OBTAINING BIOEMULSIONS STRUCTURED AS "NETWORKS" BY INNOVATIVE TECHNOLOGIES

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ABSTRACT. New bioemulsions structured like "networks" were created by innovative technologies based on: elastin/zinc hydroxide/ (bolaamphiphiles mixture: bis [2-butyl (sodium bis-thioacetate) sodium dicarboxylate 1,10 decanediyl ester] and/or sucrose diester)/ acetic acid/water, for improved surface properties development with applications in leather industry. We used in this research two "bolaamphiphiles". Bolaamphiphilic molecules contain a hydrophobic skeleton (e.g., one, two, or three alkyl chains, a steroid, or a porphyrin) and two water-soluble groups on both ends. The interaction of surfactants with biopolymers in aqueous medium results in the formation of different association structures. 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. The innovation consists in the technologies for obtaining novel micro and nanostructured bioemulsions, and the compatibilisation with film forming polymers for leather surface finishing. Elastin/zinc hydroxide micro and nanocomposites have been stabilized with bolaamphiphilic surfactants mixture: bis [2-butyl (sodium bis-thioacetate) sodium dicarboxylate 1,10 decanediyl ester and sucrose diester in a 1:1 acetic acid/water ratio, to increase the uniformity of nanocomposites. Micro and nanostructured composites like "networks" developed as a result of biopolymer-surfactants interactions for elastin/zinc hydroxide/surfactants mixture couple in acetic acid/water system are reported by SEM microscopy and DLS analysis. A special class of micro and nanoarchitectures is represented by structures organized as "network" assemblies. The novel micro and nanocomposites can provide the hybrid film with increased resistance to rubbing and water, and to deformation. Environmentally-friendly substrates with smart multifunctional features can be obtained for various applications.

KEY WORDS: bolaamphiphiles, bioemulsions structured like "networks", innovative technologies, improved surface properties

OBȚINEREA UNOR BIOEMULSII STRUCTURATE SUB FORMĂ DE „REȚELE" PRIN TEHNOLOGII INOVATOARE

REZUMAT. S-au creat noi bioemulsii structurate sub formă de „rețele" utilizând tehnologii inovatoare bazate pe: elastină/hidroxid de zinc/ (amestec de bolaamfifile: bis [2-butil (bis-tioacetat de sodiu) dicarboxilat de sodiu 1,10 decanediil ester] și/sau diester de zaharoză)/ acid acetic/apă, pentru dezvoltarea unor proprietăți de suprafață îmbunătățite cu aplicații în industria pielii. Am folosit în această cercetare două „bolaamfifile". Moleculele bolaamfifile conțin un schelet hidrofob (de exemplu, unul, două sau trei lanțuri alchil, un steroid sau o porfirină) și două grupări solubile în apă la ambele capete. Interacțiunea agenților tensioactivi cu biopolimerii în mediu apos are ca rezultat formarea diferitelor structuri de asociere. Există diverse morfologii ale complexelor de asociere biopolimer-surfactant în funcție de structura moleculară a biopolimerului și agentului tensioactiv, de natura forțelor de interacțiune dintre solvenți și surfactant sau biopolimer. Inovația constă în tehnologiile pentru obținerea de noi bioemulsii micro și nanostructurate și compatibilitatea cu polimeri filmogeni pentru finisarea suprafeței pielii. Elastina/hidroxidul de zinc micro și nanocompozitele au fost stabilizate cu amestec de surfactanți bolaamfifili: bis [2-butil (bis-tioacetat de sodiu) dicarboxilat de sodiu 1,10 decandiil ester] și zaharoză diester într-un raport acid acetic/apă de 1:1, pentru a crește uniformitatea nanocompozitelor. Compozitele micro și nanostructurate sub formă de „rețele" dezvoltate ca rezultat al interacțiunilor biopolimer-surfactanți pentru amestecul de elastină/hidroxid de zinc/surfactanți în sistemul acid acetic/apă sunt raportate prin microscopia SEM și analiza DLS. O clasă specială de micro și nanoarhitecturi este reprezentată de structurile organizate ca ansambluri de „rețele". Noile micro și nanocompozite pot oferi filmului hibrid o rezistență sporită la frecare, la apă și la deformare. Se pot obține suporturi ecologice cu proprietăți multifuncționale inteligente pentru diverse aplicații.

CUVINTE CHEIE: bolaamfifile, bioemulsii structurate sub formă de „rețele", tehnologii inovatoare, proprietăți îmbunătățite ale suprafeței

OBTENIR DES BIOÉMULSIONS STRUCTURÉES EN « RÉSEAUX » PAR DES TECHNOLOGIES INNOVANTES

RÉSUMÉ. De nouvelles bioémulsions structurées en « réseaux » ont été créées par des technologies innovantes à base de : élastine/hydroxyde de zinc/ (mélange de bolaamphiphiles : bis [2-butyl (bis-thioacétate de sodium) dicarboxylate de sodium 1,10 décanediyl ester] et/ou diester de saccharose) / acide acétique/eau, pour le développement de propriétés de surface améliorées avec des applications dans l'industrie du cuir. On a utilisé dans cette recherche deux « bolamphiphiles ». Les molécules bolaamphiphiles contiennent un squelette hydrophobe (par exemple, une, deux ou trois chaînes alkyl, un stéroïde ou une porphyrine) et deux groupes hydrosolubles aux deux extrémités. L'interaction des tensioactifs avec les biopolymères en milieu aqueux conduit à la formation de différentes structures d'association. Il existe différentes morphologies de complexes d'association biopolymère-tensioactif en fonction de la structure moléculaire du biopolymère et du tensioactif, de la nature des forces d'interaction entre solvants et tensioactif ou biopolymère. L'innovation réside dans les technologies permettant d'obtenir de nouvelles bioémulsions micro et nanostructurées, et la compatibilisation avec des polymères filmogènes pour la finition de surface du cuir. Les micro et nanocomposites élastine/hydroxyde de zinc ont été stabilisés avec un mélange de tensioactifs bolaamphiphiles : bis [2-butyl (bis-thioacétate de sodium) dicarboxylate de sodium 1,10 décanediyl ester] et diester de saccharose dans un rapport acide acétique/eau de 1:1, pour augmenter l'uniformité des nanocomposites. Des composites de micro et nanostructures comme des « réseaux » développés à la suite d'interactions biopolymères-tensioactifs pour le couple mélange élastine/hydroxyde de zinc/tensioactifs dans un système acide acétique/eau sont rapportés par microscopie SEM et analyse DLS. Une classe particulière de micro et nanoarchitectures est représentée par des structures organisées en assemblages « en réseau ». Les nouveaux micro et nanocomposites permettent de conférer au film hybride une résistance accrue au frottement et à l'eau, à la déformation. Des supports respectueux de l'environnement avec des fonctionnalités multifonctionnelles intelligentes peuvent être obtenus pour diverses applications.

MOTS CLÉS : bolaamphiphiles, bioémulsions structurées en « réseau », technologies innovantes, propriétés de surface améliorées

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INTRODUCTION

This paper presents innovative technologies for obtaining structured bioemulsions with architectures represented by structures organized as "networks" assemblies, which have applications in leather industry, environmentally-friendly substrates. Micro and nanostructure composites like "networks" developed as the result of biopolymer-surfactants interactions for elastin/zinc hydroxide/ (surfactants mixture: bis [2-butyl (sodium bis-thioacetate) sodium dicarboxylate 1,10 decanediyl ester and sucrose diester) couple in a 1:1 acetic acid/water ratio system and are reported by SEM microscopy and DLS analysis.

Bolaamphiphiles are related to and often combined with "edge amphiphiles", where one flank of a hydrophobic core carries hydrophilic groups whereas the other edge is hydrophobic [1-7]. The terms "bolaform amphiphiles" or "bolaphiles" have also been used but do not make much sense. "Form" does not appear elsewhere in organic nomenclature, and a connection with "phile = friendly" makes sense with respect to a solvent ("amphiphile") or reaction center ("nucleophile") but not in connection with a noun describing a substitution pattern. Since the early 1980s the investigation of bipolar amphiphiles ("bolaamphiphiles") has been an expanding research area leading to an increasing number of annual publications. In 2004 several review articles appeared emphasizing the importance of this unusual class of amphiphilic molecules [1–7]. Elastin powder or hydrolyzed elastin is extracted from the bovine neck tendon or bovine heart canal by biotechnology and is processed into a hydrolysate, which makes it easier to use with most of the ingredients. It is fibrin composed of polypeptide subunits and is one of the most important structural proteins. This is because elastic protein can provide the ability to resist repeated compression and deformation. Studies have proved that elastic protein peptides have a certain degree of repair and increase moisturizing factors such as skin care [1-7].

Surfactants have the ability to change the surface tension in solution, which gives them the possibility to self-organize into structures with different shapes: core-shell, fibers, ribbons, tubes, layers, multilayers and even into "networks". These structured archetypes based on surfactants improve the properties of surfaces used as substrates.

EXPERIMENTAL

Materials and Methods

In order to obtain new nanostructured composites, the following materials have been used:

- zinc hydroxide and elastin powder from Sigma-Aldrich;
- sucrose from SERVA Feinbiochemica GmbH & Co;
- bis [2-butyl (sodium bis-thioacetate) sodium dicarboxylate 1,10 decanediyl] ester obtained in an original method at ICECHIM in a PhD Thesis [1].

The experimental techniques used in this paper consist in electronic scanning (SEM) and dynamic light scattering tests:

- a "SEM QUANTA 200" equipment from FEI company, with EDAX coupled. The samples for SEM investigations were prepared by slow evaporation in clean atmosphere at room temperature;
- a "MALVERN" Zetasizer-Nano equipment, with measuring range between 0.3 nm-60.0 microns and zeta potential determination with an accuracy of +/-2%.

A number of 5 samples of elastin/surfactant (or not)/zinc hydroxide/ acetic acid/water were prepared in the working conditions: water-acetic acid solvents at 1:1 ratio, temperature=45°C for 50 minutes with elastin-c=0.1%; zinc hydroxide-c=0.1%, Figure 1.

The samples are:

- sample 1: elastin/zinc hydroxide/bis [2-butyl (sodium bis-thioacetate) sodium dicarboxylate 1,10 decanediyl] ester/acetic acid/water with surfactant concentration: 1%, elastin concentration: 0.1%, zinc hydroxide-c=0.1%;
- sample 2: elastin/zinc hydroxide/sucrose diester/acetic acid/water with surfactant concentration: 1%, elastin concentration: 0.1%, zinc hydroxide-c=0.1%;
- sample 3: elastin/zinc hydroxide/sucrose diester and bis [2-butyl (sodium bis-thioacetate) sodium dicarboxylate 1,10

decanediyl] ester/acetic acid/water with sucrose diester concentration: 1%, elastin concentration: 0.1%, zinc hydroxide-c=0.1%; bis [2-butyl (sodium bis-thioacetate) sodium dicarboxylate 1,10 decanediyl] ester concentration: 1%;

- sample 4: elastin/acetic acid/water with water-acetic acid solvents in 1:1 ratio, elastin concentration: 1-c = 0.1%;
- sample 5: elastin/zinc hydroxide/acetic acid/ water with water-acetic acid solvents in 1:1 ratio, elastin concentration: 1-c = 0.1%.

a) *b)* *c)*

Figure 1. a) Photographic image of the 5 samples; b) Image of elastin powder; c) Image of zinc hydroxide

The "network" architectures were observed only for samples 1, 2, 3 only with surfactants, not for samples 4 and 5. The experimental techniques used to analyse the new structured bioemulsions consist in electronic scanning and dynamic light scattering.

RESULTS AND DISCUSSIONS

This paper reports original innovative technologies for obtaining bioemulsions structured like "networks", Figure 2. Bioemulsions were created by the interaction of the elastin powder/zinc hydroxide/acetic acid/ water system with two surfactants used together or just one: sucrose diester and bis [2-butyl (sodium bis-thioacetate) sodium dicarboxylate 1,10 decanediyl] ester.

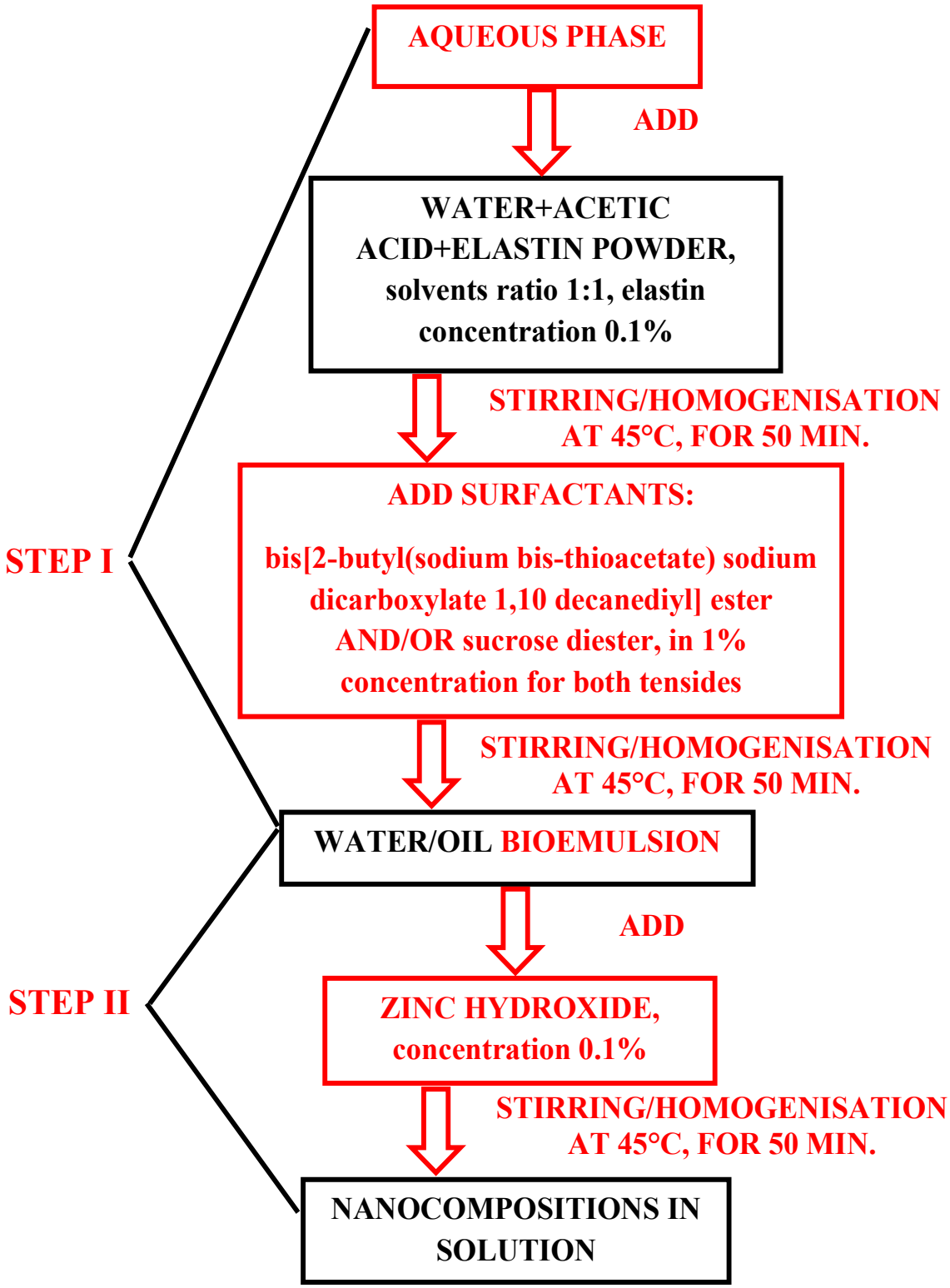


Figure 2. Two-step technological process of obtaining bioemulsion structured like “networks” and nanocompositions in solution

The original innovative technologies have two steps:

- Step I – obtaining the water-oil bioemulsion structured like "networks" by introducing in water/acetic acid at 1:1 ratio the elastin powder at concentration: 1% by stirring/ homogenization at 45°C for 50 minutes and after adding surfactants: bis [2-butyl (sodium bis-thioacetate) sodium dicarboxylate 1,10 decanediyl] ester, sucrose diester in 1:1 ratio, at concentration 1% (together or just one);
- Step II – creating the nanocompositions in solution by adding the zinc hydroxide (c=0.1%) in water-oil bioemulsion and homogenized/ stirring at 45°C for 50 minutes.

The responsible factors that control the appearance of bioemulsions structured like "networks" are: the type and concentration for surfactant and biopolymer, acetic acid/ water ratio, pH, the temperature and time of stirring, the concentration of zinc hydroxide, the hydrophilic nature of biopolymer.

The morphologies of "network" microstructures are due to the molecular structure of the biopolymer and surfactants mixtures, to the nature of interaction forces between solvents and surfactant or biopolymer in the elastin powder/sucrose diester and/or bis [2-butyl (sodium bis-thioacetate) sodium dicarboxylate 1,10 decanediyl] ester/zinc hydroxide/acetic acid/water system.

The SEM micrograph of elastin powder is shown in Figure 3.

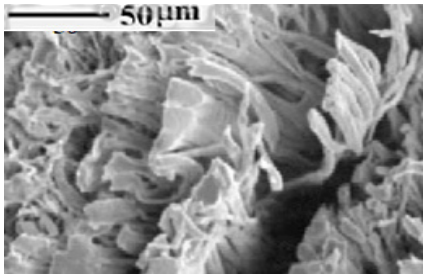
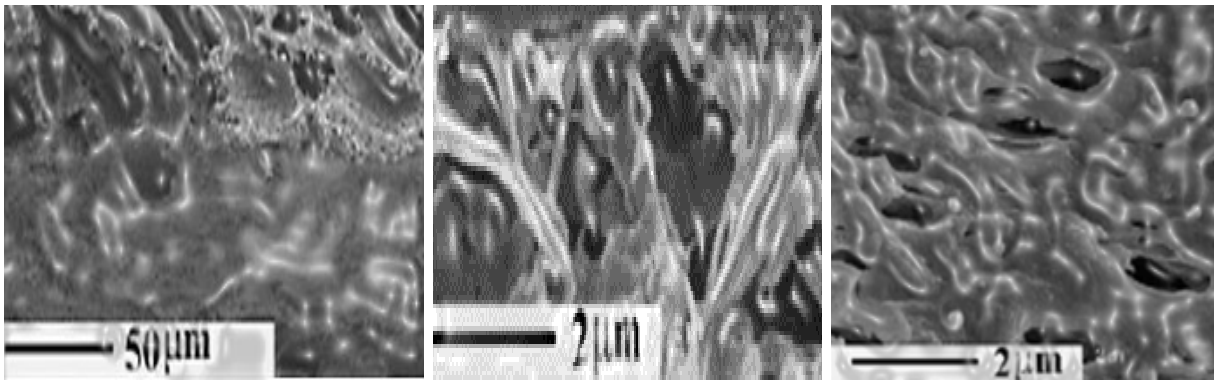


Figure 3. SEM micrograph of elastin

The association complexes with "network" morphologies appear only with surfactants, at a certain acetic acid/water/zinc hydroxide ratio, above critical concentration and for pH=4, as seen in Figure 4. SEM microscopy shows that the "network" architectures appeared only for samples: 1, 2, 3 with surfactants, not for samples 4 and 5 without tensides.



a) SEM micrograph for sample 1 *b) SEM micrograph for sample 2* *c) SEM micrograph for sample 3*

Figure 4. (a, b, c) SEM micrographs of "network" morphology in elastin/zinc hydroxide/ (surfactants mixture: bis [2-butyl (sodium bis-thioacetate) sodium dicarboxylate 1,10 decanediyl] ester and/or sucrose diester)/ acetic acid/water

The cause of the appearance for these "network" structures are the complex interactions which involve both hydrogen bonds and chemical reactions between double chain bolaamphiphile surfactant- bis [2-butyl (sodium bis-thioacetate) sodium dicarboxylate 1,10 decanediyl] ester and/or sucrose diester and elastin.

Dynamic light scattering test showed 2 types of composites: nano (50-200 nm) and microstructured (aggregate at 2mm-50 mm). The size, percentage of the particles and Zeta potential were determined and indicating the stability of nanocomposites.

CONCLUSIONS

The conducted research has led to the following results:

1. Preparation of novel micro and nanostructured bioemulsions by innovative technologies based on elastin/zinc hydroxide/ (surfactants mixture: bis [2-butyl (sodium bis-thioacetate) sodium dicarboxylate 1,10 decanediyl] ester and/or sucrose diester)/ acetic acid/water, to improve surface properties with applications in leather industry.

2. The above results bring forth aspects of the new "Smart" generation materials.

3. Further research proposes to analyse and test the possibilities of introducing other new auxiliaries (nanocomposite film) for the leather industry.

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REFERENCES

1. Varasteanu, D.S., Protein-based surfactants - Obtaining and uses, PhD Thesis, "Politehnica" University of Bucharest, **2014**.
2. Jing, S., Xing, S., Yu, L., Zhao, C., Synthesis and characterization of Ag/polypyrrole nanocomposites based on silver nanoparticles colloid, *Materia Lett*, **2007**, 61, 4528-4530, https://doi.org/10.1016/j.matlet.2007.02.045.
3. Simion, D., Gaidau, C., Berechet, D., New micro and nano-structured emulsions based on collagen and keratin hydrolysates, International Scientific Conference "Innovative solutions for sustainable development of textiles and leather industry", May 25-26, **2018**, Oradea, Romania, vol. XIX, 109-149.
4. Xu, Q., Ma, J., Zhou, J., Wang, Y., Zhang, J., Bio-based core–shell casein-based silica nano-composite latex by double-in situ polymerization: Synthesis, characterization and mechanism, *Chem Eng J*, **2013**, 228, 281-289, https://doi.org/10.1016/j.cej.2013.04.079.
5. Ma, J., Xu, Q., Zhou, J., Zhang, J., Zhang, L., Tang, H., Chen, L., Synthesis and biological response of casein-based silica nano-composite film for drug delivery system, *Colloids Surf B Biointerfaces*, **2013**, 111, 257-263, https://doi.org/10.1016/j.colsurfb.2013.06.011.
6. Ma, J., Hu, J., Zhang, Z., Polyacrylate/silica nanocomposite materials prepared by sol–gel process, *Eur Polym J*, **2007**, 43, 4169–4177, https://doi.org/10.1016/j.eurpolymj.2007.06.051.
7. Ma, J., Lu, H., Plasticity studies on leather retanned with various types of acrylic polymers, *J Am Leather Chem Assoc*, **2008**, 103, 11, 363-369.