CHEMIA
CZASOPISMO TECHNICZNE
TECHNICAL TRANSACTIONS
CHEMISTRY
WYDAWNICTWO POLITECHNIKI KRAKOWSKIEJ
1-Ch/2011
ZESZYT 8
ROK 108
ISSUE 8
YEAR 108

KAROLINA ŚLIWA, ELŻBIETA SIKORA, JAN OGONOWSKI*

APPLICATION OF WASTE WHEY IN SHAMPOOS

ZASTOSOWANIE SERWATKI W PRODUKCJI SZAMPONÓW

Abstract

Whey, for years considered waste in the dairy industry, is now more often treated as a valuable raw material for further processing. Chemically, whey contains lactose, proteins, fats, lactic acid, B group vitamins and minerals, so it can be also a natural source of valuable cosmetic components, e.g. hydrocolloids. Apart from biological activity, the functional properties of whey proteins like binding water, stabilizing foams or emulsifying properties are worthy of attention. In this work, properties of shampoos containing ultra-filtrate of cow's, sheep's and goat's milk whey were evaluated. An influence of their origin on qualities of cosmetics was examined. The obtained result showed that whey could be successfully used in hair shampoo formulation.

Keywords: whey ultra-filtrate, shampoo, waste in the dairy industry, goat's milk whey, sheep's milk whey, cow's milk whey

Streszczenie

W ostatnich latach serwatka stanowiąca odpad w przemyśle mleczarskim coraz częściej jest traktowana jako wartościowy surowiec do dalszego przerobu. Ze względu na skład chemiczny (laktoza, białka, lipidy, kwas mlekowy, witaminy z grupy B, minerały) może stanowić także naturalne źródło cennych składników kosmetycznych, w tym hydrokoloidów. Oprócz działania biologicznego na uwagę zasługują także funkcjonalne właściwości białek serwatkowych, takie jak wiązanie wody, tworzenie trwałych pian, właściwości emulgujące. W pracy oceniono właściwości szamponów zawierających ultra-filtrat serwatki z mleka krowiego, owczego i koziego. Badano wpływ rodzaju serwatki na właściwości sporządzonych kosmetyków. Przeprowadzone badania wykazały, że serwatka może być z powodzeniem stosowana w formułowaniu szamponów do włosów.

Słowa kluczowe: ultra-filtrat serwatki, szampon, odpad z przemysłu mleczarskiego, serwatka z mleka koziego, serwatka z mleka owczego, serwatka z mleka krowiego

* MSc. Eng. Karolina Śliwa, PhD. Eng. Elżbieta Sikora, Prof. PhD. Eng. Jan Ogonowski, Institute of Organic Chemistry and Technology, Faculty of Chemical Engineering and Technology, Cracow University of Technology.

1. Introduction

Milk and dairy products have provided very important nutrients for centuries. Milk can be extensively used. Dairy products include, for example, casein and whey. Among yogurt, kefir and buttermilk, for which a variety of manufacturers are trying to make more and more colourful packaging, we could not find whey that was not as popular as other dairy products.

Today, more than ever, the technical development of cosmetics is focused on the high quality of products, natural origin of components and environmental concerns. Hydrocolloids, like proteins or polysaccharides used as raw materials in the cosmetic industry, are examples of products which have functional properties and biological activity. They are also used as moistening and nutritious ingredients of cosmetics.

Although whey contains valuable nutrients it is still treated as waste. For the sake of its chemical composition (whey contains lactose, proteins, fats, lactic acid, B group vitamins and mineral salts), it can be also a natural source of valuable cosmetic ingredients. Apart from the biological activity, the functional properties of whey proteins, like binding water, stabilizing foams, emulsifying and gelling properties, are of interest [1–12].

In this work, properties of shampoos containing ultra-filtrates of cow's, sheep's and goat's milk whey were investigated. An influence of the concentration and origin of whey on cosmetics qualities was examined.

2. Experimental

On the basis of elaborate shampoo formulas, hair washing products, containing three types of rennet milk whey ultra-filtrate, from cow's, sheep's and goat's milk were obtained. In order to compare the thickening properties of whey proteins, a base shampoo formula (B) containing sodium chloride was prepared. The ingredients used in the shampoo formulation are shown in Table 1. Table 2 presents the whey's characteristics and table 3 shows the shampoo formulas.

The shampoos were prepared at room temperature, using the mechanical stirrer IKA RW 20, rotation rate=250 RPM. All the ingredients were mixed up in water in the following order: primary detergent (SLES), secondary detergents (Betaine and Cocamide DEA), preservative, sequestrate (EDTA), and the whey ultra-filtrate to obtain a homogeneous final product.

In our previous study it was proved that the shampoos with the addition of preservative (methylchloroisothiazolinone, methylisothiazolinone) meet the microbiological standards required for cosmetics products. In this paper, functional and organoleptic properties of shampoo products were studied [13]. The measurement of pH was carried out with the Mettler Toledo Seven Easy pH meter equipped with a glass Inlab 410 electrode. The surface tension measurement was performed by bubble pressure method [14]. The foaming ability (e.g. volume and stability of the foam) was examined by the Ross-Miles method [15]. Rheological properties of the products were determined with the Brookfield Rheometer R/S Plus, equipped with a cone/plate (C75-1) system, in the shear rate range of 1 to 100 (s^{-1}), at the temperature T = 293 K.

Table 1

Ingredients used in shampoo formulation

INCI name	Producer
Sodium laureth-2 sulphate (SLES)	Rokita
Cocamidopropyl betaine	Goldschmidt
Cocamide DEA	Chemco
Propylene glycol	PPH POCh Gliwice
Methylchloroisothiazolinone Methylisothiazolinone	Rohm and Hass
Dissolvine EDTA	Akzo Nobel
Cheese whey	University of Agriculture in Krakow
Sodium chloride	Cenos Sp z o. o.
Aqua	Distilled water

Table 2

Characteristics of ultra-filtrates (UF) of rennet cow's, sheep's and goat's milk whey used in shampoo formulation [8]

Ingredient	Cow's Whey	Goat's Whey	Sheep's Whey
Lactic Acid [%]	0.15	0.13	0.13
pH	6.5	6.38	6.4
Density [g/cm^3]	1.0255	1.0295	1.0320
Fat [%]	0.7	1.4	1.2
Dry residue [%]	7.12	9.47	10.05
Total ash [%]	0.45	0.69	0.50
Protein [%]	1.36	2.01	2.52
Lactose [%]	4.84	5.6	6.17

Table 3

Shampoo formulation

Ingredient	Content (% by weight)					
Ultra-filtrates of whey	–	20	30	40	50	60
SLES	25	25	25	25	25	25
Cocamidopropyl betaine	10	10	10	10	10	10
Cocamide DEA	3	3	3	3	3	3
Dissolvine EDTA	0.1	0.1	0.1	0.1	0.1	0.1
Propylne glycol	1	1	1	1	1	1
Methylchloroisothiazolinone Methylisothiazolinone	0.08	0.08	0.08	0.08	0.08	0.08
NaCl	3	–	–	–	–	–
Water	to 100	to 100	to 100	to 100	to 100	to 100

3. Results and discussion

The obtained results showed that the origin of whey applied for the shampoo formulation significantly influences its organoleptic properties. Each kind of the ultrafiltrates had its own, specific colour and smell which influenced the quality of the final products. The shampoo containing cow's milk whey was clear and colourless. The shampoo with goat's milk whey was lightly cream-coloured and the shampoo containing sheep's milk whey was milky and lightly yellow.

All of the studied shampoos showed a pH value in a range of 5.9 - 6.2. From the data presented in table 4 we can see that the origin of ultrafiltrate does not affect the acidity of the shampoo. The concentration of the ultra-filtrate only insignificantly influenced the shampoos pH.

Table 4

Shampoos pH

Shampoo	pH					
	0%	20%	30%	40%	50%	60%
CW	–	5.9	5.9	6.0	6.1	6.2
GW	–	6.0	6.2	6.2	6.1	6.0
SW	–	6.2	6.2	6.1	6.1	6.1
B	6.2	–	–	–	–	–
CW – shampoo with cow's milk whey GW – shampoo with goat's milk whey SW – shampoo with sheep's milk whey B – base shampoo (thickened with NaCl)						

On the basis of the obtained results we can conclude that the presence of whey beneficially influences the foaming ability of the shampoo. In the case of all whey-containing shampoos, the foaming ability was higher than that of the base shampoo (Table 5). Moreover, in all cases a high foam stability index was observed.

Table 5

Foaming ability and foam stability index of shampoos studied

Shampoo	Foam volume [cm^3]											
	0%		20%		30%		40%		50%		60%	
	V_o	V_5	V_o	V_5	V_o	V_5	V_o	V_5	V_o	V_5	V_o	V_5
CW	–	–	740	740	–	–	740	740	780	780	750	750
GW	–	–	760	760	765	765	750	750	750	750	740	740
SW	–	–	750	740	750	745	780	780	850	845	770	770
B	730	710										
V_o initial foam volume–foaming ability V_5 foam volume after 5 min–foam stability index												

All of the prepared products had comparable surface-active properties. Shampoos with a 20–40% whey content of whey from goat's milk had a slightly higher value of surface tension. The kind of whey and its concentration did not affect the washing properties of shampoos. It is understandable because the surface tension of shampoos depends on the kind and concentration of surface-active agents. In the shampoos studied SLES was applied as the primary detergent. Alkyl ether sulphates, used as the primary detergents in the shampoo formulations, show very good washing properties and foaming abilities, but these surfactants can irritate the skin and eyes and cause excessive degreasing of hair. The last problem can be overcome just by the addition of whey. In the cosmetic industry proteins are known as ingredients which decrease the irritating potential of anionic surfactants.

Table 6

Surface tension of shampoos studied

Shampoo	Surface tension [10^{-3}N/m]					
	0%	20%	30%	40%	50%	60%
CW	–	21.3	22.4	24.6	25.9	22.4
GW	–	44.7	51.4	49.2	29.1	26.8
SW	–	28.0	30.2	26.8	28.0	31.3
B	30.2	–	–	–	–	–

Rheological properties are of great importance in cosmetic products. They affect both the stability and the sensory properties of a product (clarity, ease of outflow from a bottle, consistency in a packet). The proper consistency is associated with better efficiency of a product. Very good consistency was obtained for cheese whey as a raw material for shampoo formulations, with no need for adding other viscosity control substances. Whey proteins and mineral salts were effective thickeners for the shampoo. Figure 1 shows that the whey type affected the viscosity of the shampoo. Formulations containing sheep's milk whey had higher viscosity than others enriched with cow's and goat's milk whey.

Thickening properties of the whey ultra-filtrate are connected with the content of mineral salts (NaCl, KCl, $Ca_3(PO_4)_2$). The effect of electrolytes on the viscosity of surfactant systems is the result of increased ionic density of the solution, which subsequently affects the size and shape of micelles. The observed effect was probably the consequence of differences in the presence of mineral salts and protein content in the whey (Table 2).

The analysis of the viscosity curves (Fig. 1) shows that the products thickened with whey ultra-filtrates are non-Newtonian rheopectic fluids, exhibiting shear thinning.

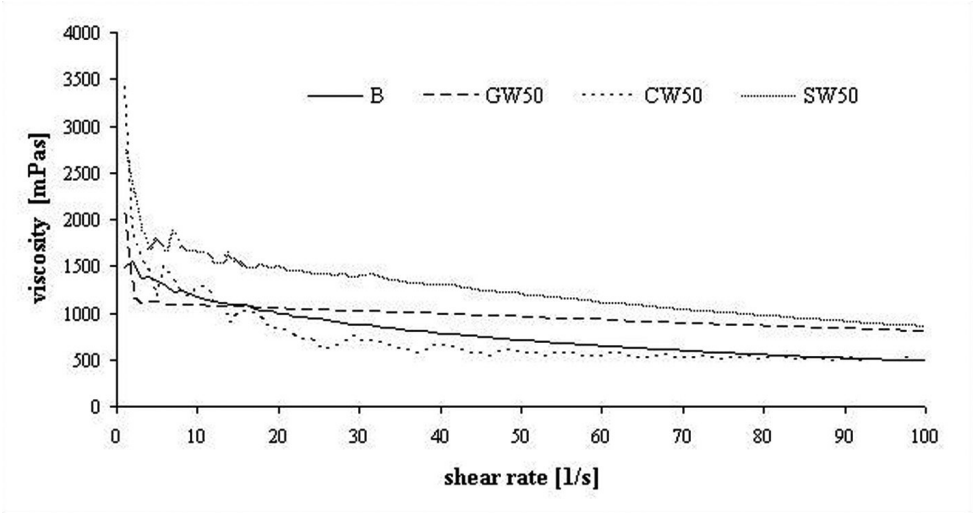

Fig. 1. Viscosity curves of shampoos containing different rennet whey ultra-filtrates (CW50 – shampoo with cow's milk whey (50%), GW50 – shampoo with goat's milk whey (50%), SW50 – shampoo with sheep's milk whey (50%)).

Rys. 1. Krzywe lepkości szamponów zawierających ultra-filtrat różnych rodzajów serwatki podpuszczkowej (CW50 – szampon z serwatki mleka krowiego (50%), GW50 – szampon z serwatki mleka koziego (50%), SW50 – szampon z serwatki mleka owczego (50%)).

4. Conclusions

On the basis of the obtained results we can conclude that cow's, sheep's and goat's milk whey can be used as a valuable ingredient of shampoos, source of vitamins, proteins and fat. The addition of whey of different origin and concentration, does not affect the washing properties of the shampoos but it has an effect on their functional properties, such as consistency and foaming ability. Particularly, it has a significant influence on the rheological properties of the products. The highest viscosity was achieved for the shampoo containing sheep's milk whey.

The use of whey as a cosmetics ingredient would become another application of waste and, on the other hand, we would obtain cosmetic products containing natural raw materials.

References

[1] Rosemary R.D., Walzem L., *Health enhancing properties of whey proteins and whey fractions. Applications monograph, nutritional and beverage*, Dairy Export Council, 1999, 1-8.

[2] Euston S.R., Finnigan S.R., Hirst R.L., *Aggregation Kinetics in Heated Whey Protein Stabilized Emulsions*, Food Hydrocolloids 2000, 155-161.
[3] Audic J.-L., Chaufer B., Daufin G., *Non-food applications of milk components and dairy co-products: A review*, Lait, 83, 2003, 417-438.
[4] Patino R.M.J., Nino R.R.M., Sanchez C.C., *Protein – emulsifier interactions at the air-water interface*, Current Opinion in Colloid and Interface Science, 8, 2003, 387-395.
[5] Renard D., Robert P., Faucheron S., Sanchez C., *Rheological properties of mixed gels made of microparticulated whey proteins and β-lactoglobulin*, Colloids and Surface, 12, 1999, 113-121.
[6] Fachin L., Viotto W.H., *Effect of pH and heat treatment of cheese whey on solubility and emulsifying properties of whey protein concentrate producet by ultrafiltration*, International Dairy Journal, 15, 2005, 325-332.
[7] Wakabayashi H., Yamauchi K., Takase M., *Lactoferricin research, technology and applications*, International Dairy Journal, 16, 2006, 1241-1251.
[8] Kalicka D., dane niepublikowane, stanowiące fragment opracowywanej rozprawy doktorskiej, Uniwersytet Rolniczy w Krakowie.
[9] Lutz R., Aserin A., Wicker L., Garti N., *Double emulsions stabilized by a charged complex of modified pectin and whey protein isolate*, Colloids and Surfaces B: Biointerfaces, 72, 2009, 121-127.
[10] Herbert G., CA 2101622 (Jan 30, 1995).
[11] Collins D.F., Mammone T., Marenus K.D., US 6203805B1 (Mar 20, 2001).
[12] Śliwa K., Sikora E., Ogonowski J., *Kosmetyczne zastosowania serwatki*, Wiadomości Chemiczne, 64, 2010, 507-532.
[13] PN-C-77002, Szampony w płynie do włosów i płyny do kąpieli. Wymagania i badania, Grudzień 1997.
[14] Ogonowski J., Tomaszkiewicz-Potępa A., *Analiza związków powierzchniowo-czynnych*, Wydawnictwo IGSMIE PAN, Kraków 2004, 15-17.
[15] PN-ISO696:1994, Środki powierzchniowo czynne. Oznaczanie zdolności pianotwórczych zmodyfikowaną metodą Ross-Miles'a, Grudzień 1994.