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RENEWABLE COMPOSITES BASED ON OAK ACORN EXTRACT, COLLAGEN AND WHEY, WITH APPLICATIONS IN LEATHER PROCESSING

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Abstract: *This research elaborated novel biotechnologies for including active substances from oak acorn extract, collagen and whey, and glyceraldehydes, obtaining novel stable systems-bioactive compounds, with application in leather processing. The bioactive composites with different concentrations of oak acorn extract, collagen hydrolysate processed from leather waste, and whey were used with or without glyceraldehydes for sheepskin tanning. The new biocomposites and processed leathers were characterized by physical-chemical microscopy and spectral methods. The characterizations allowed selecting the suitable technology for skin processing as a potential alternative to classical technologies. The composites with higher concentrations of acorn extracts in combination with glyceraldehyde showed the best performances in collagen crosslinking. We estimate that the new ecological leathers processed with renewable materials will generate biodegradable waste and leather products with wearing durability and higher biodegradability at the end of their life cycle.*

Key words: *renewable compounds based on oak acorn extract, collagen and whey; innovative biotechnologies; leather processing in leather industry*

1. INTRODUCTION

The oak is part of the *Fagaceae* family and is widespread in the temperate climates of Europe, Asia and some regions of North Africa. In Romania and Serbia, it is found mainly in plain and hilly areas, in meadows, and depressions. The oak blooms in May, its flowers are monoeciously arranged in catkins. Its fruits are achenes, are called acorns, and grow in groups of 2-5 on a peduncle (Fig.1). The acorn seed is known as a high-calorie nutrient (339 kcal/100 g), rich in vitamin C, magnesium, and calcium, and is still used for the preparation of traditional “acorn coffee”.

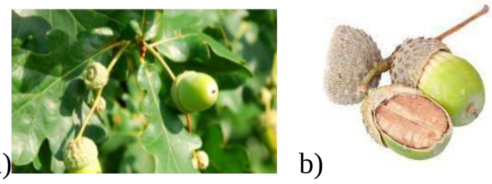
a)  b)

Fig. 1: Oak acorn (a) and seed acorn (b) [1]

Other active substances found in oak acorn are quercitanic acid, ellagic and gallic acid, bitter principles, tannin, quercin, fluroglucin, pectic substances, resins, calcium oxalate, pentadigalloylglucose, cyclogallifaric acid and carbohydrates. These give them astringent, antiseptic, surface hemostatic, anti-inflammatory, antioxidant [2,3] and deodorant effects. The interest in sustainable raw materials and alternatives to wood-origin tannins with a negative impact on ~~forest~~ deforestation oriented the research to tree and bush fruits rich in tannin like oak acorn, tara pods, and sea buckthorn branches [4-6]. The novelty of this work is represented by the combination of collagen hydrolysate and whey powders, with vegetable ones from oak acorn extract, and the formulation as a renewable composite with tanning and filling properties. The other renewable materials were the glyceraldehydes prepared from glycerin, another sustainable raw material, by catalytic oxidation. The new composites based on oak acorn extract, collagen hydrolysate whey and glyceraldehydes were characterized by physical-chemical methods, UV-VIS and FTIR-ATR spectroscopy, dynamic light scattering, and optical microscopy. The new composites experimented for skin tanning in combination with two types of glyceraldehydes for designing biodegradable leathers with ecological impact on the environment for leather waste and leather products.

2. MATERIALS AND METHODS

The following renewable raw materials have been used: acorn seed powder (Skap, Kosmaj, Serbia), leather waste (ICPI plant production), whey powder (Managis Serv SRL, Romania), and glycerine. The acorn powder has a composition of 57% carbohydrate, 5.14% protein, 5.14% fat, and traces of phosphorous, potassium, calcium, magnesium, manganese, and iron. The acorn seed extract was prepared by boiling the acorn seed powder in water, at 90°C, for 1 hour. The extract was separated from the residue by centrifuging for 30 minutes and was dried in an oven at 60°C (Fig.2.a). The collagen hydrolysate was prepared by the chemical-enzymatic method, according to our previously published papers [7]. The main characteristics of collagen hydrolysate (Fig.2.b) are 10% volatile matter, 94.06 % protein substance, pH of 4.40 (10% dispersion). The composition of whey powder (Fig.2c) is 13.3% volatile matter, 72% carbohydrate, 12.5% protein, 0.7% fat, and 1.5% salts. The glyceraldehyde (Fig.2d) was prepared by catalytic oxidation of glycerin according to literature methods [8].

a) b) c) d)

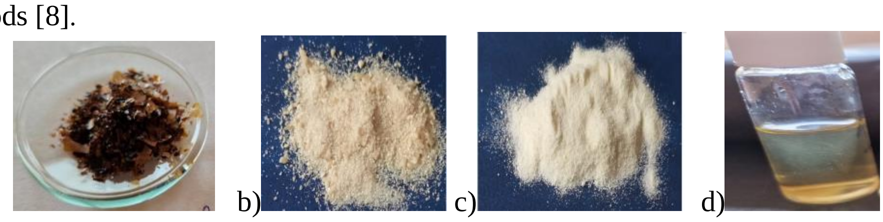


Fig. 2: The images of a) acorn seed extract, b) collagen hydrolysate, c) whey powder and d) glyceraldehyde

The renewable composites were prepared by mixing the collagen hydrolysate with whey and acorn seed extract for 4 hours at 45°C, followed by oven drying at 60°C and solid composites ball milling. Three different concentrations of acorn seed extracts were used and three composites were obtained, SZC1, SZC2 and SZC3 (Fig 3).

Fig.3: New composites for skin tanning: a) SZC1, b) SZC2 and c) SZC3

The new products were characterized by physical-chemical methods (SR EN ISO 4684: 2006 for volatile matter, SR EN ISO 4047: 2002 for total ash, SR ISO 5397: 1996 for protein substance, STAS 8619/3:1990 for pH, and Folin Ciocalteu method for total phenols), optical microscopy (confocal optical microscopy with 532 nm -CW, 636 nm -CW or ps-mode and 774 nm-120 fs excitation sources), UV-VIS (GBC,model 918) and FTIR-ATR spectroscopy (Thermo Scientific™ Nicolet™ iS50 FTIR-ATR), dynamic light scattering (Zetasizer-Nano ZS MALVERN).

3. RESULTS AND DISSCUSSION

The main physical-chemical characteristics of new composites are presented in Table 1.

Table 1. Physical-chemical characteristics of composites SZC1, SZC2, and SZC3

Characteristics	Values		
	SZC1	**SZC2**	**SZC3**
Volatile matter, %	7.04	7.44	7.83
Total ash, %	4.01	4.89	5.5
Protein content, %	20.30	22.50	23,80
pH 1:10, pH units	4.9	4.6	4.5
Total phenols, mg catechin /100 g product	0.035	0.056	0.065

The physical-chemical characteristics showed that the total phenols content is low as compared to the protein content due to the protein content of all components, collagen hydrolysate, whey, and acorn seeds. The UV-VIS spectra of 0.3% solutions of composites and components are presented in Figure 4. The FTIR-ATR spectra of solid samples of SZC1, SZC2, SZC3, collagen hydrolysate, whey, and oak acorn seed extract are illustrated in Figure 5.

An interaction between oak acorn seed extract and collagen is observed in the powders, the most obvious being for the highest content of oak acorn seed extract-SZC3 in the field of 1000-1500 cm^{-1}, and for 3000 cm^{-1}, specific wavenumbers for oak acorn seed extract The FTIR spectrum of glyceraldehyde (not shown here) allowed identifying the absorption-specific peaks of 1419 cm^{-1}-1043 cm^{-1} wavenumbers and of C=O groups at 1400 cm^{-1}, which confirmed the conversion of hydroxyl groups into carbonyl groups.

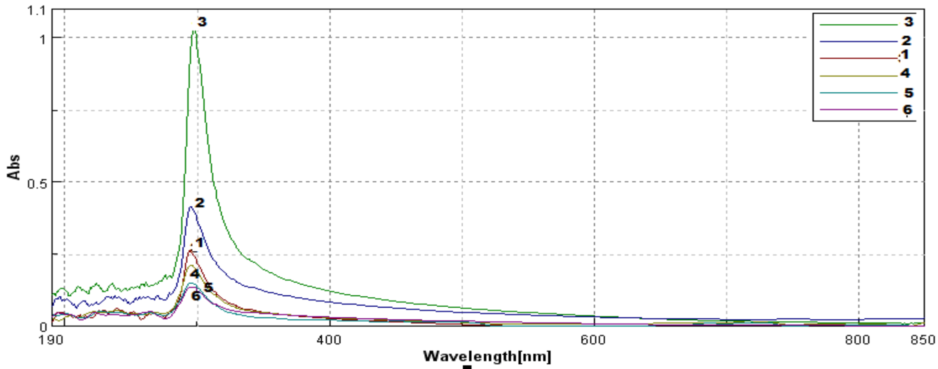


Fig. 4: The UV-VIS spectra for samples: **1**-SZC1, **2**-SZC2,**3**-SZC3, **4**-Collagen hydrolysate, **5**-Whey, **6**-Oak acorn seed extract

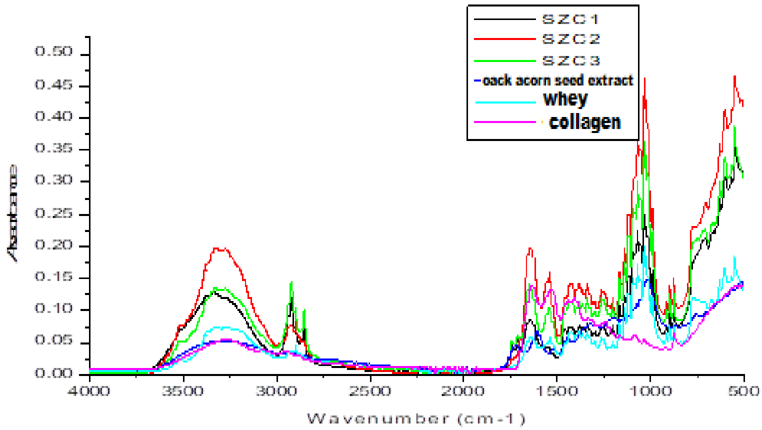


Fig. 5: The FTIR-ATR spectra of powder samples: **1**-SZC1, **2**-SZC2,**3**-SZC3, **4**-collagen hydrolysate, **5**-whey, **6**-oak acorn seed extract

The average particle size, polydispersity, and zeta potential of new composites and glyceraldehyde are presented in Table 2 and can give information on particles' ability to interreact with skin. The increase of the concentration of oak acorn seed extract has an influence on composite average particle size and polydispersity, premises for collagen binding. The opposite charges of composites and glyceraldehyde suggests a good combination for skin tanning.

Table 2. The average particle sizes, polydispersity, and zeta potential of SZC composites, and glyceraldehyde

Tanning product	Average particle size, nm	Particle sizes, nm /share, %	Polydispersity	Zeta potential, mV
SZC1	561.30	479.56/85.36	0.497	-24.5
		79.30/21.95		
SZC2	760.10	313.33/72.76	0.661	-25.7
		211.86/27.23		
SZC3	832.96	538.03/71.33	0.795	-22.8
		92.46/28.67		
Glyceraldehyde	585.60	544.70/79.00	0.489	11.78
		4227/21.00		

The optical microscopy of composite solutions confirmed the agglomeration of the particles of SZC3 particles as compared to the other composites (Fig. 6).

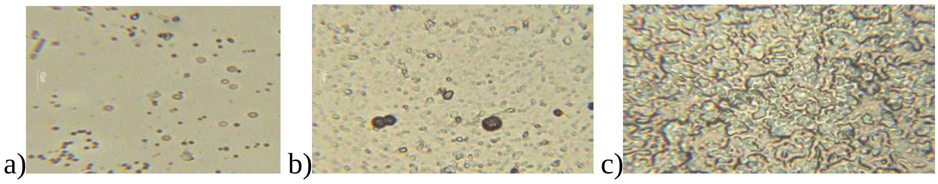


Fig.6: Optical microscopy images (1000x) for samples: a) SZC1, b) SZC2, c) SZC3 0.3% solutions

The experiments on sheepskin tanning with new composites and combinations of composites and glyceraldehyde showed that the combination of composite SZC3 and glyceraldehyde allowed suitable crosslinking of the collagen (Fig.7a).

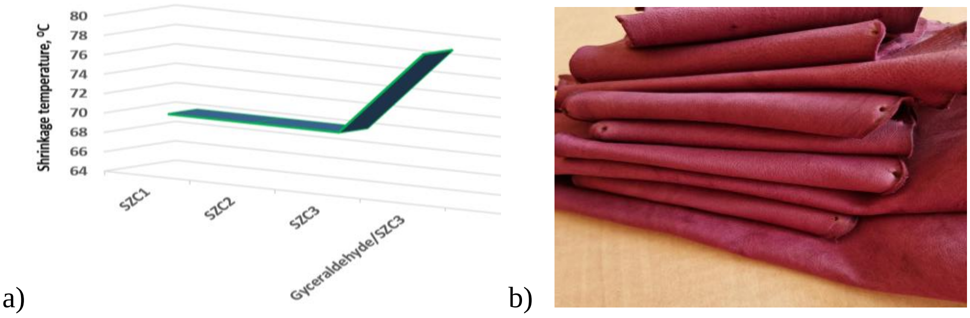


Fig.7: The shrinkage temperature of tanned sheepskins with SZC composites and combinations with glyceraldehyde (a) and sheepskin samples (b).

The FTIR-ATR spectra of tanning composites: SZC1, SZC2, SZC3 and tanned sheepskin leathers processed with different combinations are illustrated in Figure 8.

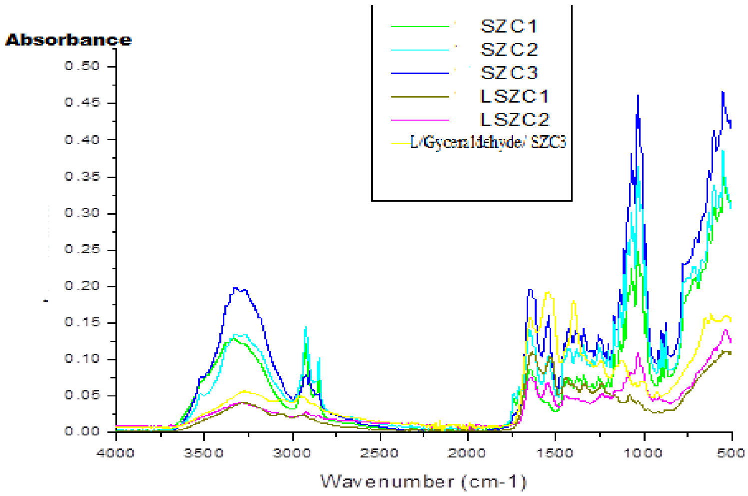


Fig. 8: The FTIR-ATR spectra for composite powders and tanned sheepskin leathers:
1-SZC1, **2**-SZC2,**3**-SZC3, **4**-LSZC1, **5**-LSZC2, **6**-L/Gyceraldehyde/ SZC3

Fig.8 showed an interaction between acorn oak extract and leather, highlighted by a maximum at the wavenumber =3000 cm^{-1}, specific oak acorn seed extract (Fig.5). The strongest interaction between oak acorn seed extract and leather occurs for the combination of gyceraldeyde with SZC3, LGlyceraldehyde/SZC3.

The potential of using renewable composites and combinations with ecological aldehydes were suggested as alternative for lower biodegradable commercial technologies and materials. Further investigations will be continued to improve tanning and material characterization in order to optimize products.

4. CONCLUSIONS

In this research were created novel biotechnologies for including active substances from oak acorn seed extracts, collagen hydrolysate, whey, and glyceraldehyde, as ecological, renewable alternatives for lower biodegradable commercial products.

The composites based on oak acorn seed extract, collagen hydrolysate and whey (SZC1, SZC2, SZC2), and the glyceraldehyde, were characterized by: UV-VIS and FTIR-ATR spectroscopy, dynamic light scattering and, optical microscopy, showing the increase of the particle size of composites with acorn seed extract concentration. The experiments on sheepskin tanning showed that the combinations of glyceraldehyde and SZC3 composite allowed crosslinking of collagen and offer a potential ecological tanning alternative. The particle size, zeta potential values as well as the ATR-FTIR analyses confirmed the conclusions of the research which will continue with tanning optimization and leather characterization.

ACKNOWLEDGEMENTS

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