as reinforcements in inorganic composites taking into account some aspect regarding the manufacturing processes, possible advantages, disadvantages and material performance improving methods. Some aspects to be considered in an environmental impact assessment by life cycle assessment (LCA) of the vegetal fiber composites are also discussed.

1. MINERAL MATRIX – VEGETAL FIBERS COMPOSITE MATERIAL

Apart from cellulose insulation which is already used at large scale in some world countries, vegetal fiber reinforced concrete, fiber reinforced cement and fiber reinforced gypsum are the materials which are gaining the attention of builders as new building materials. The contained vegetal fibers are included in the composition as a mean of reinforcement of the structural integrity. The concept of using natural fibers as reinforcement is not new. Fibers have been used for reinforcement since ancient times. Historically, horsehair was used in mortar and straw in mud bricks. Cement, which is considered the mineral matrix is a complex material that evolves with time introducing specific considerations to the interactions among the particles. Portland cement, the most widely used in the building industry and building materials production is mainly a mixture of calcium silicates (Ca_3SiO_5 , Ca_2SiO_4) tricalcium aluminate ($Ca_3Al_2O_6$) tetracalcium-aluminatferrite $Ca_4Al_2Fe_2O_{10}$ and gypsum (calcium sulphate dehydrate) [7].

Since 1950's asbestos, glass fibers and synthetic polymeric fibers have been used for

mixing and reinforcement of this type of building materials. Inorganic matrix-vegetal fiber composite materials have been designed to replace the classical fiber reinforced building materials (gypsum, concrete and cement composites). Asbestos banning due to its implication in human health problems [8] has led to an increasing interest in vegetal fibers as replacement materials for asbestos reinforced products of building components in combination with cement mortar or cement pastes matrices for low cost housing. The best potential for the using these materials is through their conversion into various kinds of building panels and blocks.

Other reason for including fibers in concrete and cement material is the control some of the cracking phenomena, figure 1, caused either by drying or by other factors [5, 9- 25]. The effects of introducing fibers in cement and concrete materials are the reduced bleeding of water and resistance to impact, abrasion, shatter, ductility and flexural resistance [5].

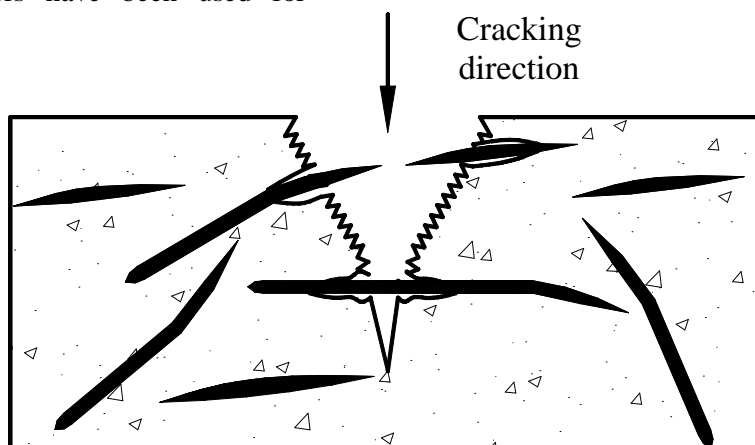


Fig. 1 Vegetal fiber cement composite cracking and cracking prevention principle

1.1. Sources of vegetal fibers

According to Mohr et al. [14] vegetal fibers used in cement-based matrices can be divided into two categories – unprocessed vegetal fibers and processed natural fibers. The unprocessed natural fibers are available in many different countries and represent a continuously renewable resource. These fibers are obtained at low cost and energy consumption through the use of locally available manpower and technology. Such fibers are used in the manufacturing of low fiber content composites and occasionally have been used in manufacturing

thin sheet high fiber content composites. The processed vegetal fibers category should refer to any fiber that has been subjected to a processing stage such as pulping or other treatment that removes natural chemical constituents. A third category may be added if waste vegetal fibrous materials such as agricultural residues and waste paper products are to be taken into consideration.

Vegetal fiber reinforced concretes are materials which may contain a weight percentage of 1- 3% or more vegetal fibers [9,10]. However, regarding the weight percentage of the vegetal fiber cement composites there is relatively large intervals

since this percentage depend on the final product destination. Several applications of vegetal fibers as reinforcements for cement based composites are further exemplified.

Sevastano et al. [11] have obtained and tested vegetal fiber-mortar reinforced composite and found that introducing vegetal fibers increases the flexural toughness of the mortar matrix with up to 40%. However the same authors indicate as a major possible deficit of vegetal fiber-mortar based materials is a lower resistance to weathering due to biodegradation of vegetal fibers under the test conditions.

Li et al. [12] have studied the mechanical and physical properties of hemp fiber reinforced concrete and concluded that the most important variable that influenced these properties is the weight content of vegetal fibers (hemp). Other variables such as mixing method, aggregate size and fiber length have been found to have a less influence.

Bentchikou et al. [13] have studied the effect of integrating recovered paper fibers into the composition cement paste. They concluded that adding cellulose fibers in the cement paste

composition decreases the thermal conductivity, which remained constant above 10% by weight vegetal fiber content, while the mechanical strength (compressive strength) increases and stabilizes around 16% fiber content. The newly proposed cement materials with content of recovered cellulose fibers from waste paper satisfied the standards for roofing tiles and wall construction boards.

1.2. Vegetal fiber cement composites production

Cement-fiber composites production techniques have been divided in two main categories: the cast-in-place technique and the precast manufacturing techniques [15]. These techniques can be generalized as cast-in-place techniques and precast manufacturing techniques. Most attention and research efforts through the last two decades have focused on precast manufacturing techniques, which include the Hatschek, slurry/dewatering, extrusion process and the cast in place process. Several stages are necessary for the production of the cement – vegetal fiber mixture, as described in figure 2.

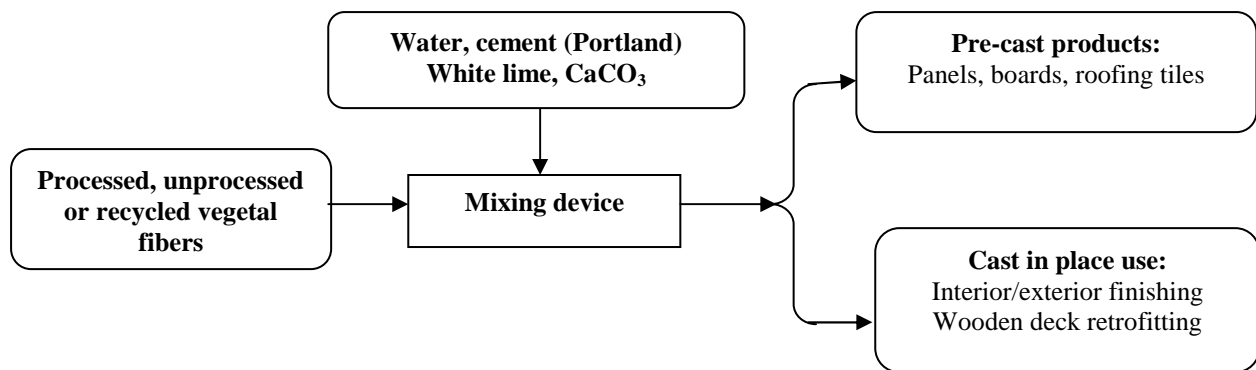


Fig. 2. Stages in making of vegetal fiber reinforced cement based composites [16]

The **Hatschek process** is performed through the formation of a thin laminate of dewatered fiber-cement water slurry – figure 3. By stacking of laminates while they are still wet, the final product can be formed to the desired thickness. In this process, the stacked laminates are obtained through continuous winding of the laminate around a cylindrical form. The cylindrical product can be kept in the form of a pipe or cut to form a thin sheet, while the cement matrix is still plastic. Up to 12% of fiber weight fraction can be incorporated in cement composites by the Hatschek process [15-17].

Dewatering process consists of making a slurry form using high speed mixing and agitation

until the vegetal fibers are suspended in the slurry and well mixed with the cement. The mix is then left to settle and the excess water is removed using a vacuum process. The resulting de-watered material (vegetal fibers, cement, and less water) is then pressed in the final shape. Balaguru and Shah [18] reported a fiber weight percentage up to 12% can be easily incorporated in the composite using this method. More recently, Bayasi states that even up to of 65% fibers by mass can be used for fiber-cement composites [19].

Extrusion process, relatively new to the fiber-cement industry, involves the forming of a cohesive, fiber-cement composite by forcing it through a die that can be adjusted to the desired

shape. Extruded composites may incorporate up to 8% fibers by weight. The sections of extruded fiber cement composite are then cut to the desired length. This method can produce composites with high density matrix and fiber packing, achieving low porosity, and strengthening of the fiber matrix bond [20, 21].

Cast-in-place process for using vegetal cellulosic fibers in cement-based materials has received relatively little attention. This might be due to the fact that the fiber weight fraction that can be used in this method is limited to a maximum of

about 2% by mass due to the difficulties associated with mixing and placing composites with high fiber mass fraction [22, 23]. Fibers distribution is also a main problem faced by the wider application of this technique. This technique involves in-situ molding and casting methods similar to those used with normal concrete or mortar. High range water reducer is usually needed for proper dispersion of the fibers and placing and compaction of the composite.

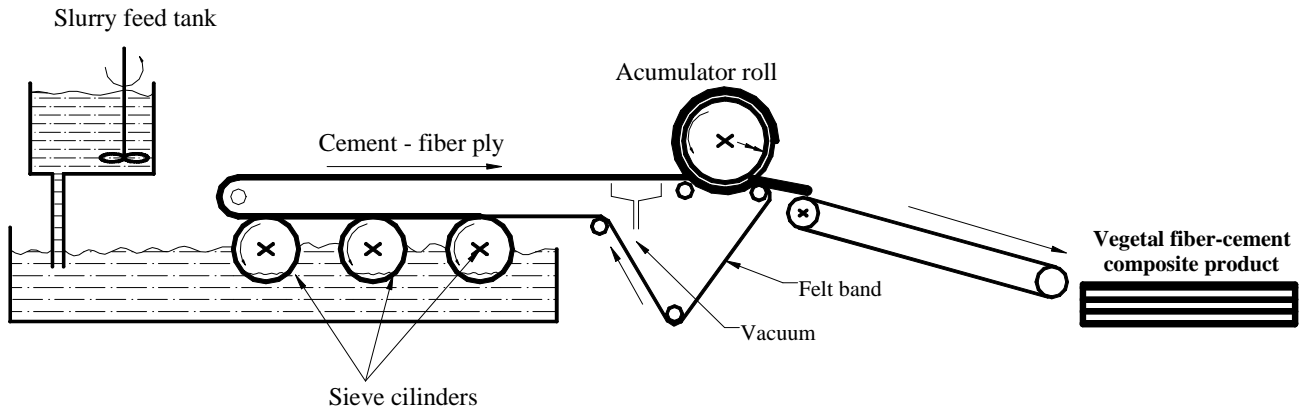


Fig. 3. Representation of an industrial cement-fiber precast manufacturing process (redrawn from [17])

A typical example of producing pre-cast vegetal fibers-cement composites is that of Agopyan et al. [24], which have obtained and studied the mechanical properties of some wall panels and roofing tiles obtained from several categories of cement materials reinforced with vegetal fibers (up to 2% by weight) such as coir fibres, sisal fibers and eucalyptus cellulose pulp and they stated that if adequate mixing ratios are used it is possible to obtain better and environmentally friendly materials. In case of thermomechanical pulping, the obtained fibers can typically be used at higher mass fractions, due to their shorter fiber length and stiffer cell wall.

Several types of pulp fiber treatments (carbonate filling and silica fume depositing) have been developed to permit uniform fiber distribution during cement composite forming process [25-28]. Bilba et al. [25,29] have evidenced that some chemical treatment of vegetal fibers to remove the water soluble sugars and easily hydrolysable compounds may improve the setting and the hydration temperature, two important properties in

manufacturing of the vegetal fiber-cement composites. Fire resistance of the vegetal fiber cement composites is easily achieved due to the higher content of inorganic material.

Kraft pulp fiber suspension problems were avoided by using aligned fiber sheets manufactured by a dynamic sheet former that can be adjusted for various fiber sheet thickness and degree of fiber alignment [30]. To achieve similar performance to distributed fiber composites, equivalent fiber mass fractions of the fiber sheets are smaller than that of distributed fibers. One problem under constant debate and research, since vegetal fibers have become the replacement of the banned asbestos in the production of roofing cement composites, is cement retention and water drainage during sheet formation. Asbestos fibers have natural affinity for cement, since they are mostly silicates. As a solution to the retention problem, flocculants such as polyacrylamides have been proposed for improving the retention of cement and drainage and therefore the productivity [7].

2. FACTORS AFFECTING VEGETAL FIBER – CEMENT COMPOSITES MECHANICAL PROPERTIES

As a general rule, the mechanical properties values are dictated by the needs in the use phase of the proposed vegetal fiber cement composites [31-36]. Since these vegetal fibers are natural, the necessity to understand their long term behavior is extremely important, because they are considered as having a low capacity to maintain their properties with time. Vegetal fiber – cement composites' mechanical properties are also the result of the control of manufacturing process. Durability represents actual challenge and concerns all construction materials.

2.1. Mechanical properties influence factors

Most of the works in the field present several identified factors that influence the mechanical properties of vegetal fiber-cement composites as well as the durability. These factors are:

1. Fiber weight/volume fraction. Several groups of authors have identified that increasing fiber fraction in composites leads to an increase of the mechanical properties. The improvement of the mechanical properties continues up to a certain limit which is variable by the type of composite. Roma et al. [36] have produced with several formulations of cement-based matrices reinforced with sisal and eucalyptus fibers. The physical properties of the tiles were more influenced by the fiber content of the composite than by the type of reinforcement. Fiber alignment in the composite material seems to significantly affect the mechanical behavior of vegetal fiber cement composites. According to Mohr et al. [30] fiber sheet alignment does significantly affect mechanical behavior, indicating that fiber alignment is achieved during the production process.

2. Cement matrix composition plays an important role in durability and mechanical resistance of all cementitious materials. As already mentioned and proved by Gram, Toledo et al. [31-33], the pH of the matrix may affect the integrity of the vegetal fibers during the production or use phase. Some attempts for improving the durability as well as mechanical resistance are mentioned by Mohr et al. [14] and include the use of artificial pozzolans or other components for lowering the pH.

3. Vegetal fiber source type is expected to influence the properties of the vegetal fiber – cement composites due to significant differences

that naturally occur between the vegetal fiber due to the different fiber chemical composition and fiber length [2]. However literature studies [15] indicates that using wood pulp as reinforcement for cement composites does not significantly affect the mechanical properties. Contradictory results have been obtained by Blankenhorn et al. [37], who obtained significant differences in mechanical strength of vegetal fiber – composite materials containing various types of wood fibers. The best results obtained by using softwood kraft pulp fiber as reinforcement were attributed to the higher length/diameter ratio. In case of non-wood fibers, the higher aspect ratio is expected to also influence the behaviour of the fiber cement composites.

4. Fiber processing such as prehydrolysis, pulping and bleaching and other already mentioned are expected to influence the properties of the vegetal fiber composite materials, since all of this treatments alter the chemical composition of the fiber [25-29]. It has been found that increased α -cellulose content of the vegetal fiber used for reinforcement of the cement materials leads to an increase of mechanical properties. Bleaching of the vegetal fiber induces higher mechanical properties, but reduces the durability due to the removal of the protective lignin layer [38].

5. Beating of vegetal fibers is an important wet mechanical treatment method in paper production. As beating increases fiber specific surface, the bond between the cement matrix and fibers increase, moreover beating improves the fibers' ability to retain particles and maintain sufficient drainage rate. It was found that beating negatively affects some of the mechanical properties while improving other. The flexural strength was found to increase with beating to an optimum level (for CSF of about 550 or 45°C) but reduced after that level. Mohr et al. showed that mechanical parameters values for unbeaten fiber composites were significantly greater than those of beaten fiber composites [14].

6. Fiber moisture state. Since both of the components of the vegetal fiber-cement composites are susceptible of water absorption from the environment, it is expected that humidity of the material to play an important role in its mechanical strength. Literature data on the vegetal fiber mechanical properties under different moisture states indicates that an increase of water content leads to the weakening of the vegetal fiber – cement matrix bond and even to failure of the material under certain conditions [39]. The initial drying state of a fiber also affects its dimensional stability during subsequent wetting and drying [14].

7. Curing conditions play an important role on the composite behavior, which has been

attributed primarily to the influence of curing on the matrix properties. Two curing methods that are generally used in wood fiber cement composites are air/moist curing (normal pressure and temperature) and autoclave curing (high pressure and temperature). Bentur and Mindess [40] showed that the effect of the autoclave curing conditions lead to worse results in terms of mechanical strength that compared to normal air or moisture curing has been reported.

2.2. Testing of vegetal fiber cement reinforced composites

The analysis of vegetal fiber cement reinforced composites should also concern these newly proposed materials, since the fiber cement interface changes occur as a result of environmental factors effect on the vegetal fiber reinforced material. Testing the durability of vegetal fibers reinforced building materials is usually performed by wet/dry cycle and freeze/thaw cycle. These tests are also referred as accelerated aging, while sometimes exposure to real environment conditions is preferred.

Wet/dry cycle test means exposing the building material to several wetting and drying cycles, usually 25 times or more. During the wetting it is believed that the strongly alkaline environment generated strongly affects the fiber integrity causing depolymerisation of fiber components and loss of strength. Various studies, such as those performed by Gram [31], Toledo [32] and Toledo et al. [33] indicate that mechanical property loss of unprocessed vegetal fiber reinforced cement matrix composites is caused by lignin and hemicelluloses dissolution phenomenon which occurs during the wetting cycle of the reinforced composites due to the alkalinity of the water present in the pores. Alkalinity of the water present in pores is the result of common component of cement mixtures – calcium hydroxide. $\text{Ca}(\text{OH})_2$ was also believed to induce fiber degradation by “mineralisation” the name given to precipitation of CaCO_3 in the lumen, walls and voids of the fibres. Contradictory results, in terms of constant mechanical properties after 25 wet-dry cycles, were obtained by Mohr et al. [34] when using kraft pulp fiber for reinforcing cement composites. This is explainable by the lower content of hemicellulose and lignin of the kraft pulp fibers, which are removed during the kraft pulping process.

In case of **freeze/thaw** cycle testing it has been shown that vegetal fiber reinforcement of the cement and concrete building materials durability is improved due to a fiber protection of against cracking. Some of mechanical properties were still

lost. Mohr et. al. [30] recently concluded that the presence of fibers, such as pulp fibers, is expected to be less damaged by freeze/thaw cycles by minimizing the propagation of cracks.

3. SOME ASPECTS REGARDING THE ENVIRONMENTAL IMPACT OF VEGETAL FIBER-COMPOSITE MATERIALS

Most of the building materials and practices have a large ecological footprint. The large majority of these materials are energy intensive. Building waste constitutes a large percentage of landfill volume [41]. Vegetal fibers-cement composites are structural materials made from renewable resources. These materials are being researched and developed to replace less eco-friendly structural and non-structural materials used in the building industry. Life cycle assessment (LCA) of products is the most widely used method in establishing the probable environmental impact of a given product or service. The most common definition of LCA is the investigation and evaluation of the environmental impacts of a given product or service caused or necessitated by its existence. The goal of LCA is to assess and balances all the possible impact of the product from its very beginning to its life end. The impact categories taken into account in the LCA studies are: carcinogenic substances, respiratory diseases, climate changes, ozone depletion, ionizing radiation, acidification and eutrophication, ecotoxicity, land use, mineral resource depletion and fossil fuels [42].

There are several standardized LCA methodologies mentioned, but most of them include the same phases: goal and scope definition, inventory analysis, impact assessment and interpretation of the results. The procedures of life cycle assessment (LCA) are part of the ISO 14000 environmental management standards: in ISO 14040:2006 and 14044:2006. (ISO 14044 replaced earlier versions of ISO 14041 to ISO 14043 [41,42]. The role of the LCA studies is considerable important in the design of sustainable buildings. The concept of *zero emission building* referring to building with low to none environmental impact has been lately promoted through the LCA studies [42]. In case of vegetal fiber composites, a simplified life cycle approach may be visualized in figure 4. Vegetal fiber production green house gases emission are generally lower than in case of artificial fibers [47]. However, additional information might be needed in case of industrial crops which may involve additional resources and

energy consumption which are to be measured and included in LCA studies [42,43].

As regarding the *functional unit*, the most used is the mass weight of the material produced or the unit of product. Xu et al. [44] have introduced a new term called *material service density*, which is defined as the volume of material satisfying a specific strength requirement.

Raw materials

The rationale behind this is that specific volumes of different materials are required to withstand a given mechanical load. When agricultural wastes are used as sources of vegetal fibers this issue should be carefully analyzed [40-47].

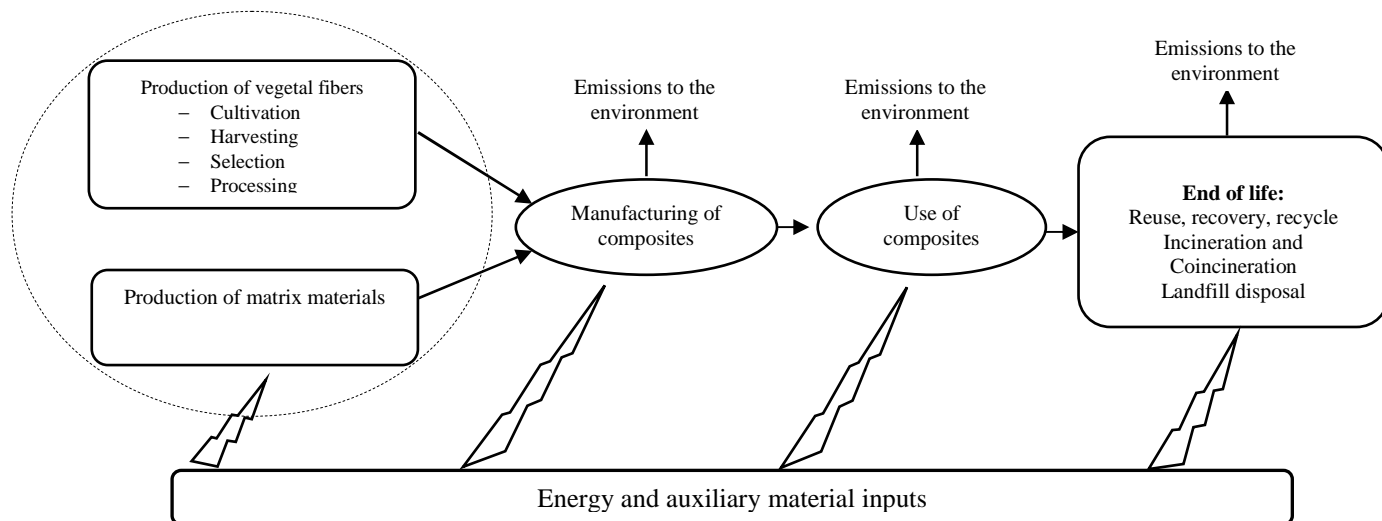


Fig. 4. Simplified schematic approach of vegetal fiber reinforced composite material life cycle

CONCLUSIONS

Sustainable development in the production of different materials means integration of natural and renewable resources into processes and products. Uses of vegetal fibers as potential reinforcement for cement composites materials are an adequate example for the above mentioned integration.

Integration of vegetal fiber into fiber cement composites used in housing and different building activities has occurred from the need of preventing cracking and replacing toxic asbestos fibers. Several manufacturing techniques are outlined together with the most important factors affecting resulted composites properties and durability. Since the number of vegetal fiber resources is relatively high and vegetal fiber cement composites outcome in various combinations, it is relatively difficult to generalize the influence factors mentioned to all vegetal fiber cement composites. The performances affecting factors include the vegetal fiber volume&weight fraction, cement matrix composition, vegetal fiber source and degree of processing and curing conditions.

Vegetal fiber cement composites have been proven to have a lower overall life cycle environmental impact and better environmental compatibility when compared with synthetic fiber based composites. Vegetal fiber use in cement

composites contributes also to their carbon footprint reduction due to atmospheric CO₂ consumption. Assessing the potential environmental impact by LCA studies of composites produced by incorporating agricultural or waste paper products as vegetal fiber sources may lead to better results than in the case of cropped vegetal fibers sources use.

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PROPRIETĂȚILE ȘI APLICAȚIILE POTENȚIALE ALE CHITOSANULUI ÎN FABRICAREA HÂRTIEI

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Rezumat

Chitosanul este un biopolimer cationic, constituit din unități D-glucozaminice, care se obține din resurse regenerabile (chitina). Chitosanul prezintă versatilitate chimică ridicată, ce permite sinteza a numeroși derivați cu proprietăți specifice (capacitate de coagulare/floculare, capacitate de a forma filme și pelicule, biodegradabilitate, activitate antimicrobiană, biocompatibilitate, etc.). Aceste proprietăți specifice permit numeroase aplicații ale chitosanului, în cele mai diverse domenii, precum medicină, cosmetică, industria alimentară, tratarea apelor uzate, industria hârtiei, etc. În această lucrare se prezintă un studiu de literatură privind proprietățile specifice ale chitosanului și derivaților săi, precum și aplicațiile potențiale ale acestora la fabricarea hârtiei. Acest studiu evidențiază faptul că chitosanul reprezintă o sursă potențială de bio-aditivi multifuncționali pentru fabricarea hârtiei, care trebuie exploatată în scopul îmbunătățirii profilului ecologic al industriei papetare.

Cuvinte cheie: *chitosan, biomateriale, biocompatibilitate, biodegradabil*

Abstract

The chitosan is a cationic biopolymer consisting of D-glucosamine units, which is obtained from renewable resources (chitin). It has high chemical versatility, which allows synthesis of a large number of derivatives with specific properties (coagulation / flocculation capacity, ability to form films, biodegradability, antimicrobial activity, biocompatibility, etc.). These special properties allow many applications of chitosan, in various areas, such as medicine, cosmetics, food industry, wastewater treatment, paper industry, etc. This paper presents a brief review on the specific properties of the chitosan and its derivatives, as well as their potential applications in papermaking. This study underlines that chitosan derivatives represents a potential source of multifunctional bio-additives for papermaking, which has to be exploited in order to improve the environmental profile of paper industry.

Key words: *chitosan, biomaterials, biocompatibility, biodegradable*

INTRODUCERE

Chitosanul este principalul derivat al chitinei, care este al doilea polimer natural, ca abundență după celuloză și care se regăsește în natură în exoscheletul crustaceelor și al artropodelor, precum și în unele alge sau în membranele celulelor unor fungi. În formă naturală, chitosanul se găsește doar în unele ciuperci din familia *Mucoraceae* [1].

Chitina și chitosanul sunt descrise în literatură ca fiind polizaharide cu structură liniară și masă moleculară ridicată, formate din unități

variabile de N-acetil-2-amino-2-dezoxi-D-glucoză și 2-amino-2-dezoxi-D-glucoză legate între ele prin punți glucozidice $\beta(1-4)$. Principala deosebire dintre structura chitinei și chitosanului constă în conținutul de unități 2-amino-2-dezoxi-D-glucoză, care în cazul chitinei este neglijabil (fig. 1a), în timp ce chitosanul are un număr semnificativ de grupe amino eliberate prin dezacetilate (fig. 1b). Prezența grupării $-NH_2$ libere, cu capacitate de ionizare în mediu acid este răspunzătoare de solubilitatea chitosanului în acizi organici diluați (ex. acid acetic) și de asemenea determină încărcarea cationică a acestuia[1-6].

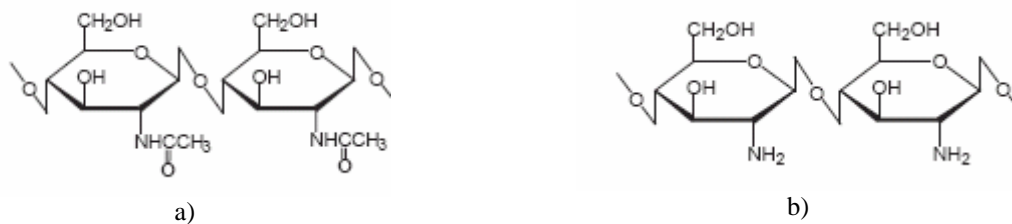


Fig. 1 Structura chimică a chitinei (a) și a chitosanului (b) [6]

Importanța chitinei și chitosanului a crescut substanțial în ultima perioadă, pe de o parte datorită faptului că acestea reprezintă surse de chimicale regenerabile și biodegradabile, iar pe de altă parte datorită unei cunoașteri mai bune a funcționalității lor prin numeroase aplicații curente în biologie, farmacie, biotehnologie, medicină.

Chitina se estimează a avea o producție anuală în jur de 10 gigatone pe an [7]. Importanța chitinei și a derivaților săi în ultimii ani este evidențiată și prin numărul mare de publicații apărute în ultimul deceniu (Tabelul 1, sursa: baza de date SCOPUS, publicații apărute după anul 2000).

Tabelul 1 Numărul publicațiilor științifice referitoare la chitină și chitosan

Cuvânt cheie	Sinteze de literatură	Articole	Brevete
Chitină (fără Chitosan)	182	2741	9064
Chitosan (fără Chitină)	401	5959	2004
Chitină și Chitosan	119	2040	1180

În esență, chitosanul se obține prin dezacetilarea chitinei. În funcție de condițiile de dezacetilare și materia primă folosită se pot obține un număr mare de derivați care diferă prin gradul de dezacetilare (40-99%) [8] și masa moleculară ($5 \cdot 10^4$ - $2 \cdot 10^6$ Da) [9]. Alți autori definesc chitosanul ca derivatul care are în structura sa mai mult de 60% de unități 2-amino-2-deoxi-D-glucoză [10, 11]. Chitosanul se remarcă în cadrul

familiei de polimeri naturali, non-toxici, biodegradabili și biocompatibili, a căror importanță devine tot mai evidentă. Aplicațiile potențiale ale acestui polimer natural sunt estimate la un număr mai mare de 200 [1, 2], fiind utilizat în diverse domenii: industria alimentară, purificarea apelor uzate, industria farmaceutică, cosmetice și altele prezentate în figura 3 [1, 2].

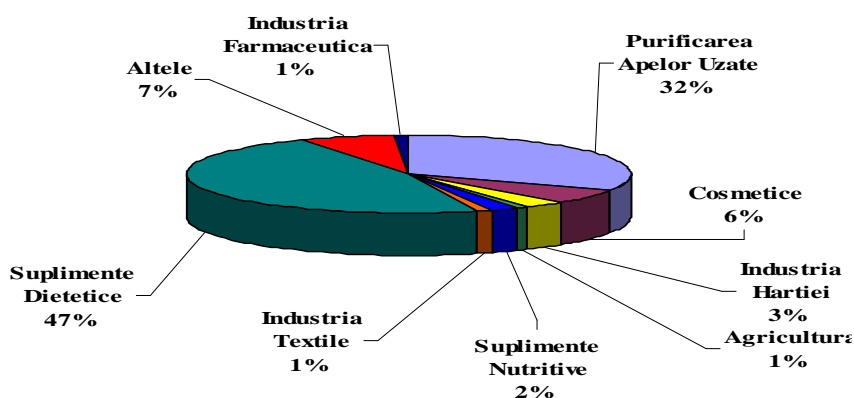


Fig. 2 Distribuția consumului de chitosan în diferite domenii de aplicație [1]

OBȚINEREA CHITOSANULUI

După cum s-a menționat mai sus, chitina este prezentă în numeroase surse naturale,

chitinele comerciale fiind de obicei izolate din crustacee marine, datorită cantității mari de deșeuri disponibile în urma prelucrării produselor piscicole. Exoscheletul crustaceelor este format

din 30-40% proteine, 30-50% carbonat de calciu și chitină în proporție de 20-30%. De asemenea, acestea conțin pigmenți de natură lipidică, cum ar fi carotenoide (astaxanthin, astathin, cantaxantină, luteină și p-caroten). Compoziția exoscheletului crustaceelor variază în funcție de speciile de crustacee și de sezon [1]. Extracția chitinei începe

cu un tratament în mediu acid pentru dizolvarea carbonatului de calciu, urmată de dizolvarea proteinelor în mediu alcalin și apoi de o etapă de depigmentare, necesară pentru obținerea unui produs final incolor, în principal prin eliminarea astaxantinei [10].

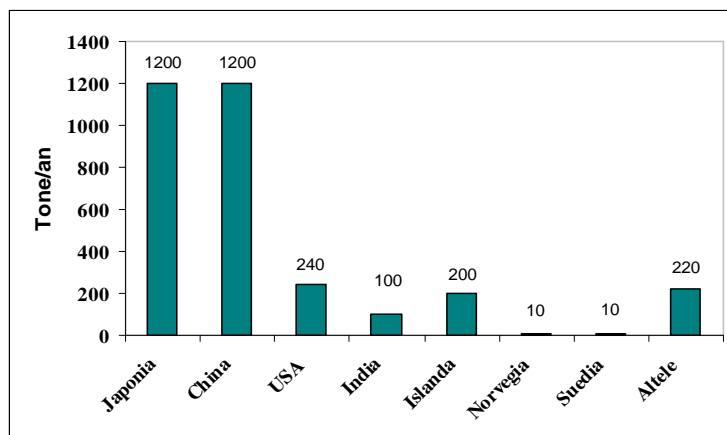


Fig. 3 Producția mondială de chitosan a principalelor țări producătoare [13]

Chitosanul se prepară prin hidroliza alcalină a grupărilor de acetamidă prezente pe lanțul macromolecular al chitinei, la carbonul C2 al unităților glucozidice [3]. Alături de acțiunea soluțiilor alcaline este de obicei necesar și un tratament termic pentru a obține o dezacetilare parțială a chitinei (grad de acetilare mai mic de 40%). De obicei, se utilizează hidroxidul de sodiu sau de potasiu cu o concentrație de 30-50% (w/w) la temperaturi ridicate în jur de 100°C.

În general, sunt cunoscute două metode de obținere a chitosanului din chitină: dezacetilarea în sistem eterogen a chitinei aflată în stare solidă și dezacetilarea în mediu omogen a chitinei umflată anterior în mediu apos, la vid. În ambele situații, reacția de dezacetilare implică utilizarea de soluții alcaline concentrate și timp de procesare lung, care poate varia de la 1h la aproximativ 80h. Unii autori [14-16] descriu metode alternative de

prelucrare, dezvoltate pentru a reduce timpul de procesare lung și costurile mari ale substanțelor chimice necesare pentru o dezacetilare avansată a chitinei. Factorii care afectează gradul de dezacetilare includ: tratamentul aplicat chitinei anterior procesării, concentrația soluțiilor alcaline utilizate, mărimea particulelor și densitatea chitinei [10]. În practică, gradul de dezacetilare maxim ce se poate obține în urma unui singur tratament alcalin este de aproximativ 75-85% [1, 17]. Metoda de prelucrare a chitinei este de asemenea un factor important care afectează totalitatea proprietăților fizico-chimice ale produsului final. Studiile au demonstrat în mod clar, că proprietățile specifice chitosanului (în special masa moleculară și gradul de acetilare) depind în mare măsură de condițiile procesului de obținere a acestuia [1, 9, 18-21].

PROPRIETĂȚILE CHITOSANULUI

Grupările acetyl și amino din structura chitosanului au fără îndoială un rol crucial în evidențierea proprietăților unice atât biologice, cât și chimice ale chitosanului: caracter de polielectrolit, densitate de sarcină cationică, proprietăți de coagulare, de adsorbție a ionilor metalici [12, 22], precum și proprietăți antibacteriene și antifungice ridicate [4, 5, 23, 25].

Proprietăți biologice

- Biocompatibilitate
 - Polimer natural;
 - Biodegradabil în organismele cu metabolism normal;
 - Non-toxic.
- Afinitate mare pentru celulele mamiferelor și a microorganismelor;
- Hemostatic;
- Bacteriostatic, antifungic;
- Prezintă efecte antitumorale;
- Imunomodulator [1, 2, 25 (a, b), 34].

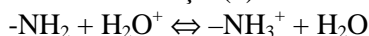
Proprietăți chimice ale chitosanului

Proprietățile chimice ale chitosanului sunt următoarele:

- Este un polimer cationic;
- Are grupare amino liberă în poziția C2;
- Are grupări hidroxil primare și secundare în pozițiile C3 și C6;
- Formează chelați cu ionii metalelor tranzitive,
- Este un polimer cu configurație liniară;
- Gruparea amino poate suferi mai multe reacții chimice ca: acetilare, alchilare, cuaternizare și grefare. Aceste reacții oferă o gamă largă de compuși cu proprietăți specifice;
- Grupările hidroxil sunt susceptibile de reacții de: O-acetilare, legături de hidrogen cu molecule polare, grefare, etc. [1-3, 13, 14, 26, 34].

Proprietăți importante pentru aplicații în fabricarea hârtiei

Polielectrolit cationic: În mediu slab acid soluțiile de chitosan disociază conform echilibrului chimic din relația (1):



Apariția sarcinilor pozitive pe lanțul polimerului este răspunzătoare de caracterul de polielectrolit al chitosanului și influențează proprietățile acestuia. Densitatea de sarcină cationică și implicit proprietățile chitosanului sunt influențate substanțial de nivelul pH-ului soluției. La o valoare a pH-ului mai mică de 6, grupele amino sunt protonate și încărcate pozitiv, conferind astfel chitosanului comportament policationic. La o valoare a pH-ului ridicată (mai mare decât 6,5), grupările amino sunt deprotonate, iar polimerul își pierde sarcina cationică și devine insolubil [26].

Capacitatea de a forma pelicule și filme: Una dintre cele mai interesante proprietăți ale chitosanului este abilitatea sa de a forma pelicule. Soluțiile slab acide de chitosan pot fi ușor transformate în membrane (filme) sau pelicule cu proprietăți mecanice și proprietăți de permeabilitate bune. Altă proprietate specifică chitosanului este biodegradabilitatea [15, 37].

Biodegradabilitatea: Sub acțiunea enzimatică a diferitelor hidrolaze, chitosanul este depolimerizat, conducând la eliberarea de oligozaharide netoxice de lungime variabilă, care pot fi metabolizate sau eliminate [24]. Cinetica degradării este invers proporțională cu gradul de cristalinitate, care este controlat în principal de gradul de dezacetilare. De asemenea, biodegradabilitatea este influențată și de grupările

acetil, deoarece absența sau distribuția omogenă a acestora conduc la grade foarte mici de degradare enzimatică. Mai multe studii evidențiază faptul că viteza de degradare enzimatică este influențată și de lungimea lanțurilor polimerice [24]. Astfel, este important controlarea atât a mecanismului cât și a vitezei de degradare deoarece acestea sunt esențiale în aplicațiile ulterioare ale chitosanului în domeniul regenerării țesuturilor.

Posibilitatea de modificare chimică: Una din cele mai importante proprietăți ale chitosanului este capacitatea mare de reacție datorată prezenței grupării amino și a celor două grupe hidroxilice pe unitatea glucozidică, care pot suferi mai multe reacții chimice, cum ar fi: acetilare, alchilare, cuaternizare, grefare, precum și O-acetilare sau formare de legături de hidrogen cu molecule polare, etc., oferind o gamă largă de compuși cu proprietăți specifice [1-3, 9, 25 (a, b)].

APLICAȚII ALE CHITOSANULUI ÎN INDUSTRIA HÂRTIEI

Aplicații ale chitosanului

Chitosanul prezintă un mare potențial pentru o gamă largă de aplicații, ca urmare a biodegradabilității sale, biocompatibilității, activității antimicrobiane, non-toxicității și versatilității sale chimice. Primele aplicații ale chitosanului în fabricarea hârtiei se bazează pe capacitatea acestuia de a forma filme uniforme și flexibile și se referă la tratarea la suprafață a unor hârtii speciale, așa cum este spre exemplu hârtia fotografică. În ultimul deceniu, s-a constatat un interes crescut pentru aplicațiile chitosanului și a derivaților săi, atât ca aditiv în partea umedă a mașinii de fabricat hârtie, cât și ca agent de tratare la suprafață.

influența chitosanului asupra fenomenelor de coagulare/floculare și efectele lor asupra proceselor de retenție și deshidratare a pastei de hârtie; capacitatea chitosanului de a dezvolta legături de hidrogen și respectiv, de a contribui la îmbunătățirea indicilor de rezistență în stare umedă și uscată a hârtiei. Rezultatele obținute au demonstrat eficiența chitosanului ca aditiv multifuncțional la fabricarea hârtiei, având efecte pozitive atât asupra proceselor de bază (retenție, deshidratare) [30], cât și asupra proprietăților produsului finit - îmbunătățirea opacității hârtiei prin creșterea conținutului de material de umplere reținut în hârtie, îmbunătățirea gradului de înclieiere datorită creșterii retenției aditivului de înclieiere (alchilidimeretenă) și mărirea rezistenței la tracțiune a hârtiei. Densitatea cationică a

chitosanului mult mai mare, comparativ cu amidonul cu cel mai înalt grad de substituție, conduce la fenomene de heterofloculare a materialului fin și de umplere, cu efecte pozitive atât asupra retenției și a vitezei de deshidratare, dar și asupra proprietăților fizico-mecanice ale hârtiei [26-29].

Aplicații ale derivaților de chitosan

Totuși, aplicarea chitosanului în procesul de fabricare a hârtiei ridică unele probleme legate în principal de insolubilitatea acestuia în apă și de dificultățile inerente de preparare și dozare în pasta de hârtie. În acest context, unul dintre obiectivele cercetărilor a fost și este în continuare modificarea chitosanului prin diverse reacții de alchilare, carboximetilare, eterificare, etc. și obținerea unor derivați solubili în apă, cu proprietăți specifice noi și cu un domeniu larg de aplicație. Având în moleculă grupe amino primare alifatică, chitosanul suferă reacții tipice aminelor, dintre care acilarea la atomul de azot și formarea bazelor Schiff sunt cele mai importante. Derivații de chitosan sunt astfel ușor de obținut în condiții de reacție moderate, la temperatura camerei, sub formă de aldoimine și ketimine cu aldehide și respectiv cetone [32-36]

Derivații de chitosan pot fi clasificați în două categorii: prima categorie de derivați se obține prin reacții chimice care au loc la gruparea amino liberă (-NH₂) rezultând N-derivați, iar a

doua categorie cuprinde O-derivați rezultați în urma reacțiilor chimice ce au loc la nivelul grupărilor hidroxil (-OH) primare și secundare (din pozițiile C3 și C6). Marea majoritate a reacțiilor de modificare a chitosanului nu sunt specifice, astfel rezultând compuși ce aparțin ambelor categorii [3, 18- 21, 31-36]. Dintre derivații chitosanului ce au fost aplicați în domeniul papetar și au avut efecte pozitive asupra principalelor procese de la fabricarea hârtiei (retenție, deshidratare, formare) și/sau asupra proprietăților hârtiei enumerăm: carboximetil chitosanul, chitosanul alchilat, cuaternizat și cianoetilat.

Carboximetil-chitosanul: Carboximetil-chitosanul este sintetizat în condiții alcaline prin reacția chitosanului cu acidul monocloracetic. Procesul de sinteză presupune o serie de etape: dispersarea chitosanului în alcool izopropilic; menținerea chitosanului sub agitare în mediu alcalin prin adăugarea unei soluții de NaOH (la 25⁰ C); adăugarea acidului monocloracetic; ridicarea temperaturii mediului de reacție la 60⁰ C; corectarea pH-ului la valoarea 7 cu acid acetic glacial; filtrarea și spălarea produsului cu alcool metilic 70%; filtrarea și uscarea produsului timp de 12 h la o temperatură de 60⁰C. Se obține astfel un derivat al chitosanului solubil în apă cu caracter amfoter [27, 32, 33, 37]. Reacția chimică de obținere și structura derivatului de chitosan este prezentată în figura 4.

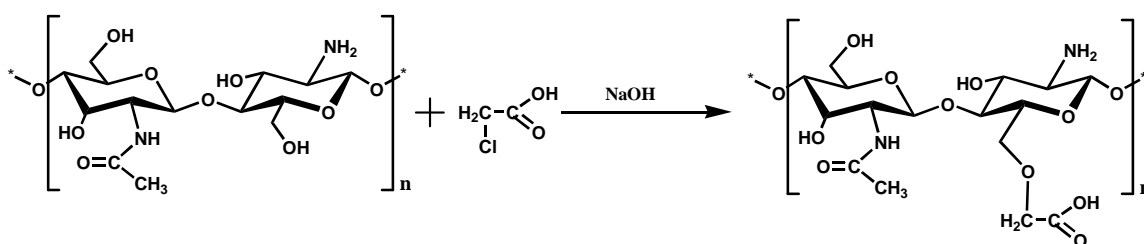


Fig. 4 Reacția de obținere a chitosanului O-carboximetilat [33]

Testarea ca aditiv în masă a carboximetil-chitosanului (CMCh) în diferite combinații, cu alți aditivi clasici utilizați la fabricarea hârtiei, au arătat că acesta influențează pozitiv retenția și formarea, iar prin combinarea acestuia cu chitosan într-un sistem bicomponent, conduce la valori mai ridicate ale vitezei de deshidratare decât sistemele clasice cu microparticule (poliacrilamidă cationică-bentonită). Probele de hârtie obținute cu carboximetilchitosan prezintă proprietăți fizico-mecanice bune, iar proprietățile optice și cele de rezistență la atacul micro-organismelor sunt superioare sistemelor care utilizează amidon cationic pentru creșterea rezistenței în stare uscată.

Proprietățile mecanice și optice ale hârtiei reflectă o formare bună în cazul utilizării carboximetilchitosanului, care poate fi rezultatul unui mecanism de microagregare de tip rețea. Efectele pozitive ale CMCh-lui asupra retenției/deshidratării, fără a avea influență negativă asupra gradului de alb, oferă motive destul de bune pentru utilizarea acestui aditiv în procesul de fabricare a hârtiilor cu opacitate și grad de alb ridicate [27, 28, 37, 38].

De asemenea, alte date experimentale anterioare [29 (b)] evidențiază efectele benefice pe care le are carboximetil-chitosanul prin aplicarea acestuia la suprafața hârtiei, și anume

îmbunătățirea indicilor de rezistență în stare uscată, efect comparabil cu cel obținut în cazul derivaților de celuloză (metilceluloza și carboximetilceluloza), utilizați în mod curent în astfel de aplicații. Prin utilizarea CMCh-lui la suprafața hârtiei, acesta nu provoacă modificări dimensionale ale acesteia. Alte date experimentale [39] menționează faptul că prin imersarea hârtiei în soluție de CMCh se înregistrează creșteri ale

indicilor de rezistență mecanică, precum și a rezistenței dielectrice a hârtiilor tratate.

Chitosanul alchilat: În funcție de agentul de alchilare folosit în reacție (aldehidă cu un anumit număr de atomi de carbon) se obține chitosanul cu un substituent alchil la gruparea amino cu lungime diferită a lanțului de atomi de carbon. Reacția de obținere a N-alchil chitosanului este prezentată în figura 5.

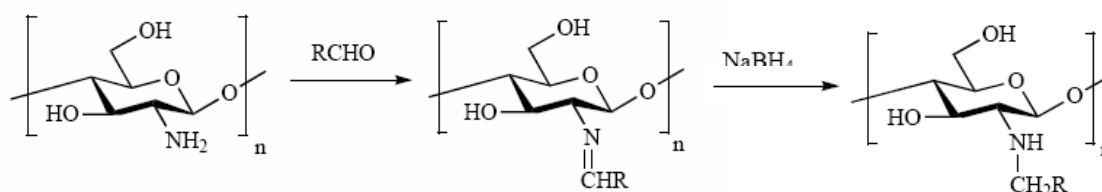


Fig. 5 Structura chimică a N-alchil chitosanului [40]

Spre deosebire de chitosanul nemodificat, chitosanul alchilat prezintă avantajul solubilității sale în apă, fiind mult mai ușor de preparat în soluție și nu produce scăderi importante ale pH-ului extractului apos al hârtiei tratate menținându-se slab alcalin [29 (b)]. Cel mai important efect produs de chitosanul alchilat este reducerea substanțială a absorbției apei în prezența alchilmercetenei (scăderea substanțială a indicelui Cobb₆₀). De asemenea, aplicarea la suprafața hârtiei a chitosanului alchilat a avut ca

efect creșterea ușoară a rezistențelor mecanice ale hârtiilor tratate [5, 29 (a, b)].

Chitosanul cuaternizat: Chitosanul cuaternizat este cunoscut ca având o activitate antimicrobiană deosebită, ceea ce îl recomandă a fi un material indicat pentru tratamente atât în masă, cât și la suprafața hârtiei. Solubilitatea sa în apă constituie de asemenea un real avantaj față de chitosanul nemodificat. Reacția de obținere a chitosanului cuaternizat este prezentată în figura 6.

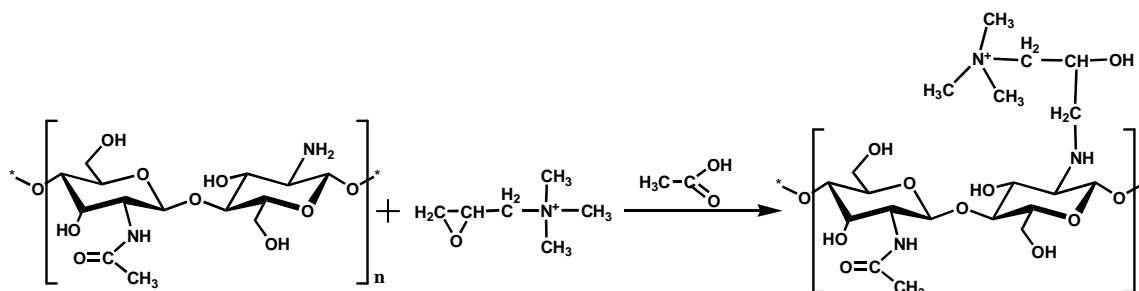


Fig. 6 Reacția de obținere a chitosanului cuaternizat [40]

Utilizările în domeniu papetar a acestui derivat au demonstrat o creștere spectaculoasă a indicilor de rezistență în stare uscată a hârtiei, în special lungimea de rupere și rezistența la plesnire înregistrând creșteri importante. Aceste efecte pot fi puse pe seama capacității de coagulare a derivatului cuaternizat, determinând interacțiuni sinergice ce pot conduce la optimizarea procesului de fabricare a hârtiei [29 (b), 40].

Chitosanul cianoetil: Proprietățile dielectrice, precum și stabilitatea termică a foilor de hârtie tratate cu cianoetil-chitosan înregistrează creșteri semnificative, comparativ cu carboximetil chitosanul și chitosanul nemodificat [41].

Adăugarea în pastă a cianoetil chitosanului îmbunătățește proprietățile mecanice ale probelor de hârtie. De asemenea, s-a observat că prin adăugarea în masă la fabricarea hârtiei a cianoetil chitosanului, valorile corespunzătoare lungimii de rupere sunt mai mari, decât cele obținute prin utilizarea derivatului cianoetil în tratamentele de suprafață. Pe de altă parte, valorile rezistenței la sfâșiere sunt mai mari în cazul în care derivatul ciano-etilat este utilizat în tratamente de suprafață [42]. Reacția de obținere a cianoetil chitosanului este reprezentată în figura 7.

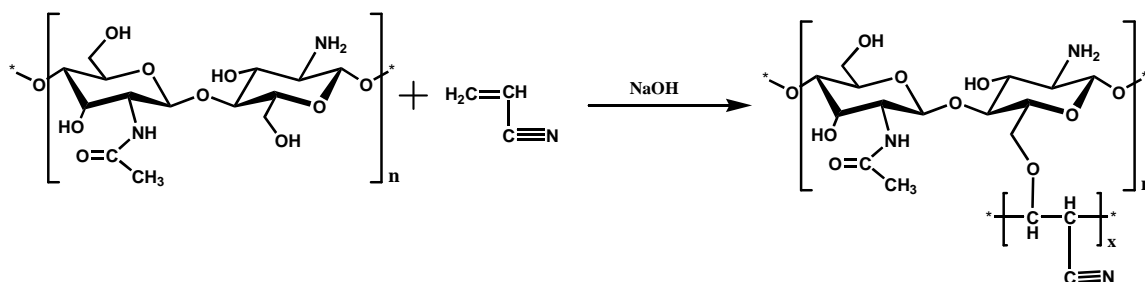


Fig. 7 Reacția de obținere a cianoetil chitosanului [42]

CONCLUZII

Chitosanul și derivații săi posedă un potențial extraordinar într-un domeniu larg de aplicații, datorită unei combinații unice de proprietăți specifice: biocompatibilitate față de țesuturile vii, nontoxicitate, activitate antimicrobiană și antifungică, capacitate de coagulare, capacitate mare de reacție, selectivitate, etc.

Cercetările efectuate în domeniul utilizării acestei clase de compuși la fabricarea hârtiei au evoluat odată cu dezvoltarea procedeele de obținere a chitinei și chitosanului, cu toate acestea prețul relativ ridicat al acestor compuși comparativ cu prețurile chimicalelor utilizate în prezent în industria de fabricare a hârtiei încă mai prezintă un impediment în utilizarea lor la scară largă. Prețul ridicat al chitosanului comercializat în prezent se datorează în primul rând purității ridicate, deoarece acesta se produce în special pentru aplicații medicale, farmaceutice și în industria alimentară. Totuși, s-a constatat că dacă se ia în considerație multifuncționalitatea chitosanului ca aditiv la fabricarea hârtiei (aditiv de coagulare/floculare, aditiv pentru rezistență în stare umedă, activitatea antimicrobiană, ș.a) raportul cost/eficacitate se poate reduce considerabil.

În ultimul timp, foarte multe publicații și patente vizează obținerea și privind aplicațiile unor derivați de chitosan ca bio-aditivi pentru tratarea în masă sau la suprafață a hârtiei. Cercetările privind modificarea chitosanului pentru aplicații specifice în fabricarea hârtiei (ex. carboximetil chitosan, chitosan cuaternizat și alchilat, cianoetil chitosan, etc) pot conduce la apariția unei clase noi de bio-aditivi multifuncționali care ar putea substitui mare parte din polimerii sintetici utilizați în prezent.

Acest studiu de literatură evidențiază faptul că chitosanul reprezintă o sursă potențială de bio-aditivi multifuncționali pentru fabricarea hârtiei, care trebuie exploatată în scopul îmbunătățirii profilului ecologic al industriei papetare.

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CONSIDERAȚII PRIVIND EVALUAREA CICLULUI DE VIAȚĂ AL HÂRTIEI (LCA)

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Rezumat

În prima parte, lucrarea prezintă analiza și evaluarea impacturilor potențiale asupra mediului al produselor și proceselor prin evaluarea ciclului de viață, cu noțiuni generale despre definirea conceptului de LCA și fazele unui studiu LCA, respectiv definirea scopului și a domeniului de aplicare, analiza inventarului, evaluarea impactului, interpretarea datelor rezultate și aplicațiile directe ale LCA.

În partea a doua a lucrării este prezentat un studiu de caz privind analiza și evaluarea impacturilor potențiale asupra mediului a tehnologiei de fabricație a hârtiei tissue, prin tehnici LCA.

Cuvinte cheie: *Hârtie, Evaluarea ciclului de viață, Impact de mediu, Hârtie tissue*

Abstract

In the first part, the paper presents the analysis and evaluation of potential environmental impacts of products and processes by life cycle assessment, with general notions about the LCA concept definition and the main stages of an LCA study, the goal and field definition, inventory analysis, impact assessment, resulted data interpretation and LCA direct applications, respectively.

The second part of the paper presents a case study concerning the analysis and evaluation of potential environmental impacts of the tissue paper making technology, by LCA techniques.

Key words: *Paper, Life Cycle Assessment, Environmental Impact, Tissue paper*

ANALIZA ȘI EVALUAREA IMPACTURILOR POTENȚIALE ASUPRA MEDIULUI AL PRODUSELOR ȘI PROCESELOR PRIN EVALUAREA CICLULUI DE VIAȚĂ

Evaluarea ciclului de viață (*Life Cycle Assessment*) încorporează aspecte privind calitatea mediului în procesul de luare a deciziilor referitoare la practicile de producție. Creșterea conștientizării asupra importanței protecției mediului și a impacturilor posibile asociate produselor fabricate și consumate, a mărit interesul pentru dezvoltarea metodelor pentru o mai bună înțelegere și reducere a acestor impacturi.

LCA este o tehnică de interpretare și evaluare a intrărilor, ieșirilor, aspectelor de mediu și a impacturilor potențiale de mediu asociate unui sistem-produs pe durata ciclului său de viață, de la achiziția materiilor prime, continuând cu producția, activitățile de marketing, utilizarea și post-utilizarea [1].

Conceptul de LCA își are originea în inițiativele Societății Europene de Toxicologie, Mediu și Chimie (SETAC), care a inițiat o serie de activități pentru a stabili un cadru tehnic de evaluare a ciclului de viață. Rezultatele acestor activități au fost baza standardelor pentru evaluarea ciclului de viață elaborate, în 1994, de ISO – Organizarea Internațională de Standardizare [2].

SR EN ISO 14040 (2002), *Management de mediu – Evaluarea ciclului de viață – Principii și cadru de lucru* este primul standard din seria LCA, care furnizează principiile și cadrul de lucru, precum și unele cerințe metodologice pentru conducerea studiilor LCA. Conform ISO 14040, LCA este o tehnică pentru evaluarea aspectelor de mediu și a impacturilor potențiale asociate unui produs, proces sau serviciu, prin parcurgerea următoarelor etape [2,3]:

- realizarea unui inventar pentru elementele relevante de intrare (constituite din totalitatea materiilor prime, materialelor sau energiei care intră într-un proces elementar) și ieșire (constituite din toate elementele sau datele care rezultă din executarea unei sarcini sau a unui lot de lucrări) ale unui sistem produs;
 - evaluarea impacturilor potențiale de mediu asociate acelor intrări și ieșiri;
 - interpretarea rezultatelor analizei inventarului și a fazelor de evaluare a impacturilor în relație cu obiectivele studiate.
- LCA poate contribui la [1]:
- identificarea oportunităților de îmbunătățire a aspectelor de mediu generate de produse în diferite puncte din ciclul lor de viață;
 - luarea deciziilor în industrie, organizații guvernamentale și neguvernamentale (de exemplu planificarea strategică, stabilirea priorităților, proiectarea sau reproiectarea produselor sau a proceselor);
 - selectarea indicatorilor relevanți ai performanței de mediu, inclusiv a tehnicilor de măsurare;
 - marketing (de exemplu declarații de mediu, schema de eco-etichetare sau declarația de mediu pentru produs).

LCA este una dintre tehnicile de management de mediu (de exemplu evaluarea riscului, evaluarea performanței de mediu, auditarea de mediu și evaluarea impactului de mediu) și poate să nu fie cea mai potrivită tehnică pentru a fi utilizată în toate situațiile. În mod special LCA nu tratează aspectele economice sau sociale ale produsului. LCA identifică în totalitate resursele utilizate și deșeurile generate în toate compartimentele de mediu (aer, apă și sol) pe parcursul întregului ciclu de viață al unui produs sau serviciu, fiind în prezent singurul instrument aplicat pentru a evalua produsele și procesele sub aspectul impactului de mediu [4].

Fazele unui studiu LCA

Un sistem-produs este definit ca un ansamblu de unități de proces intercorelate din punct de vedere material și energetic, care îndeplinesc una sau mai multe funcții definite [1].

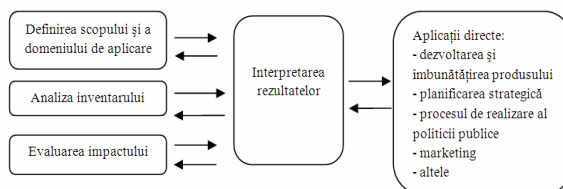


Fig. 1 Fazele studiului LCA

Fazele unui ciclu de viață sunt evidențiate în Schema de evaluare a ciclului de viață în figura 1, acestea cuprinzând:

A. definirea scopului studiului de evaluare a ciclului de viață și a domeniului de aplicare - stabilește elemente cheie a studiului: definirea sistemului, scopul, domeniul de aplicare, ipotezele principale care stabilesc granițele sistemului (conceptual, geografic și temporal) precum și calitatea datelor utilizate. Domeniul de aplicare e dat de *unitatea funcțională*: unitatea de produs sau serviciu a cărui impact asupra mediului va fi evaluat sau comparat, exprimată în termeni de cantitate de produs [5,6];

B. analiza de inventar a ciclului de viață (ICV) – proces tehnic de colectare și calcul a datelor, de cuantificare a intrărilor și ieșirilor din sistem, așa cum sunt definite în domeniul de aplicare. Intrările și ieșirile pot include utilizarea resurselor și evacuările în aer, apă și sol. Aceste date constituie intrarea pentru evaluarea impactului ciclului de viață [7];

C. evaluarea impactului ciclului de viață - proces de identificare și caracterizare a potențialelor efecte produse de mediu, de sistemul din cadrul studiului [8]. Acest proces implică asocierea datelor inventarului cu impacturile de mediu specifice și încercarea de a înțelege impacturile acestora;

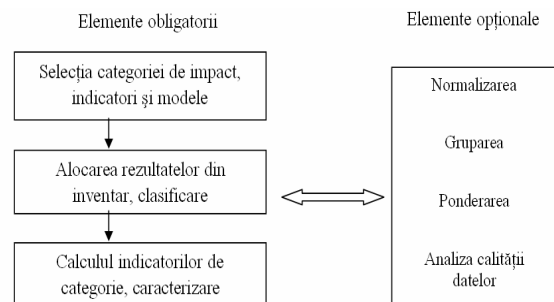


Fig. 2 Elemente ale etapei LCIA în acord cu SR EN ISO 14042/2002

D. interpretarea datelor rezultate în urma studiului de evaluare – rezultatele sunt prezentate sintetic, prezentându-se sursele critice

de impact și soluțiile de reducere a acestora. Se parcurg toate etapele procesului LCA pentru a se verifica coerența ipotezelor și calitatea datelor. Toate intrările necesare, emisiile din mai multe etape și operațiunile din ciclul de viață sunt considerate frontiere în cadrul sistemului;

E. **aplicațiile directe ale LCA.** Conform SR EN ISO 14040/2002 aplicațiile LCA ies în afara domeniului Evaluării Ciclului de Viață, fiind un instrument de management a mediului folosit pentru [9]:

- a oferi o imagine completă a interacțiunilor cu mediul înconjurător;
- a identifica impactul de mediu major precum și etapele ciclului de viață care contribuie la aceste efecte;
- a lua decizii în industrie, organizații guvernamentale și neguvernamentale;
- a selecta indicatorii relevanți ai performanței de mediu inclusiv ai tehnicilor de măsurare.

Avantaje ale aplicațiilor LCA [10]:

- LCA este un instrument de comparație, poate fi utilizat pentru a compara performanțele generale vizavi de mediu în pofida diferențelor dintre produse sau procese;
- LCA este un instrument cuprinzător, fiind în esență un proces de contabilizare prin intermediul căruia sunt listate și apoi însumate toate intrările necesare și emisiile pentru un sistem dat.

STUDIUL DE CAZ. ANALIZA ȘI EVALUAREA IMPACTURILOR POTENȚIALE ASUPRA MEDIULUI A TEHNOLOGIEI DE FABRICAȚIE A HĂRTIEI TISSUE, PRIN TEHNICI LCA

Analiza inventarului ciclului de viață (ICV)

I. Definirea și prezentarea grafică a sistemelor-produs

Unitatea analizată este o unitate neintegrată de fabricare a hârtiei, care desfășoară următoarele **activități principale** [11]:

- A. Fabricarea hârtiei pentru carton ondulat
- B. Fabricarea hârtiei tissue

Aceste activități cad sub incidența Directivei IPPC 96/61/EC, care a fost transpusă în

legislația națională prin OUG 34/2002, aprobată prin Legea 645/2002.

Cele două activități principale sunt deservite de următoarele **instalații auxiliare**, comune [11]:

C. Instalații energetice pentru producerea aburului tehnologic, respectiv: cazane energetice CET

D. Instalațiile de epurare a apelor uzate

E. Depozitarea finală a deșeurilor solide

Pentru acest studiu de caz se vor analiza și evalua impacturile potențiale asupra mediului ale tehnologiei de fabricație a hârtiei tissue, prin tehnici LCA.

În figura 3 se prezintă grafic limita instalației IPPC, care produce și comercializează hârtia tissue, care este și limita sistem-produs, din perspectiva analizei LCA. Limita sistem-produs se consideră punerea produsului pe piață către utilizatori.

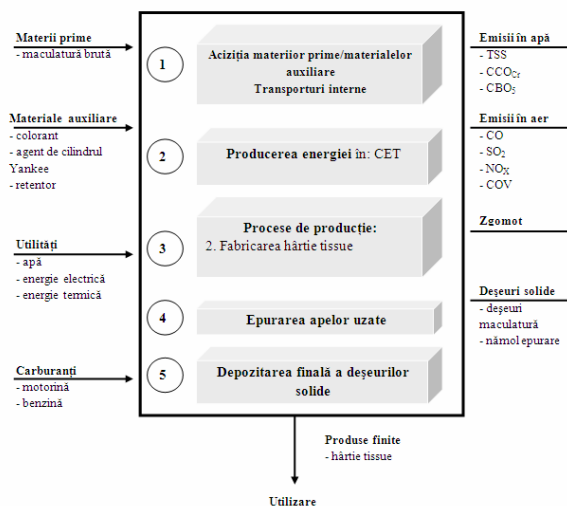


Fig.3 Limita sistem-produs

Principalii utilizatori de hârtie sunt producătorii de confecții din hârtie tissue.

După utilizare, acest sortiment de hârtie poate fi colectate sub formă de maculatură, care se reciclează la fabricarea altor sortimente papetare cu caracteristici de rezistență mai reduse: hârtii igienice etc.

În anul 2009, S.C. VRANCART S.A. Adjud a realizat următorul nivel de producție pentru hârtia tissue [12]:

Nr. crt.	Denumire sortiment	Producție realizată 2009, tone
1.	Hârtie tissue	22 664,93

II. Descrierea sistemului-produs

Din perspectiva analizei LCA, sistemul-produs hârtia de tissue cuprinde următoarele elemente [11]:

a) Unități de proces

- Achiziția de materii prime, materiale auxiliare și combustibili de către agentul economic cu mijloacele proprii de transport (transportul cu mijloace mobile, care este comun cu sistemul-produs al hârtiei pentru carton ondulat)
- Producerea energiei termice prin arderea gazelor naturale în CET
- Fabricarea hârtiei tissue inclusiv prepararea pastei de maculatură
- Epurarea apelor uzate în instalația de tratare fizico – chimică și biologică

b) Fluxurile elementare de intrare în sistem sunt:

- ⇒ materii prime:
 - maculatură brută din ziare și reviste, sorturile I, II, III
- ⇒ materiale auxiliare:
 - colorant
 - agent șpreere cilindrul Yankee
 - retentor
- ⇒ utilități:
 - apă
 - energie electrică
 - energie termică
- ⇒ Combustibili pentru mijloacele de transport intern

c) Fluxurile elementare de ieșire din sistemul-produs sunt:

- ⇒ **Emisiile în apă:**
 - Suspensii
 - CCO_{Cr}
 - CBO₅
 - Ape uzate epurate

⇒ **Emisiile poluante în aer** (rezultate de la arderea gazelor naturale în CET)

- CO
- COV
- SO₂
- NO_x

⇒ **Deșeuri solide:**

- Deșeuri de la sortarea maculaturii
- Nămolul primar din treapta de epurare fizico – chimică

d) Produs finit: Hârtia tissue

Utilitatea funcțională specifică hârtiei este tona de hârtie absolut uscată, Bdt, cu toate că în cazul bilanțurilor de fibră și apă se ia în considerare umiditatea efectivă a hârtiri (6 – 8%)

III. Identificarea și cuantificarea categoriilor de date ale Inventarului Ciclului de Viață – ICV

Pentru cuantificarea categoriilor de date ale ICV, s-au avut în vedere:

- Nivelul producției realizate în anul 2009
- Realizările de consumuri totale și specifice pentru anul 2009
- Măsurătorile de emisii în apă și aer efectuate în anul 2009
- Factorii de emisie pentru anumiți indicatori de poluare a aerului

Datele colectate, din înregistrările societății, din măsurători sau din calcule și estimări sunt prezentate în tabelele 1, 2 și 3 în care se centralizează toate datele de intrări și ieșiri, exprimate atât în cantități totale anuale (t, kg/an) cât și în cantități specifice, precum și celelalte unități de proces auxiliare și comune [12, 13].

Tabelul 1 Producția de hârtie tissue = 22664,93 t

Nr. Crt.	Denumire categorii de date ale ICV	Cantitate totală U.M./an	Cantități specifice U.M./Adt (UIM/Bdt)
0	1	2	3
I	INTRĂRI		
1.	Materii prime <ul style="list-style-type: none"> • Maculatură brută totală 	29635,289 t	1,382 t/Bdt
2.	Materiale auxiliare <ul style="list-style-type: none"> • Colorant • Agent șpreere cilindrul Yankee • Retentor 	42,533 t 23,4 t 5,5 t	1,87 kg/Bdt 1,03 kg/Bdt 0,24 kg/Bdt
3.	Utilități <ul style="list-style-type: none"> • Apă • Energie electrică • Energie termică 	621580,686 m ³ 21218215,6 m ³ 34001,69 m ³	27,42 m ³ /Bdt 936,169 m ³ /Bdt 1,5 m ³ /Bdt

II	IEȘIRI		
1.	Emisiile în apă (evacuare Siret – după treapta biologică) <ul style="list-style-type: none"> • Debit ape epurate • TSS • CCO_{Cr} • CBO₅ 	552848 m ³ 1029,882 t 192,41 t 76,36 t	24,39 m ³ /Bdt 48,44 kg/Bdt 8,49 kg/Bdt 3,37 kg/Bdt
2.	Emisiile în aer (de la CET) <ul style="list-style-type: none"> • CO • SO_x • NO_x • COV 	37,87 t 4,82 t 24,28 t 0,833 t	1,67 kg/Bdt 0,21 kg/Bdt 1,07 kg/Bdt 0,036 kg/Bdt
3.	Deșeuri solide <ul style="list-style-type: none"> • Deșeuri sortare maculatură • Nămolul epurare 	1833,6 t 3985,9 t	80,9 kg/Bdt 175,8 kg/Bdt

Tabelul 2 Transportul mijloacelor mobile - 2009

Nr.c rt.	Denumire categorii de date ale ICV	Cantitate totală U.M./an
I	INTRĂRI	
	<ul style="list-style-type: none"> • Benzină • Motorină 	46332,576 kg 277119,92 kg
II	IEȘIRI	
	Emisiile în aer <ul style="list-style-type: none"> • CO • CO₂ • NO_x • SO₂ • Pulberi 	29,958 t 1029,56 t 11,9 t 2,862 t 1,267 t

Tabelul 3 CENTRALIZATOR

Nr.c rt.	Denumire categorii de date ale ICV	Cantitate totală U.M./an		
0	1	2		
I	INTRĂRI			
1.	Materii prime <ul style="list-style-type: none"> • Maculatură brută 	29635,289 t		
2.	Materiale auxiliare <ul style="list-style-type: none"> • Colorant • Agent șpreere cilindru Yankee • Retentor 	42,533 t 23,4 t 5,5 t		
3.	Utilități <ul style="list-style-type: none"> • Apă • Energie electrică • Energie termică 	621580,686 m ³ 21218215,6 m ³ 34001,69 m ³		
II	IEȘIRI			
1.	Emisiile în apă <ul style="list-style-type: none"> • Debit ape uzate • TSS • CCO_{Cr} • CBO₅ 	552848 m ³ 1029,882 t 192,41 t 76,36 t		
2.	Emisiile în aer	TOTAL	CET	Trans. mijl. mobile
	<ul style="list-style-type: none"> • COV • Pulberi • SO₂ • NO_x • SO_x • CO • CO₂ 	0,833 t 1,267 t 2,862 t 36,18 t 4,82 t 67,828 t 1029,56 t	0,833 t 24,28 t 4,82 t 37,87 t	1,267 t 2,862 t 11,9 t 29,958 t 1029,56 t
3.	Deșeuri solide <ul style="list-style-type: none"> • Deșeuri sortare maculatură • Nămolul epurare 	1833,6 t 3985,9 t		
4.	Produse finite <ul style="list-style-type: none"> • Hârtie tissue 	22 664,93 t		

IV. Bilanțuri între intrări și ieșiri

Bilanțul intrărilor și ieșirilor la fabricarea hârtiei tissue se prezintă în tabelul 4.

Tabelul 4 Bilanțul intrări-ieșiri

INTRĂRI		IEȘIRI	
- Maculatură	29635,289 t	• Hârtie	22664,93 t
- Aditivi chimici	71,433 t	• TSS	1029,882 t
		• CCO _{Cr}	192,41 t
		• Refuz sortare	1833,6 t
		• Nămol	3985,9 t
TOTAL	29706,722 t		29706,722 t

Repartizarea pierderilor de materii prime și materiale auxiliare între produsul finit și factorii

de mediu apă și nămol de la epurarea mecanică se prezintă în tabelul 5.

Tabelul 5 Repartizarea pierderilor de materii prime și materiale

Materie primă/ materiale auxiliare	În produsul finit		În apă		Deșeuri solide	
	%	t	%	t	%	t
Maculatură	76	22577,11	0,1	29,63	23,9	7082,83
Colorant	90	38,28	10	4,25	0	0
Retentor	100	5,5	0	0	0	0

Producerea energiei

Consumul de energie electrică pentru fabricarea hârtiei tissue este:

Consumul de energie electrică	21218215,6 m ³
-------------------------------	---------------------------

Consumul de energie termică pentru fabricarea hârtiei tissue este:

Consumul de energie termică	34001,69 m ³
-----------------------------	-------------------------

Evaluarea impactului asociat hârtiei tissue asupra mediului și comparația cu valorile limită de referință a indicatorilor de mediu conform BREF/ BAT/ PPI, sau proiectate

I. Evaluarea performanței globale de mediu pe unități de proces și pe total

a) Emisii în apă

Indicatori	Hârtie tissue	
	U.M.	%
- Debit ape uzate	552848 m ³	100
- TSS	1029,882 t	100
- CCO _{Cr}	192,41 t	100
- CBO ₅	76,36 t	100

Se precizează faptul că, de la celelalte unități de proces nu rezultă cantități semnificative de emisii poluante în apă, de aceea nu au fost luate în considerare.

b) Emisii în aer

Indicatori	Transport mijl. mobile		Producerea energiei	
	t	%	t	%
Pulberi	1,267 t	100	0	0
SO ₂	2,862 t	100	0	0
NO _x	11,9 t	32,89	24,28	67,11
CO	29,958 t	44,17	37,87	55,83
CO ₂	1029,56 t	100	0	0
COV	0	0	0,833	100
SO _x	0	0	4,82	100

Din datele prezentate rezultă că ponderea cea mai mare la impactul asupra aerului pentru principalii indicatori o au următoarele unități de proces:

- pulberi : transporturile interne
- SO₂ : transporturile interne
- NO_x : generarea energiei termice
- CO : generarea energiei termice
- CO₂ : transporturile interne
- COV : generarea energiei termice
- SO_x : generarea energiei termice

c) Deșeuri solide

Indicatori	Hârtie tissue	
	t	%
Refuz sortare maculatură	1833,6	100
Nămol primar și biologic epurare	3985,9	100

II. Profilul de mediu al hârtiei tissue, comparativ cu nivelurile valorilor limită de referință BREF /BAT /PPI a indicatorilor de mediu

a) Consumul de resurse naturale

Nr. crt.	Indicator	U.M.	Consumuri specifice 2009	Consum asociat BAT
1.	Maculatură	t/Adt	1,382	1,25
2.	Apă	m ³ /Adt	27,42	25

b) Utilizarea energiei

Nr. crt.	Indicator	U.M.	Consumuri specifice 2009	Consum asociat BAT
1.	Energie electrică	m ³ / Adt	936,169	1055
2.	Energie termică	m ³ / Adt	1,5	4,6

c) Emisiile în mediu

• **Emisii în apă** (după epurarea biologică)

Nr. crt.	Indicator	U.M.	Consumuri specifice 2009	Consum asociat BAT
1.	TSS	Kg/ Adt	48,44	0,4
2.	CCO _{Cr}	Kg/ Adt	8,49	4
3.	CBO ₅	Kg/ Adt	3,37	0,4
4.	Apă	m ³ / Adt	24,39	25

• **Emisii în aer** – din generarea energiei termice și transporturi interne

Nr. crt.	Indicator	U.M.	Nivel 2009	Nivel	
				asociat BAT	propus
1.	CO ₂	Kg/ Bdt	-	-	-
2.	NO _x	Kg/ Bdt	1,07	0,2	0,2
3.	Pulberi	Kg/ Bdt	-	0,01	0,01
4.	SO ₂	Kg/ Bdt	-	0,03	0,03
5.	CO	Kg/ Bdt	-	-	-

Se înregistrează depășiri importante la emisiile de NO_x.

• **Deșeuri solide**

Nr. crt.	Indicator	U.M.	Nivel 2004	Nivel asociat BAT
1.	Refuz sortare maculatură	Kg/ Adt	80,9	50 - 100
2.	Nămol epurare	Kg/ Adt	175,3	

Se înregistrează valori mai mari, comparativ cu nivelul asociat utilizării BAT la unele consumuri și emisii.

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Domeniul major de intervenție 3.2 „Formare si sprijin pentru intreprinderi si angajati pentru promovarea adaptabilitatii ”

Programe de sprijin organizațional și formare profesională pentru personalul anagajt din sectorul de celuloză, hârtie și carton în vederea adaptării la dinamica pieței interne și internaționale”
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Perioada de implementare: decembrie 2010 – noiembrie 2013

Parteneri

- Institutul de Cercetare-Dezvoltare pentru Celuloză și Hârtie – **SC Ceprohart SA Brăila – solicitant**
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- Patronatul Industriei de celuloză și Hârtie din România - **ROMPAP- partener 3**

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Obiectivul general al proiectului este orientat în direcția dezvoltării unui cadru instituțional și metodologic eficient de îmbunătățire a nivelului de pregătire profesională și a condițiilor de sănătate și securitate la locul de muncă pentru angajații și angajatorii din sectorul românesc de celuloză, hârtie și carton în vederea creșterii adaptabilității, mobilității și flexibilității acestora la cerințele unui mediu economic în continuă schimbare.

Activități principale

1. Dezvoltarea și implementarea metodelor inovatoare de organizare a muncii în scopul optimizării proceselor de producție, îmbunătățirii condițiilor de munca și adaptării

angajatorilor la inovațiile tehnice și organizatoriale

- Realizarea unui studiu documentar privind bunele practici și tendințe la nivel european privind organizarea muncii
- Analiza diagnostic a modelului organizațional existent la nivelul grupului tintaA4.3Definirea unui model organizațional inovator
- Elaborare model organizațional și metodologie de aplicare
- Realizarea a 4 exercitii pilot de aplicare a modelului organizațional inovator la nivelul grupului tinta
- Organizarea unor „ateliere de lucru” pentru manageri (48 persoane cu funcții de conducere) în vederea dezvoltării de aptitudini necesare pentru implementarea noilor modele de organizare a muncii: 6 workshop-uri, câte 1/regiune (SE, SM, NE, Centru, NV, BI)
- Organizarea unor campanii de instruire și informare privind reglementările din domeniul SSM, pentru personalul de execuție și cel cu atribuții de medicina muncii (120 angajati): 6 campanii de informare a câte 3 zile, câte 1/regiune (SE, SM, NE, Centru, NV, BI)
- Realizarea unor sesiuni de instructaj pentru lucratori în vederea ridicării gradului de specializare în efectuarea individuală a reglajelor tehnologice (autorizarea a 120 angajati pe echipamente de munca): 6 sesiuni

de instructaj (cate 3 zile) - 1/regiune (SE, SM, NE, Centru, NV, BI)

- Realizarea unor exercitii pilot de evaluare a riscurilor la posturile de munca reprezentative (10 posturi)
- Elaborarea unor pachete de solutii si propuneri de prevenire si protectie pentru factorii de risc cu nivel peste cel acceptat.

Cursuri de instruire:

1. Specializarea si instruirea personalului in domeniul introducerii conceptelor moderne de fabricatie, noilor tehnologii si procese tehnologice:

Modul 1: Noutati si perspective in domeniul fabricarii hartiilor si cartoanelor, inclusiv a sortimentelor papetare cu aplicatii speciale;

Modul 2: Noutati si perspective in procesul de fabricare a cartonului ondulat si ambalajelor din carton ondulat;

Modul 3: Tehnologii inovative de sortare si reciclare a hartiilor si cartoanelor recuperate;

Modul 4: Noi alternative de utilizare, transformare si valorificare a biomasei vegetale;

Modul 5: Posibilitati de aplicare a proceselor biotehnologice in industria de celuloza si hartie;

Modul 6: Introducerea conceptelor moderne de fabricatie in scopul cresterii competitivitatii si productivitatii intreprinderilor din sectorul de celuloza, hartie si carton;

Modul 7: Concepte moderne de aplicare si utilizare a sistemelor de aditivi in procesele de fabricare a hartiei si cartonului

2. Program de instruire si perfectionare in domeniul protectiei mediului si dezvoltarii durabile

Modul 8: Protectia mediului si asigurarea controlului poluarii in industria de celuloza si hartie;

Modul 9 Introducerea conceptului de dezvoltare durabila aplicabil in industria de celuloza si hartie;

Modul 10 Tehnologii de valorificare/integrare in mediu a deseurilor din industria de celuloza si hartie;

Modul 11 Analiza impactului asupra mediului al produselor si proceselor din industria de celuloza si hartie prin evaluarea ciclului de viata (LCA) ;

Modul 12 Asigurarea SSM in intreprinderi cu particularizare la fabricile din sectorul de celuloza, hartie si carton

3. Imbunatatirea competentelor angajatilor in domeniul proceselor organizationale, inovarii tehnice si tehnologice

Modul 13: Imbunatatirea competentelor in domeniul MRU;

Modul 14 Management organizational si strategii de firma;

Modul 15 Competente antreprenoriale;

Modul 16 Managementul proiectelor;

Modul 17: Auditor in domeniul calitatii;

Modul 18: Auditor de mediu;

Modul 19 : Managementul inovarii;

Modul 20: Managementul diversitatii in intreprinderi

4. Actualizarea si imbunatatirea competentelor in domeniul TIC

Modul 21: Operator introducere, validare si prelucrare date;

Modul 22: Operator proiectare asistata de calculator

Informații suplimentare:

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