



## Green nanostructured biodegradable materials

### Short Review

#### Part I

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**Abstract:** The article presents a brief overview of the work in producing and studying of environment friendly nanostructured polymeric composites. Preparation technology and main applications of the nanocellulose (NanoCell) is described. Novel environment friendly hydrophobic polymer composites were developed. These composites consist of a thick layer of cellulose substrate and a thin protective layer of a biodegradable polymer. Various types of the layer composites and their applications in production of packaging materials are described. The proposed biodegradable nanocomposite coating increases strength of the natural packaging materials and serves effective barrier against water and grease. Wastes of the novel polymer materials can be utilized in two ways: by repulping and by biodegradation. Widespread usage of the proposed polymer composite materials will bring about an improvement in the ecological state of the environment. Method for preparation of the reactive nanocellulose biocarrier and discussion about its biomedical and cosmetic applications are described as well

**Keywords:** nanocellulose, biocarrier, biodegradable materials, nanocomposite polymer coating, packaging materials, ecological safety.

## INTRODUCTION

Conventional disposable packaging items such as containers, trays, plates, bowls, and others, are commonly made from polystyrene or other synthetic hydrophobic plastics and also from paper or paperboard coated commonly with polyethylene. These materials are durable, moisture-resistant and grease-resistant.

The disposable items are produced by the industry in great quantities and are relatively inexpensive. After usage, these biostable goods are discarded in the environment and therefore create serious ecological problems [1-4]. Packaging waste forms a significant part of municipal solid waste and has caused increasing environmental concerns, resulting in a strengthening of various regulations aimed at reducing the amounts generated. Plastic waste imposes negative externalities

such as greenhouse gas emissions or ecological damage. It is usually non-biodegradable and therefore can remain as waste in the environment for a very long time; it may pose risks to human health and the environment; in some cases, it can be difficult to reuse and/or recycle. The expected lifetime of polystyrene materials, for example, is several hundred years. Recycling of plastic items is an expensive process. Moreover, in some countries the recycled plastics are prohibited as a material for production packaging for food.

Among other materials, a wide range of oil-based polymers is currently used in packaging applications. These are virtually all non-biodegradable, and some are difficult to recycle or reuse due to being complex composites having varying levels of contamination

The annual world consumption of non-biodegradable plastic packaging is about 200million tons. More 150 million tons are annual world consumption of paper and board packaging. The consumption of coated paper and board are about 45 million tons per year. The global paper packaging market was \$213.8 billion in 2014 and is estimated to reach \$306.73 billion by 2020 growing at a Compound Annual Growth Rate (CAGR) of 6.2%. Of the paper packaging market, paperboard is estimated to be the fastest growing market with a forecasted growth rate of 7.5% during the period 2014-2020 [5, 6].

Figures 1 [7] and 2 [8] illustrate stable growth of production and consumption of plastic packaging materials in Europe.

In 2008, total generation of post-consumer plastic waste in EU-27, Norway and Switzerland was 24.9 Mt. Packaging is by far the largest contributor to plastic waste at 63%.

Due to biostability of synthetic materials the tendency to use biodegradable disposable packaging materials has steadily increased in the last decade. Recently, significant progress has been made in the development of biodegradable plastics,

largely from renewable natural resources, to produce biodegradable materials with similar functionality to that of oil-based polymers.

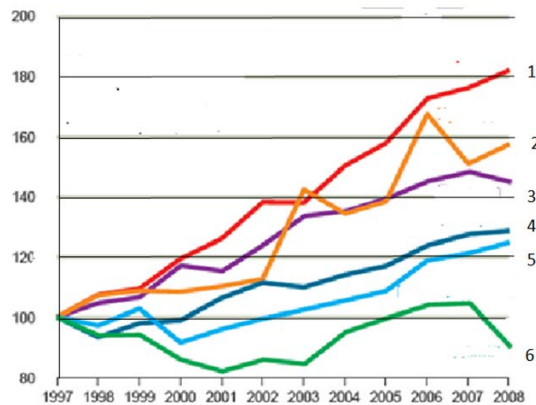


Figure 1. Tendency of production of plastic packages in Europe (Index = 100 in 1997 ) : 1- Germany, 2- Ireland, 3- Belgium, 4- Sweden, 5- Great Britain , 6-Denmark .

The expansion in these bio-based materials has several potential benefits for greenhouse gas balances and other environmental impacts over whole life cycles and in the use of renewable, rather than finite resources. It is intended that use of biodegradable materials will contribute to sustainability and reduction in the environmental impact associated with disposal of oil-based polymers.

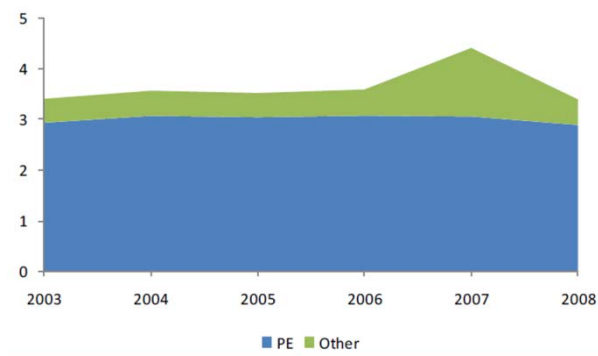


Figure 2. Volume of plastic and bags produced in EU, 2003-2008 (Mt)

The main approach has been the manufacture of inexpensive goods from biodegradable and compostable natural materials such as starch, cellulose, proteins etc. [9-14]. However, these natural biodegradable materials has several

shortcomings, the most important being susceptibility to water, grease and various other liquids. The starch binder is water-soluble and penetrable to grease.

This chapter discusses the potential impacts of biodegradable packaging materials and their waste management, particularly via composting. It presents the key issues that inform judgements of the benefits these materials have in relation to conventional, petrochemical-based counterparts. Specific examples are given from new research on biodegradability in simulated 'home' composting systems. It is the view of the authors that biodegradable packaging materials are most suitable for single-use disposable applications where the post-consumer waste can be locally composted.

Cellulose materials - papers and cardboards, are widely used in the manufacturing of packaging. These materials are ecologically safe because they can undergo biodegradation and repulping. However, cellulose packaging is hydrophilic and porous and therefore swells in water. When exposed to water or significant amounts of water vapor, these packaging materials lose form-stability and become susceptible to breakage. Therefore, it fails to protect packaged products from the negative effects of water, greases, vapors, gases and other environmental factors. In order to give them barrier properties, cellulose substrates are laminated or coated with polyolefins (polyethylene, polypropylene) and other synthetic hydrophobic polymers. Despite the fact that cellulose-polyolefin composites possess good barrier properties, their prospective application is problematic for ecological reasons. Since they are non-biodegradable and non-repulping as papers or cardboards, and non-recyclable as common plastics, cellulose-polyolefin composites waste accumulates on dumps in immense amounts and pollutes the environment. This creates a sharp ecological problem.

To overcome the shortcomings of the natural hydrophilic materials, it is necessary to develop advanced, environmentally friendly, hydrophobic polymer materials that are capable of recycling and biodegradation..

The most attempts to manufacture biodegradable packaging were focused on developing biodegradable plastic films. Creation of biodegradable packaging products based on improving low barrier properties of cellulose-based materials by coating with special polymer composition. Moreover, the coated cellulose material is recyclable and biodegradable, like as ordinary paper or cardboard. These products can be included also into pulp composition.

In this chapter, the technology of novel protective nanocoatings on surface of natural biodegradable packaging materials is described.

One from the most developed fields of the nano-technology is nanoplastics containing polymer binders and inorganic nanofillers, such as clay, silica, chalk, titanium dioxide, ceramics, etc. However, the inorganic nanofillers have the following disadvantages:

- High density increases weight of composites and articles;
- High abrasibility decreases life time of an equipment;
- High hardness hinders polishing of coatings;
- Low bonding ability with organic polymers hinders strength rising;
- Bio-stability hinders production biodegradable plastics;
- Settling ability in liquid systems causes to phases separation.

In contrast with nanoinorganic, nanoorganic fillers can contain various functional groups allowing them bonded with an organic polymer that leads to strength rising of the plastics. Moreover, organic nano-fillers such as nanocellulose will have low' density, low hardness and abrasibility, as well as increased settling stability of dispersions, etc. Besides, nano-organic fillers made from cellulose are biodegradable. Therefore, our aim was development preparation method of nano-cellulose and study main application fields of the new nanoproducts.

This chapter discusses the potential impacts of biodegradable packaging materials and their waste management, particularly via composting. It presents the

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key issues that inform judgments of the benefits these materials have in relation to conventional, petrochemical-based counterparts. Specific examples are given from new research on biodegradability in simulated ‘home’ composting systems. It is the view of the authors that biodegradable packaging materials are most suitable for single-use disposable applications where the post-consumer waste can be locally composted.



Skin has difficult multi-layer structure comprising exterior layer – stratum corneum, middle layer – epidermis and inner layer – dermis [15]. To prophylactic skin care, the cosmetic remedies can be used that act mainly on the skin exterior layer. In the case of skin injury or disease, a specific biocide (drug) is used that should be penetrate inside the skin through pores having average size of 50  $\mu\text{m}$ . In order to prevent by-effects, improve effectiveness and impart the slow-release effect, as well as to extend application areas, a chemical attachment of the biocide to appropriate carrier should be performed.

Restricted materials are suitable as carrier of biologically active substances (BAS) in biology, medicine and cosmetics. This carrier should meet the following requirements:

- It should be generally recognized as safe (GRAS);
- To contain fine particles having a gentle sensation ;
- To be insoluble in water, oils and various organic solvents;
- To be able to modification in order to forming specific reactive groups capable to bound BAS
- To be stable to attached BAS;
- Not inhibit the attached BAS ;
- Not interact with other ingredients of the drug composition.

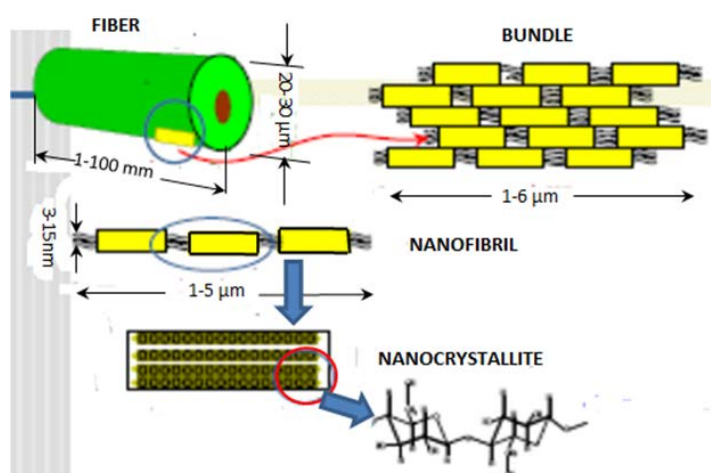
Microcrystalline cellulose (MCC) belongs to the GRAS-substances [16]. However, coarse particles (50-200  $\mu\text{m}$ ) and inertness hinder grafting of BAS to MCC and transdermal delivery of the particles through skin pores. To use cellulose particles as biocarrier, it is needed to reduce the size of the particles to nanoscale and turn the material in a reactive.

Method for preparation of the reactive nano-cellulose biocarrier and discussion about some its biomedical and cosmetic applications are presented.

## NANO-CELLULOSE AND ITS APPLICATIONS

### Materials and methods

As it known cellulose is the main building material of flora which forms the cellular walls of trees and other higher plants. The structure of a molecule of cellulose (Figure 3) is a high-chain polysaccharide consisting of n-glycosidic residues, linked by ether bridges (1,4- $\beta$  - glycosidic linkages)



**Figure 3.** Structure of cellulose

Bleached wood cellulose (95% Alfa Cellulose, DP = 1180) was used as a raw material for preparation of the nano-cellulose (NanoCell).

NanoCell- products were manufactured by process showing in Table 1[17].

**Table 1.** Main stages for manufacturing of the nanocellulose

Stage	Process	Product
1	Chemical depolymerization of the	Wet Cake
2	Treatment of the microcrystalline	NanoCell -
3	Centrifugal concentrating and	NanoCell-paste
4	Freeze drying and vortex super-fine	NanoCell-

The initial cellulose raw material is cut on pieces and they are put in a glass reactor. A water solution containing the acidic catalyst, modifier is poured into reactor. The reactor is hermetically closed with a cover and the reaction system is kept at increased temperature for short time and then cooled. The cellulose slum' is filtered and wet cake is diluted up to 1-5% transferred in Gaulin-type homogenizer and an inhibitor and a dispersing agent is added to the slurry. The dispersion is mechanically homogenized at 500-1000 bar and NanoCell dispersion is collected. This dispersion can be concentrated by centrifugation up to 25-30% solid paste of NanoCell. To producing dry NanoCell- powder. NanoCell-paste can be freeze-dried and disintegrated by vortex super-fine mill

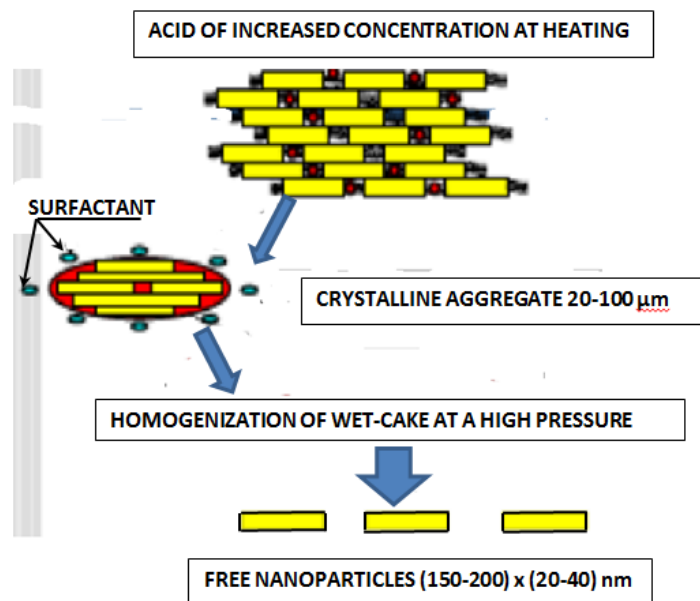
Process of NanoCell production is illustrated in Figure 4.

Testing of NanoCell-materials and compositions was carried out by means of the following methods:

- XRD (Rigaku-Ultima Plus Diffractometer);
- SEM (Hitachi S-430);
- Viscometry (Ostwald's capillary viscometer);



- Laser-Light Scattering (Malvern's Mastersizer-2000 tester);
- Mechanical tests (LLOYD LR 50K instrument).



**Figure 4.** Process of NanoCell production

### Using of the viscometry method for NanoCell investigations

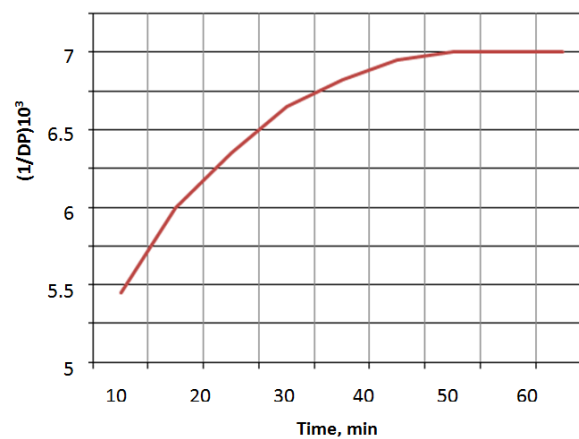
This method is based on theoretical conceptions and experimental data about super molecular structure of cellulose and its change during chemical treatments [E3-E5]. It is known that cellulose micro-fibrils contain amorphous regions and crystallites linked with intramolecular valence bonds. The amorphous regions are weak places of micro-fibrils accessible to chemical reagents, while crystallites are strong and inaccessible structural elements. Therefore, chemical treatment of cellulose with destructive reagents leads to breaking of chains in weak amorphous regions only and to decreasing in degree polymerization (DP) of cellulose (chemical cutting). After finishing of the depolymerization process in amorphous regions, the about constant DP-value "Level-off DP" (LODP) is reached. This value conforms to average DP of cellulose crystallites. The viscometry method is usually used for testing DP and LODP. If LODP was determined experimentally, the average length ( $L$ ) of elementary<sup>7</sup> cellulose crystallites can be calculated:

$$L = l \cdot LODP$$

where  $l = 0.517$  nm is length of glucopyranose link of cellulose,

### *Testing results*

The dependence of DP on time of chemical cutting of cellulose chains in amorphous regions was investigated. As can be seen from Figure 5 [17], DP of the studied wood cellulose decreases until reaches about constant value corresponding to LODP. The determined LODP value of the studied NanoCell was 141. Then average length of elementary crystallites of NanoCell is:  $L = 0.517 \text{ nm} \cdot 141 \approx 73 \text{ nm}$ .



**Figure 5.** Degree of polymerization of wood cellulose as function of chemical cutting time

### **Investigation of the NanoCell by XRD method**

The dry NanoCell powder was selected for X-ray analysis. The tablets were pressed from dry powder in order to obtaining X-ray diffractograms. The following characteristics of the sample can be calculated from XRD investigations [19, 21]:

- Degree of Crystallinity:

$$DC = (S_c / S_0) \cdot 100\%,$$

where  $S_c$  - total surface of crystalline peaks;  $S_0$  - total surface of diffractogram.

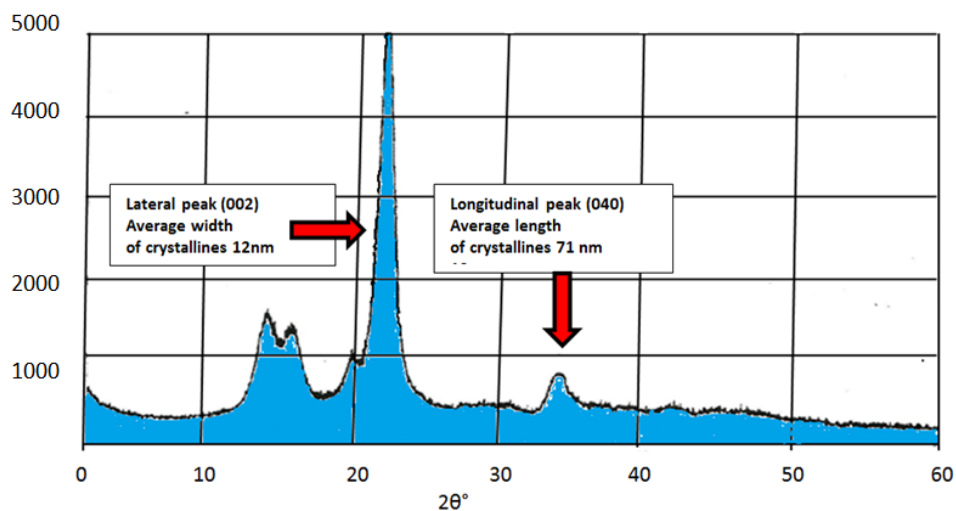
- Average size of an elementary crystal (length –  $L_0$  and width –  $H_0$ ) was calculated in accordance with the equation:

$$L_0 \text{ (or } H_0) = [(\mathbf{B}_0 \cos\theta) / \lambda]^2 - (\delta / \mathbf{d})^2]^{-1}$$

where  $\mathbf{B}_0$  - corrected width of the peak;  $\theta$ - diffraction angle;  $\mathbf{d}$  - inecrplanar distance;  $\delta$  - lattice distortion of the second type;  $\lambda$ - length of  $\text{CuK}_\alpha$  X-ray wave (0.15418 nm).

### Testing results

XRD of the NanoCell sample (Figure 6 [17]) was carried out using "Rigaku-Ultmia Plus" diffractometer.



**Figure 6.** XRD of NanoCell with Cl-crystalline modification

- Degree of crystallinity: **DC** = 81%.

Lateral peak (002) has the following parameters:  $\theta = 11.25^\circ$ ;  $d = 0.395$  nm;

$B_0 = 0.02045$  radian;  $\delta = 0.040$ .

Calculated width of the elementary crystallites of NanoCeil:

$$H_0 = [(0.02045 \cdot 0.9898 / 0.15418)^2 - (0.04 / 0.395)^2]^{-1} = 12 \text{ nm.}$$

- Longitudinal peak (040) has the following parameters:

$\theta = 17.35^\circ$ ;  $d = 0.2585$  nm;  $B_0 = 0.02$  radian;  $\delta = 0.0318$ .

Calculated length of the elementary crystallites of NanoCeil:

$$L_0 = [(0.02 \cdot 0.9545 / 0.15418)^2 - (0.0318 / 0.2585)^2]^{-1} = 71 \text{ nm.}$$

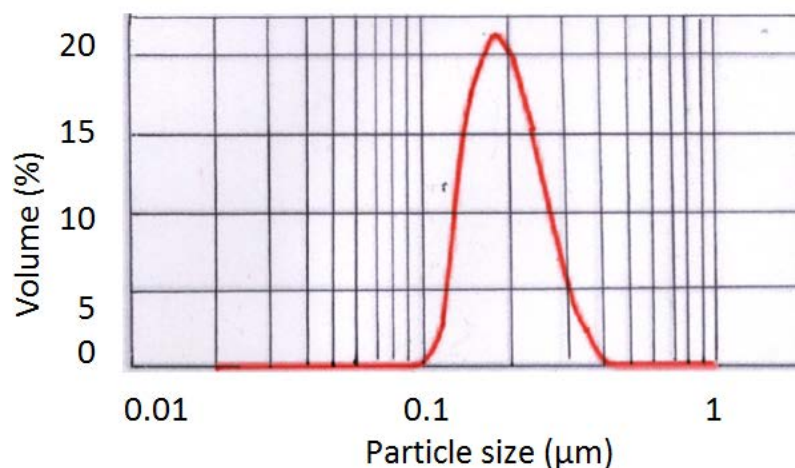
As it is follows from XRD-results, the NanoCeil has Cl-crystalline modification. The elementary nano- crystallites are an isometric having length 71 nm and width 12 nm.

So, both the viscometry and XRD methods evidence about nano-scale structure of elementary crystallites of NanoCell -samples.

NanoCell powder usually contains aggregates of the elementary crystallites. In order to find size of crystalline aggregates methods of Laser Light Scattering and SEM were used.

### Method of Laser-Light Scattering (LLS)

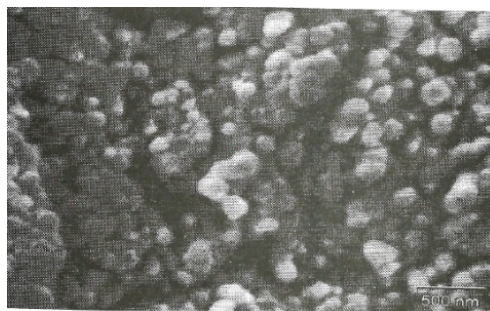
This method underlies of Malvern's Mastersizer- 2000 Apparatus for measuring particle size distribution (PSD) and average particle size ( $D_{0.5}$ ) of various dispersions and powders. As it is follows from testing results (Figure 7 [17]). NanoCell-dispersion contains small nano-crystalline aggregates with average size  $D_{0.5}$  about 200 nm.



**Figure 7.** PSD-curve of the NanoCell-dispersion

### **Using of the SEM-method for NanoCell investigations**

Dry powder of the NanoCell was prepared for SEM-investigation by chemical cutting of the initial cellulose, blending, homogenization, freeze-drying and mechanical disintegration. In order to improve contrast the NanoCell powder was preliminary coated by gold. As seen from Figure 8 [17] this sample contains ellipsoidal shape nanoparticles with average diameter 100-300 nm. This is correlated with LLS results.

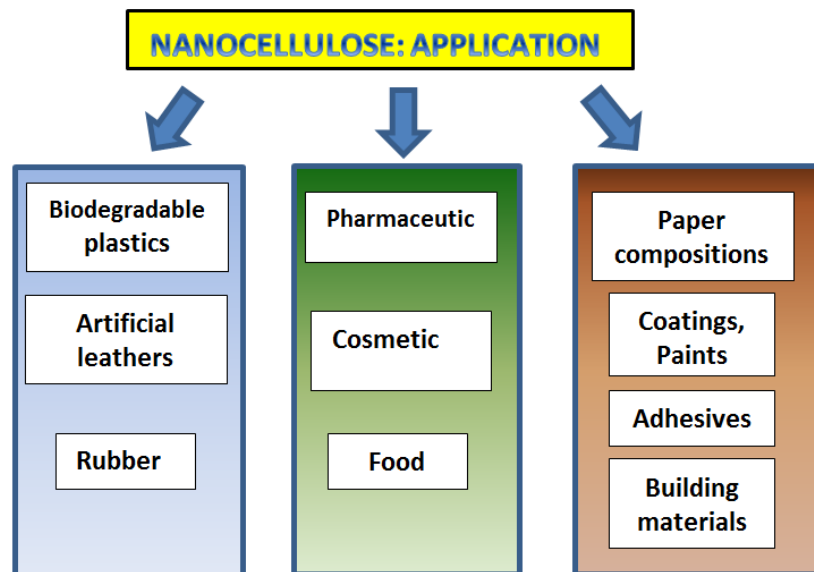


**Figure 8.** Scanning Electron Micrograph of the NanoCell sample

### **Potential application, preparation and investigation of composite materials based on NanoCell**

Nanocellulose can be widely used in various fields of consumer industry, pharmaceuticals and construction owing to its unique physical and chemical

properties, including correspondence to requirements of environmental safety. Some potential fields of application of NanoCell are shown in Figure 9.



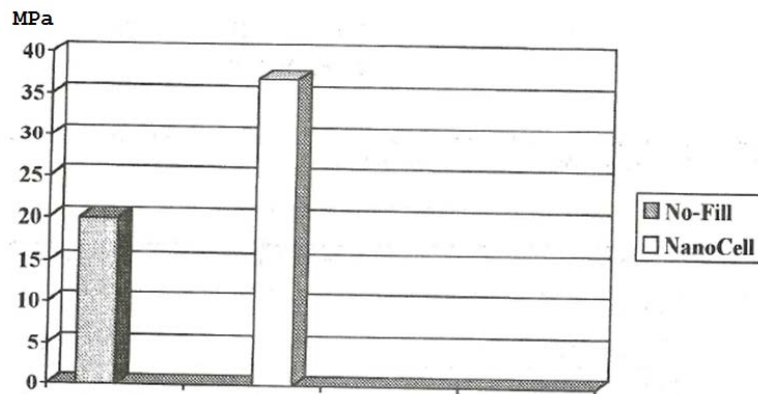
**Figure 9.** Some potential fields of application of NanoCell

The following NanoCell-containing materials were prepared:

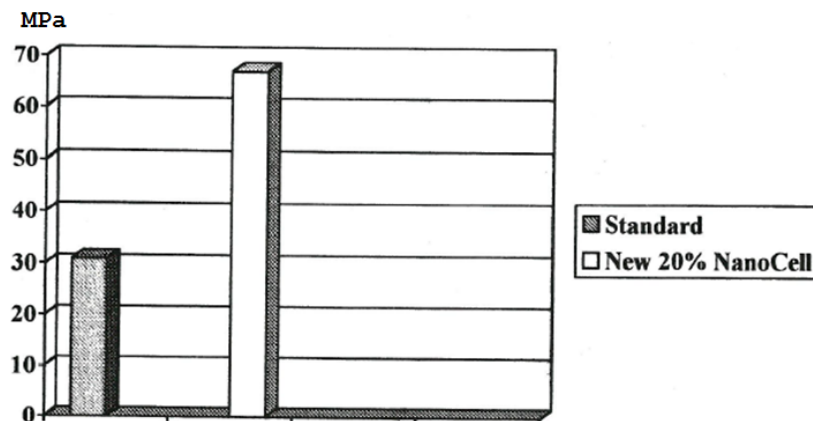
- PVC-plastic filled with NanoCell-powder;
- Biodegradable PCL-polymer filled with NanoCell-powder;
- Paper pulp water-based composition filled with NanoCell-paste;
- Glue composition containing Polyvinyl acetate latex, DOP and NanoCell-paste;
- Water-based paint composition containing UCAR-Latex,  $\text{TiO}_2$ , GCC.  
NanoCell-paste and assistant agents (disperser, surfactant, thickener, etc.)

As it can see from mechanical testing (Figures 10, 11 [17]) introducing of the NanoCell leads to considerable increasing in strength of PVC, PCL and paper materials. Moreover, filling of PCL with NanoCell contributes to increasing of

biodegradation ability of the composite polymer material (Figure 12[17]).



**Figure 10.** Tensile Strength (MPa) of initial PVC and PVC filled with 15% of NanoCell powder

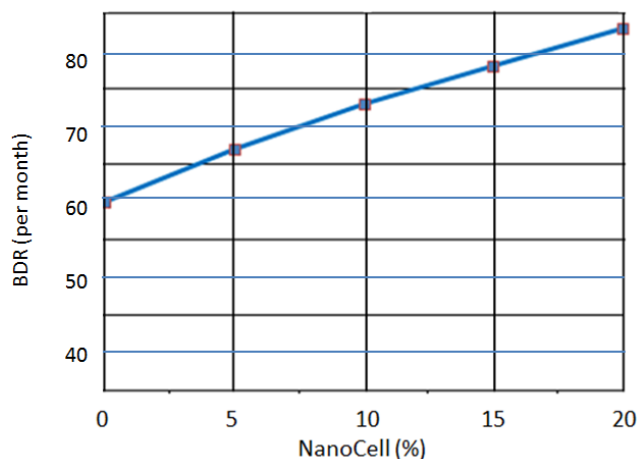


**Figure 11.** Tensile Strength (MPa) of initial paper and paper containing 20% of NanoCell

Introducing of NanoCell in the glue composition permits improving tackiness and gluing strength (Table 2 [17]).

**Table 2.** Properties of Wood's Glues

Properties	Standard	NanoCell-
<b>Tackiness, Pa</b>	70	120
<b>Strength ,</b>	6.4	6.7



**Figure 12.** Bio-decomposition rate (BDR) of PCL plastics filled with NanoCell

Besides, water-based paint compositions containing  $TiO_2$ -pigment, GCC-filler, NanoCell as an extender, UCAR binder and medium were prepared. Paint coatings were applied on to opacity charts of Sheen Instruments using the 100 microns bar applicator. Opacity value (contrast ratio) of the dn paint coating was measured by Sheen Opac Reflect meter. NanoCell showed excellent extender properties for the paint containing mineral pigments. Introduction a low amount of the NanoCell into the paint composition permits replacing a significant amount of  $TiO_2$ -pigment without changing in paint opacity value (Table 3 [17]).

**Table 3.** Characteristics of interior paint compositions based on UCAR-binder (Pigment volume concentration = 60%)

Components	Composition.	
	No 1	No 2
TiO	20	13
GCC	30	30
UCAR-	25	28
Medium	25	29
Characteristic		
TiO -Saving.	0	35
Opacity	0.94	0.95





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## PROCESSING OF BIODEGRADABLE PACKAGING MATERIALS

### Biodegradable packaging material GreetCoat™

Hydrophobic synthetic polymers are widely used for production of packaging and others goods. These polymers have excellent protection properties, but they are highly resistant to biodegradation that caused polluting of the environment.

To solve the burning ecological problem of biostable polymeric wastes, various companies have been working out innovative polymers and polymeric materials that can be biodegradable: Biopol, Mater-Bi, Bioflex, PLA and others. But these polymeric materials have common disadvantages, like complicated technology, limiting in raw materials, high cost and dissatisfaction in some properties. World consumption of these biodegradable polymeric materials is only 0.1% from consumption of polyolefins and other biostable hydrophobic synthetic polymers. Therefore it is need in principal new conception for creating of hydrophobic biodegradable materials.

The goal was to provide a composition for forming a protective coating layer on a biodegradable natural material that imparts to the material improved waterproofing and grease-resistant properties. Fundamental idea was based on solution of the problem of susceptibility of natural materials to water and other liquids penetration, by filling the pores on the surface of the natural biodegradable packaging material with fine barrier particles.

Because paper and other natural materials contain micron- scale pores, filling of these micro-pores with protective biodegradable nanoscale particles closes the pores and thus makes the natural materials stable against penetration of water and other liquids. Nano-particles of cellulose in combination with some other additives appeared to be most suitable for the purpose in hand

Substrates for coating were paperboard of Weyerhaeuser Co and starch-based trays of Hartmann Co. Bleached Kraft pulp (92%  $\alpha$ -cellulose, DP=1100) of Weyerhaeuser Co was used as an initial material for preparation of cellulose

nanoparticles. Biodegradable Polycaprolactone (PCL) was delivered from Dow Plastics Co, while the natural hydrophobic agent - Carnauba wax from Strohmeyer & Arpe Co. Other suitable chemical – sulfuric acid, calcium oxide, organic solvent and some others were available from Sigma-Aldrich Co.

The initial cellulose sample was cut on pieces and mixed with water in a lab glass. Then 80 wt. % sulfuric acid (SA) was slowly added at cooling to obtain the required final concentration of SA of 60 wt. % and acid/cellulose ratio 5. The glass was placed into water bath having temperature 50°C and heated at stirring for 1 h. Hydrolyzed cellulose was separated from the acid by centrifugation at the acceleration of 4000 g for 15 min, washed and separated once again. Then calcium oxide was added to the acidic slurry to neutralize the acid and precipitate the inorganic nanofiller – calcium sulfate.

The slurry containing agglomerates of nanoparticles was added to acetone solution containing 30-35 wt. % PCL and 1.5-2 wt. % of Carnauba wax. Then this mixture was homogenized by means of Gaulin-type homogenizer with 10 circulations at 100 MPa to obtain the protective nanocomposition for coating for natural biodegradable substrates.

The substrates were coated with the liquid nanocomposition by means of rod-type lab coater and dried at 100° C for 30 min. The weight of the dry coating on the surface of paperboard was 20 g/m<sup>2</sup> and on surface of the starch-based substrate was 40 g/m<sup>2</sup>.

Particle size of the nanocoating was studied by a means of a Mastersizer-3000 apparatus of Malvern Instrument Ltd. Viscosity of the liquid compositions was measured by the Brookfield viscometer DVII at a rotation rate of 20 rpm. Water absorption of the coated substrates was determined by the Cobb test in accordance with ASTM D3285. The mechanical properties were tested by Instron 4201 - Test System. Biodegradability was evaluated by weight loss of materials at composting in wet soil under conditions described in ASTM D2020-B and ASTM D5988.

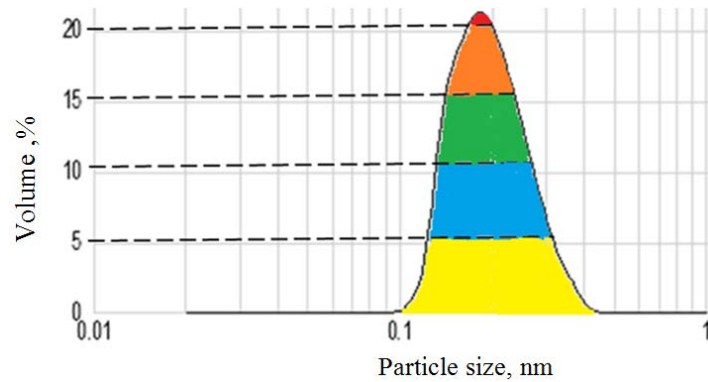
### ***Results and discussion***

After acid hydrolysis of the initial pulp and neutralization with calcium oxide about 15% wet-cake was obtained containing 60-65% nanocellulose and 35-40% inorganic nanofiller ( $\text{CaSO}_4$ ). About 100 g of the wet-cake were mixed with 200 g solution containing biodegradable polymer and natural hydrophobic agent and then homogenized. As a result the coating composition was obtained (Table 4 [22]).

Investigation showed that this composition has viscosity about 300 cP and average size of the solid particles about 170 nm (Figure 13 [22]).

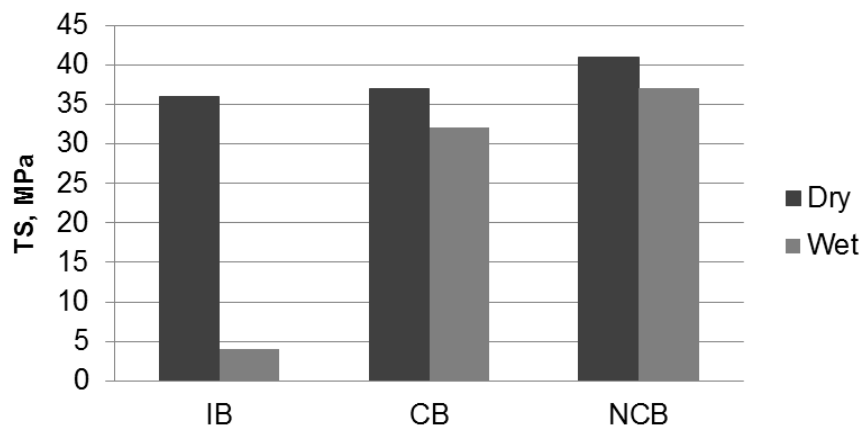
**Table 4.** Main ingredients of the coating composition

<b>Ingredient</b>	<b>Content, wt. %</b>
Solid nanocellulose	3.0-3.3
Solid inorganic nanofiller	1.8-2.0
Soluble polymer	20-23
Soluble wax	1.0-1.3
Organic solvent	42-45
Water	27-28



**Figure 13.** Size distribution of the solid nanoparticles in the coating composition

After coating of the substrates, increase of mechanical properties was observed (Figure 14[22]). Initial substrate in wet state loses about 90% of its strength, while the coated substrate after wetting, vice versa, maintains up to 90 % its strength. Besides, introduction of the nanoparticles into coating composition promotes obtaining higher mechanical properties of the coated substrate.



**Figure 14.** Tensile strength (TS) in the dry and wet state of the initial paperboard (IPB), board coated with composition without nanoparticles (CB) and board coated with composition containing nanoparticles (NCB)

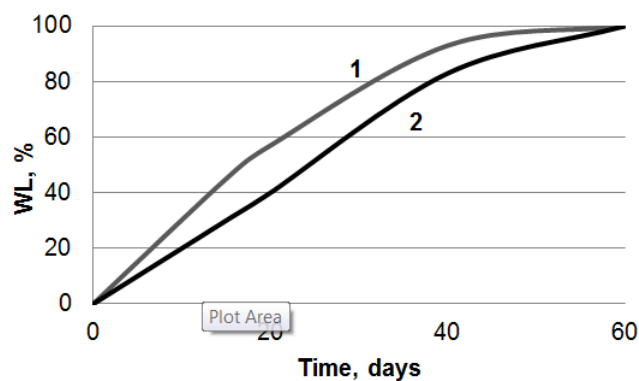
The initial substrates don't possess barrier properties to water and grease. In contrast, coating of the substrates with nanocomposition imparts to hydrophilic materials the increased barrier properties (Table 5 [22]).

**Table 5** Barrier properties of the initial (IB, IS) and nanocoated (NCB, NCS) materials

Substrate	Grease Kit No	Water Cobb <sub>30</sub> , g/m <sup>2</sup>
IB	1-2	170-200
NCB	10-11	10-15
IS	0	480-540
NCS	8-9	20-25

**Note:** IB and IS are initial board and starch-based tray; NCB and NCS are nanocoated board and starch-based tray

Due to special composition of the coating, the coated substrates decompose in the wet soil during a relative short time (Figure 15 [22]).



**Figure 15.** Weight loss (WL) of the initial (1) and nanocoated (2) paperboard due to biodestruction in wet soil

Comparative properties of the GreenCoat™ composition with the similar biodegradable package materials are shown in Tables 6, 7

**Table 6.** GreenCoat™ comparative table

Properties	Materials				
	LDPE	Bioceta	Mater-Bi	Paper	GreenCoat™
Producer	Borealis A/S Denmark	<u>Mazucchelli</u> 1849 S.p.A Italy	<u>Novamont</u> S.p.A, Italy		<u>Polymate Ltd.</u> Israel
Tensile strength, (kg/mm <sup>2</sup> )					
• Dry condition	2-3	3-4	2-3	2-4	4.5-6
• Wet condition	1.9-3	2.3-3.2	1.5-2.5	0.3-0.6	3-3.5
WVT (g/day m <sup>2</sup> )	0.1-1	5-6	5-10	20-30	4-5
O <sub>2</sub> permeability x10 <sup>13</sup> (cm <sup>3</sup> cm /cm <sup>2</sup> s Pa)	0.2-0.5	0.5-0.7	0.5-0.8	5-10	0.2-0.4
Rate of biodegradation % in wet soil (25-30% moisture 28-30°C) for 6 months	0-0.5	20-30	100	100	100
Time of biodegradation	>10 years	1 year	1-3 month	1-2 month	1-2 month

**Table 7.** Properties of cardboard coated by synthetic rubber and GreenCoat™

Properties	Rubber coating	GreenCoat™
Water absorption, Cobb-Test for 30 min, (%)	12	5
WVP (g/day m <sup>2</sup> )	5	4
O <sub>2</sub> permeability x10 <sup>13</sup> (cm <sup>3</sup> cm/cm <sup>2</sup> s Pa)	4	0.3
Resistance against oil and organic solvents (Kit number)	10	12

Patent [9] present the results of experimental investigation of the some biodegradable nanocellulose composites samples ( Table 8).

**Table 8.** Results of water penetration (Cobb test for 30 min.), grease resistance (3 Kit test number or degree), and biodegradability time (BDT- full weight loss during composting in wet soil.

Sample	Particle size (nm) in coating composition	Coating weight (g/m <sup>3</sup> )	Cobb Test (g H <sub>2</sub> O/m <sup>2</sup> )	Grease-resistance (degree)	BDT (month)
1	240	20	18	12	2
2	180	15	21	12	3
3	200	40	27	10	2
4*	6000	20	62	8	2
5*	10000	40	75	5	2

\* Comparative samples

As shown in Table 8, nanocompositions protect the natural packaging materials against water and grease, while micro-compositions containing coarse micron-scale particles have poor barrier properties. Moreover, natural packaging materials coated with the proposed nano-compositions are biodegradable and decompose fully for two to three months when composting in wet soil

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