NEW NANOSTRUCTURED COMPOSITE OBTAINED BY INNOVATIVE TECHNOLOGIES

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The paper is focused on obtaining a new nanostructured composite by innovative technologies based on: fibrillar cellulose/titanium dioxide/surfactants (bolaform- dodecandioyl-diglycine and surfactant classic-collagen hydrolysate)/ethanol/water, for improved surface properties. Innovation consists in technologies for obtaining new nanostructured composites, solubilisation/compatibilisation of their component substances for the conditioning of supports processed with the film created by evaporation of the emulsion nanocomposites. Fibrillar cellulose/titanium dioxide nanocomposites have been stabilized with bolaform surfactants in a 1:1 ratio of ethanol/water solvents in order to increase the uniformity of titanium dioxide shell nanocomposites. Nanostructured “cauliflower”-like composites developed as a result of biopolymer-surfactant interactions for fibrillar cellulose/titanium dioxide/bolaform couple in ethanol/water system are reported by SEM microscopy. The analysis by FTIR-ATR spectroscopy of bolaform, fibrillar cellulose and dynamic light scattering of 2 types of nanocomposites emulsions (with bolaform and classic surfactant emulsions) were reported. The new nanocomposites could provide the hybrid film with increased mechanical resistance to water and heat. Supports processing with the composite film improve wet/dry friction resistance, water resistance and tensile strength. Environmentally-friendly supports with smart multifunctional features are obtained for various applications.

Keywords: hybrid nanocomposites, fibrillar cellulose/titanium dioxide/surfactants, innovative technologies, improved surface properties

INTRODUCTION

A new nanostructured composite was created by innovative technologies based on fibrillar cellulose/titanium dioxide/(bolaform-dodecandioyl-diglycine and classic-collagen hydrolysate)/ethanol/water, for different applications (leather or plastics industry) (Kang, S.M. *et al.*, 2006). The trend is to develop new materials with multiple functions and added value, with low environmental impact and without harmful emissions of pollutants that can affect the climate balance (Jing, S. *et al.*, 2007). This paper brings a solution to avoid environmental pollution and meets the increasing demands for an advanced economy by capitalizing on the cellulose-based by-products from the wood industry which are currently less exploited resources (Trandafir, V. *et al.*, 2008). The high potential of using cellulose as a material for various applications: in membrane technologies for pollutant absorption, in pharmacy, etc. opens the way to obtaining new added value materials (hybrid nanocomposites) (Simion, D. *et al.*, 2009). The interaction of classic surfactants (amphiphilic molecules with a single hydrocarbon chain and a hydrophilic head group) with biopolymers in aqueous medium results in the formation of different association structures (Niculescu, M.D. *et al.*, 2013). There are various morphologies of biopolymer-surfactant association complexes depending on the molecular structure of the biopolymer and surfactant, on the nature of interaction forces between solvents and surfactant or biopolymer (Xu, Q. *et al.*, 2013). Bolaamphiphiles have the ability to self-organize at water/air or water/solvent interfaces. In solution they can self-assemble in structures such as core-shell, fibers, ribbons, tubules, planar monolayers and multilayers, depending on various factors (Ma, J. *et al.*, 2013). Compared with classic tensides, the introduction of a second hydrophilic group to the bolaamphiphiles increases their water

solubility and the critical micellar concentration, and decreases the aggregation number (Ma, J. *et al.*, 2007). pH is a basic parameter which influences the association structures (Gaidău, C. *et al.*, 2007). As an example, it is mentioned the pH-sensitive structural transformation for a peptidic bolaform. The bolaforms might be used as template in the synthesis of nanocomposites, developing nanotubes, fabrication of nanostructures assemblies with many applications. A special class of nanoarchitectures is represented by multi sheets nanostructures organized as flower-like assemblies (Ma, J. *et al.*, 2008). Such nanoarchitectures were reported, where nanosheets stack layer-by-layer onto multisheets architectures like flower petals. That hierarchical architectures had properties that made them appropriate for preparation of superhydrophobic surfaces.

EXPERIMENTAL

Materials and Methods

Materials

For obtaining of new nanostructured composites the following materials have been used: titanium dioxide from Sigma-Aldrich (nanoparticles, molecular weight 79.87 g/mol, particle size: 200 nm); tenside based on hydrolysates of collagen HCN6CV. Collagen extract - HCN6CV used as a tenside due to its specific properties was obtained by alkaline-enzymatic hydrolysis of leather waste, quality filtration and vacuum concentration in a 3:1 ratio; dodecandioyl-diglycine from Sigma-Aldrich; fibrillar cellulose from SERVA Feinbiochemica GmbH & Co. Crust leathers processed in Leather Research Department were used for finishing trials with new nanocomposites.

Nanocomposites Preparation

A number of 10 samples of fibrillar cellulose/surfactant (classic or bolaamphiphile)/titanium dioxide/ethanol/water were prepared in the following working conditions: water-ethanol solvents at ratio 1:1, temperature=60°C at 30 minutes with fibrillar cellulose-c=1%; titanium dioxide-c=0.2%, fig.1.; **samples 1, 2**: fibrillar cellulose/classic surfactant/titanium dioxide/ethanol/water with classical surfactant concentration **1-c=1%**; **2-c=2%**; **samples 3-10**: fibrillar cellulose/bolamphiphile/titanium dioxide/ethanol/water with the concentration of bolaform **3-c=1%**; **4-c=2%**; **5-c=3%**; **6-c=4%**; **7-c=5%**; **8-c=6%**; **9-c=7%**; **10-c=8%**.

Figure 1. Photographic images of 10 samples of nanostructured composites

The “cauliflower”-like architectures were observed only for bolaform (samples **3, 7, 10**) and not for the classic surfactant.

Nanocomposite Characterisation

The characterisation techniques used in this paper consist in infrared spectral analyses (FT/IR-ATR Jasco, spectrophotometer, model 4200), electronic scanning microscopy (SEM QUANTA 200”, FEI) and dynamic light scattering tests (Zetasizer Nano-ZS, MALVERN, UK) with measuring range between 0.3 nm-10.0 microns and zeta potential determination with an accuracy of +/-2%.

Leather Surface Finishing with New Nanocomposite and Characterisation

The classical technologies were performed (Table 1) by spraying different composites for waterproofing (Recipe C3), for base and for top coat layers, adding the new structured “cauliflower” emulsion in base coat (Recipe C2) or in top coat (Recipes C1 and C1_1). The difference between recipe C1 and C1_1 was the concentration of “cauliflower” emulsion, from x% to 2x% in the top coat layer.

Table 1. Different compositions for leather surface covering with new “cauliflower” emulsion

Materials	Waterproofing coat		Base coat		Top coat	
	New “cauliflower” composite emulsion	Compact acrylic binder	Pigment paste	New “cauliflower” composite emulsion	Nitrocellulose lacquer emulsion	New “cauliflower” composite emulsion
Control	-	x	x	-	x	-
Recipe C1	-	x	x	-	x	x
Recipe C1_1	-	x	x	-	x	xx
Recipe C2	-	x	x	x	x	x
Recipe C3	x	x	x	x	x	x

Sheepskin leathers covered with selected nano and micro structured “cauliflower”-like emulsion composite were analysed for resistance to abrasion (SR EN ISO 13520:2003) and for rubbing resistance at dry and wet rub cycles (SR EN ISO 11640:2013) as compared to the control sample covered with the same recipe but without the new composite.

RESULTS AND DISCUSSION

Structured nanocomposites are formed and the properties derive from the surfactants used, as well as the conditions and working parameters. This phenomenon is controlled by the concentration of biopolymer, bolaform (dodecandioyl-diglycine), titanium dioxide, the hydrophilic nature of biopolymer, ethanol/water ratio, pH=4.5.

There are various morphologies of biopolymer-surfactant association complexes depending on the molecular structure of the biopolymer and surfactant, on the nature of interaction forces between solvents and surfactant or biopolymer.

FTIR-ATR analyses (Table 2) showed that in surfactant/cellulose microemulsion systems not only physical associations are expected by means of hydrogen bonds, but also esterification reactions are possible with a different chemical structure.

Table 2. Characteristic vibration bands (cm^{-1}) in FT/IR-ATR spectra of surfactant and biopolymer

Bolaamphiphile: Dodecandioyl-diglycine; n, [cm^{-1}]	Fibrillar cellulose; n, [cm^{-1}]	Assignments
3303	3342	OH stretching
2915		NH stretching
2847	2894	CH ₂ symmetrical and asymmetrical stretching
		C=O stretching
1634	1642	amide I band, C=O stretching
1547		amide II band, NH deformation
679	667	-(CH ₂) _n -, n>3 deformation

The SEM micrograph of fibrillar cellulose is presented in Figure 2.

Figure 2. SEM micrograph of fibrillar cellulose

The association complexes with “cauliflower”-like morphologies begin to appear at high concentration of bolaform at a certain ethanol/water/titanium dioxide ratio, above critical concentration and for pH= 4.5, as seen in Fig. 3. The nanosheet microstructures built as “cauliflower”-like morphologies are the result of interaction of cellulose/titanium dioxide with glycine-based bolaamphiphile. Although bolaform and cellulose are not aromatic compounds (no π - π stacking interactions), as in the case of aniline, they succeed in creating “cauliflower”-like structures in a fibrillar cellulose/titanium dioxide/(bolaform-dodecandioyl-diglycine)/ethanol/water system.

Figure 3. SEM micrographs of “cauliflower”-like morphology in fibrillar cellulose/titanium dioxide/(bolaform-dodecandioyl-diglycine)/ethanol/water composites

Efforts in leather processing aim at beneficial effects on the environment with zero waste and low energy consumption. “Cauliflower”-like association nanostructures composites developed as the result of biopolymer-surfactant interactions for fibrillar cellulose/titanium dioxide/bolaamphiphile couple in ethanol/water system are reported.

The morphology of “cauliflower”-like association complexes is noticed only in the case of dodecandioyl-diglycine bolaamphiphile as compared with classic single chain surfactant-collagen hydrolysate. This phenomenon is controlled by the concentration of: biopolymer (fibrillar cellulose), bolaform (dodecandioyl-diglycine), titanium dioxide, the hydrophilic nature of biopolymer, ethanol/water ratio, pH.

Dynamic light scattering test showed that all three types of nanocomposites are nano and microstructured. The fibrillar cellulose/bolaform/titanium dioxide/solvents nanocomposites have sizes ranging between 40 nm, 220 nm and 5000 nm without stirring and sizes of 80 nm and 400 nm after 10 minutes of mechanical stirring. The recorded zeta potential was of -13.5 mV.

In view of testing the micro and nano “cauliflower” emulsion functionality, sample 3 from Fig. 1 was selected for quality improvement of leather surface finishing (Fig. 4) due to the special architecture and zeta potential value which can generate resistance to mechanical stress and stability in film forming polymers.

Figure 4. “Cauliflower” emulsion composite based on fibrillar cellulose/titanium dioxide/bolaform- dodecandioyl-diglycine - sample 3 from Fig. 1

Leather Surface Properties Improvement by Using Nano and Micro Structured “Cauliflower”-like Emulsion Composite

The leather surfaces covered with different recipes of finishing composites as compared to the control samples (without structured “cauliflower”-like emulsion composite) are presented in Fig. 5a). The aspect of leather surface covered with “cauliflower”-like emulsion composite showed the ability to cover imperfections and improve the final classification of leather quality as compared to control samples.

The main physical characteristics of new leather surface finishing showed resistance to wet rub and to abrasion as compared to control sample. In Fig. 5b) the control sample after the abrasion test shows cracks and the sample C1_1 surface is undamaged. In Table 3 it can be seen that the sample C1_1 has slightly better resistance to wet rubbing and substantial improvement of abrasion resistance.

Figure 5. a) Leathers covered with different compositions of finishing layers with “cauliflower” emulsion as compared to control sample (without emulsion); b) abrasion tests

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Table 3. Physical tests of leather surface covered with finishing composites with new “cauliflower” emulsion

Characteristics	M	C1	C1_1	C2	C3
Resistance to 50 wet rubbing, cycles	5/4-5	5/4-5	5/5	4-5/4	4/4-5
Resistance to abrasion, no of revolutions	25600	25600	51200	25600	25600

The main advantages of new finishing coat is the quality improvement of leather classification and durability due to the better covering power, wet rubbing and abrasion resistance provided by the new micro and nano structured “cauliflower” emulsion. The research is in progress regarding the identification of new properties of leather surface finished with the new smart structured emulsion.

CONCLUSIONS

The successful preparation of cellulose/titanium dioxide/surfactant composites with “cauliflower”-like morphology for leather finishing was presented. The analyses results showed that rubbing and abrasion resistance can be improved for more durable leather goods manufacture in the spirit of European ecological label principles.

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